EQUILIBRIUM

SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

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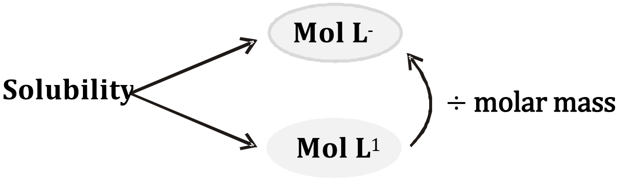
Solubility (s) and Solubility Product (Ksp)

Solubility: “Moles of a substance dissolved per unit volume of a solution.”



Classification of Salts:

If $S > 0.1$ M ⇒ Soluble Salts

If $0.01 \text{ M} < S < 0.1$ M ⇒ Partial Soluble salts

If $S < 0.01$ M ⇒ Sparingly soluble salts

Note: All salts of alkali metals and NH_4^+ ion is generally water soluble.

Examples of sparingly soluble salts are AgCl, $PbCl_2$, Hg_2Cl_2, $PbSO_4$, Ag_2CO_3, $CaSO_4$, AgCN, etc.

Process of Dissolution of Sparingly Soluble Salts

Let AB ⟶ Sparingly Soluble Salt

$$AB(s) \underset{\text{Precipitatio}}{\overset{\text{dissolution}}{\underset{}{\overset{H_2(\ell)}{\rightleftharpoons}}}} \overset{\oplus}{A}(aq) + \overset{\ominus}{B}(aq)$$

Initially, rate of dissociation > rate of ppt.

∴ more salt can be dissolved and solution is unsaturated.

But, when Saturated solution

rate of dissolution = rate of ppt ion

In a saturated solution, whatever salt is dissolved will be present in the form of its ions and therefore, concentration of ions in a saturated solution will represent solubility of the salt.

This is generally used for sparingly soluble salts. We will be dealing with the solubilities in the following type of solution

Solubility Product (K_{sp})

For a saturated solution,

$$AB \longrightarrow A^{\oplus} + B^{\ominus}$$

$$K_{eq.} = \frac{[A^+][B^-]}{[AB]} \text{[concentration of solid is constant]}$$

$$\therefore \quad \underbrace{K_{eq.}\,[AB]}_{\downarrow} = [A^+]\,[B^-]$$

$$K_{sp} = [A^+]\,[B^-]$$

Solubility product (K_{sp}) is a type of equilibrium constant, so will be dependent only on temperature for a particular salt.

Here different methods for writing K_{sp} for different types of salts are following:

(a) AB Type Salt

$$AB(s) \longrightarrow A^+(aq) + B^-(ag)$$

$$\quad s \qquad\qquad s$$

$$K_{sp} = [A^+][B^-] = s^2$$

$$s = \sqrt{K_{sp}}$$

(b) A_2B Type Salt

$$A_2\ B(\ s) \longrightarrow 2\ A^+(aq) + B^-(aq)$$

$$\quad 2s \qquad\qquad s$$

$$K_{sp} = [A^+]^2[B^-] = [2s]^2[s] = 4s^3$$

$$K_{sp} = 4s^3$$

(c) AB_3 Type Salt

$$AB_3(\ s) \longrightarrow A^{3+}(aq) + 3\ B^-(aq)$$

$$\quad s \qquad\qquad 3s$$

$$K_{sp} = [s][3s]^3 = 27s^4$$

(d) A_2B_3 Type Salt

$$A_2\ B_3(\ s) \longrightarrow 2\ A^{3+}(aq) + 3\ B^{2-}(aq)$$

$$\quad 2s \qquad\qquad 3s$$

$$K_{sp} = [2s]^2[3s]^3$$

$$K_{sp} = 108\ s^5$$

(e) AxBy Type Salt

$$AxBy \longrightarrow xA^{y+} + yB^{x-}$$

$$AxBy \longrightarrow xA^{y+} + yB^{x-}$$

$$\quad xs \qquad\qquad ys$$

$$K_{sp} = (xs)^x\ (ys)^y$$

$$K_{sp} = x^x.y^y.s^{x+y}$$

Following examples will illustrate the different type of solubilities and the effects of different factors or situation on solubility of a salt.

Simple Solubility

Let the salt is $A_x\ B_y$, in solution in water, let the solubility in H_2O = 's' M, then

$$A_xB_y \longrightarrow xA^{y+} + yB^{-x}$$

$$-xs \qquad\qquad ys$$

$$\therefore \qquad k_{sp} = (xs)^x\ (ys)^y = x^x,\ y^y.(s)^{x+y}$$

◆ **INDICATORS**

An indicator is a substance which changes its colour at the end point or neutral point of the acid-base titration i.e., the substance which is used to indicate neutral point of acid-base titration are called indicators.

At End Point $N_1V_1 = N_2V_2$

Indicators are of two types

(i) Acidic

(ii) Basic

(i) Phenolphthalein (HPh) :- HPh is acid indicator. It ionizes in water to give colourless H^+ ions and pink coloured anions.

$HPh \leftrightarrow H^+ + Ph^-$

Colourless Pink

If $[Hph] > [Ph^-] \longrightarrow$ Colourless

$[Hph] < [Ph^-] \longrightarrow$ Pink

In acidic medium the dissociation of HPh is almost nil so it gives no colour because acid suppress the ionisation of HPh due to the presence of common ion H^+ and the solution remains colourless.

$HPh \leftrightarrow H^+ + Ph^-$

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

In alkaline medium, the OH^- ions combine with H^+ ions of the indicator to form water. $HPh \;\; H^+ + Ph^-$

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

Thus Ph^- ions give pink colour in alkaline medium.

(ii) Methyl Orange (MeOH) :- It is a weak base and dissociates as :-

$MeOH \leftrightarrow Me^+ + OH^-$

Yellow Red Colourless

If $[MeOH] > [Me^+] \longrightarrow$ Yellow

$[MeOH] < [Me^+] \longrightarrow$ Red

MeOH is not dissociated in alkaline medium due to the presence of common ions OH^- and the solution remains yellow.

$$MeOH \leftrightarrow Me^{+} + OH^{-}$$

$$NaOH \longrightarrow Na^{+} + OH^{-}$$

In acidic medium OH^{-} combine with H^{+} thus increase the ionisation of MeOH. Hence yellow colour of solution change to red colour.

$$MeOH \leftrightarrow Me^{+} + OH^{-}$$

$$HCl \longrightarrow H^{+} + Cl^{-}$$

- **Modern Quinonoid Theory**

According to this theory,

(i) An acid-base indicator is a dynamic equilibrium mixture of two alternative tautometric forms ; ordinarily one form is benzenoid while the other is quinonoid.

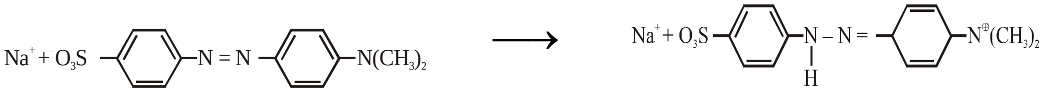
(ii) The two forms have different colors.

(iii) Out of this one form exist in acidic solution, while the other in alkaline solution.

(iv) The change in pH cause the transition of benzenoid form to quinonoid form and vice-versa and consequently change in colour.

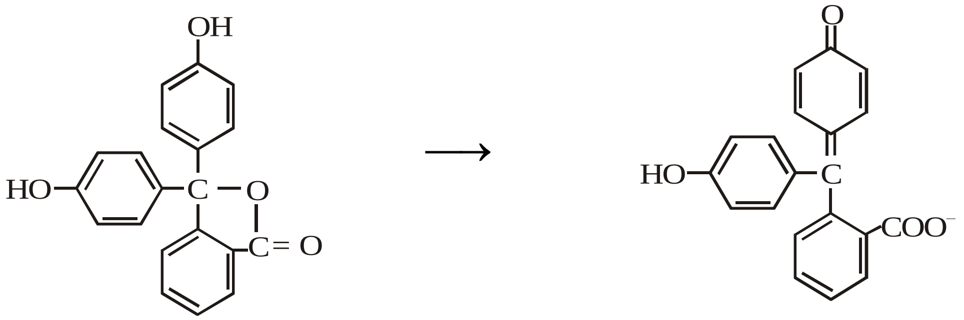
Ex.

(a) For methyl orange



Yellow benzenoid form (in bases) Red quinonoid form (in acids)

(b) For Phenolphthalein



Colourless benzenoid form (in Acid) Red quinonoid form (in Alkali)

THEORIES OF INDICATORS

(a) **Ostwald Theory :-** According to this theory

(i) Indicators are organic, aromatic weak acids or weak bases.

(ii) The colour change is due to ionisation of the acid - base indicator. The unionized form has different colour than the ionised form.

(iii) Every indicator shows colour changes in opposite medium due to the conversion of unionized part into ionized part.

For example phenolphthalein shows pink colour in basic medium and methyl orange shows red colour in acidic medium.

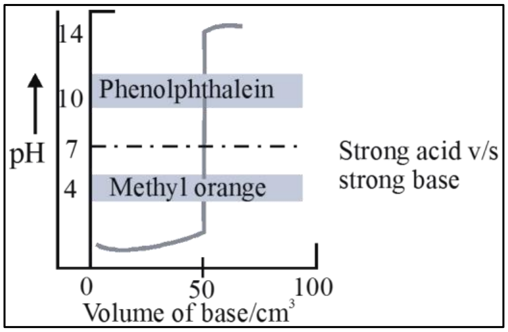
Note: For oxidation reduction (Redox) reactions indicators are not used because these reactions are very fast. Indicators are not used in coloured solution also.

◆ TITRATION OF STRONG ACID AGAINST STRONG ALKALI

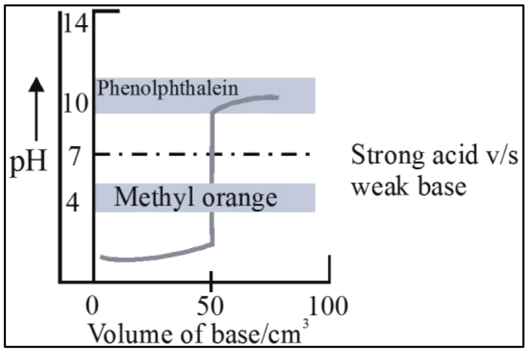
The graph (A) shows how pH changes during the titration of 50 cm^3 of 0.1 M HCl with 0.1 M NaOH.

$$NaOH\ (aq) + HCl\ (aq) \longrightarrow NaCl\ (aq) + H_2O\ (\ell)$$

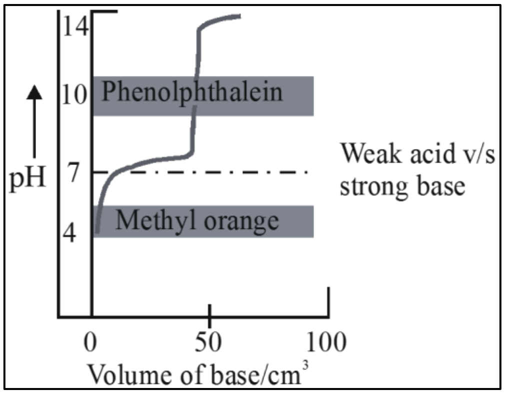
The pH of 0.1 M solution of HCl in the beginning would be 1. As alkali is added, the pH changes slowly in the beginning. However, at the equivalence point pH changes rapidly from about 3.5 to 10. It can be shown by simple calculations that pH of the solution is 3.7 when 49.8 cm^3 of 0.1 M NaOH solution have been added. The pH suddenly changes to 10 after addition of 50.1 cm^3 of the NaOH solution. Thus, any indicator having pH range between 3.5 to 10 will identify the equivalence point. This means that any one of phenolphthalein, methyl orange or bromothymol blue could be used as an indicator.


14
10
7
4
pH
Phenolphthalein
Methyl orange
Strong acid v/s strong base
0
50
100
Volume of base/cm^3

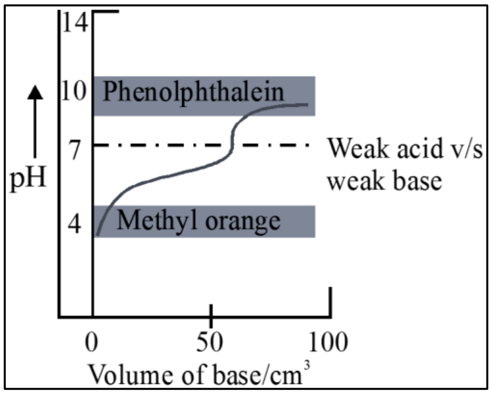
(A)


14
10
7
4
pH
Phenolphthalein
Methyl orange
Strong acid v/s weak base
0
50
100
Volume of base/cm^3

(B)


14
10
7
4
pH
Phenolphthalein
Methyl orange
Weak acid v/s strong base
0
50
100
Volume of base/cm^3

(C)


14
10
7
4
pH
Phenolphthalein
Methyl orange
Weak acid v/s weak base
0
50
100
Volume of base/cm^3

(D)

TITRATION OF STRONG ACID AGAINST WEAK ALKALI

The graph (B) shows how pH changes during titration of 50 cm^3 of 0.1 M HCl with 0.1 M NH_3.

$$HCl\ (aq) + NH_4OH\ (aq) \longrightarrow NH_4Cl\ (aq) + H_2O\ (\ell)$$

In this case, the pH changes rapidly from 3.5 to 7.0 at the equivalence point. Methyl orange, methyl red and bromocresol green are suitable indicators for this type of titration. Phenolphthalein is unsuitable because its pH range lies outside the vertical portion of the curve.

TITRATION OF WEAK ACID AGAINST STRONG BASE

The graph (C) shows how pH changes during titration of 50 cm^3 of 0.1 M CH_3COOH with 0.1 M NaOH.

$$CH_3COOH\ (aq) + NaOH\ (aq) \longrightarrow CH_3COONa\ (aq) + H_2O\ (\ell)$$

The vertical portion of this titration curve lies between pH range 7 to 10.6. Phenolphthalein is suitable indicator for this titration. Methyl orange is not suitable for this titration because its pH range lies on the flat portion of the curve.

TITRATION OF WEAK ACID AGAINST WEAK BASE

The graph (D) represents the titration curve obtained for titration of 50 cm^3 of 0.1 M CH_3COOH with 0.1 M NH_3.

$$CH_3COOH\ (aq) + NH_4OH\ (aq) \longrightarrow CH_3COONH_4\ (aq) + H_2O\ (\ell)$$

For this type of titration there is no sharp increase in pH at the equivalence point. No indicator is suitable for this type of titration.

Indicator	**pH range**	**Colour change**	**pK_a** **Neutral colour pH**
Methyl orange	3.2 – 4.5	Pink to yellow	3.7
Methyl red	4.4 – 6.5	Red to yellow	5.1
Litmus	5.5 – 7.5	Red to blue	7.0
Phenol red	6.8 – 8.4	Yellow to red	7.8
Phenolphthalein	8.3 – 10.5	Colourless to pink	9.6