Electrolyte

Acid
Base
Salt

in
Soln.
molten

Electrolyte

SE	WE
* readily ionizes	* slowly
* completely	* incomplete
* $\alpha = 1$	* $\alpha < 1$
* Eg.	* Eg.
HCl, H_2SO_4	CH_3COOH
$NaOH$	NH_4OH
$NaCl$	CH_3COONH_4

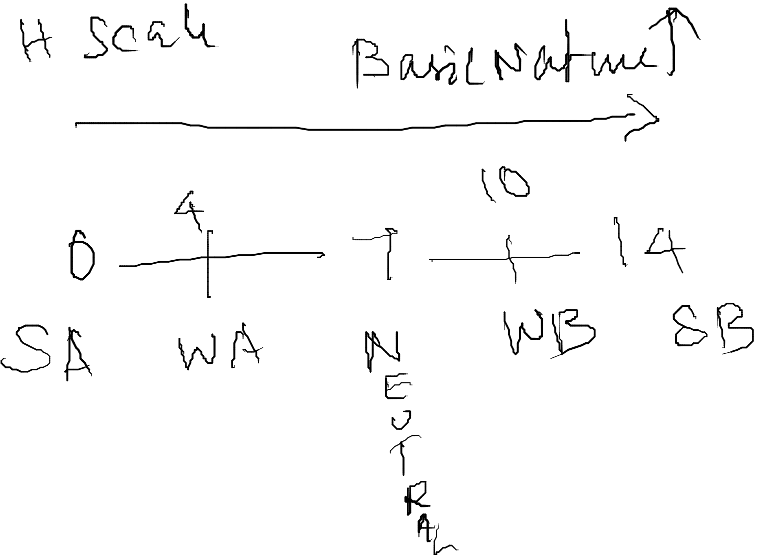
$pH = -\log[H^+]$

$= -\log[H_3O^+]$

$pOH = -\log[OH^-]$

$pH + pOH = 14$

pH scale



Buffer – resists the change in pH

- AB
  - WA + its salt of SB
  - eg. CH_3COOH + CH_3COONa
- BB
  - WB + its salt of SA
  - eg. NH_4OH, NH_4Cl

Theory of Indicators.

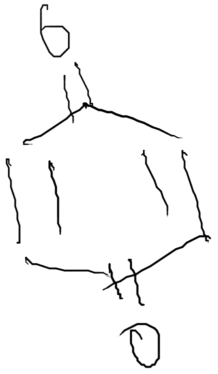
Acid – Methyl orange → Red

Base – Phenolphthalein

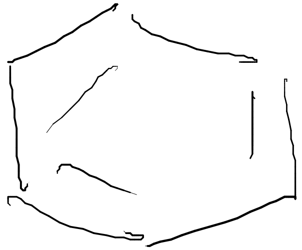
White → Pink

Colourless

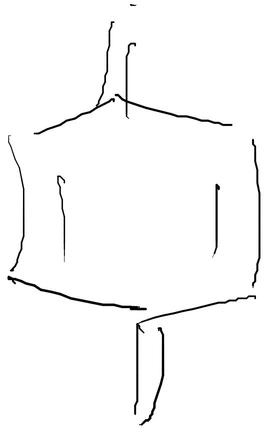
Quinonoid theory



quinone

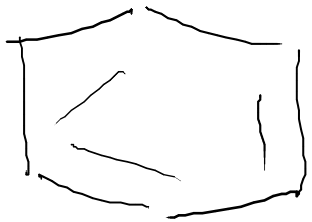


benzene



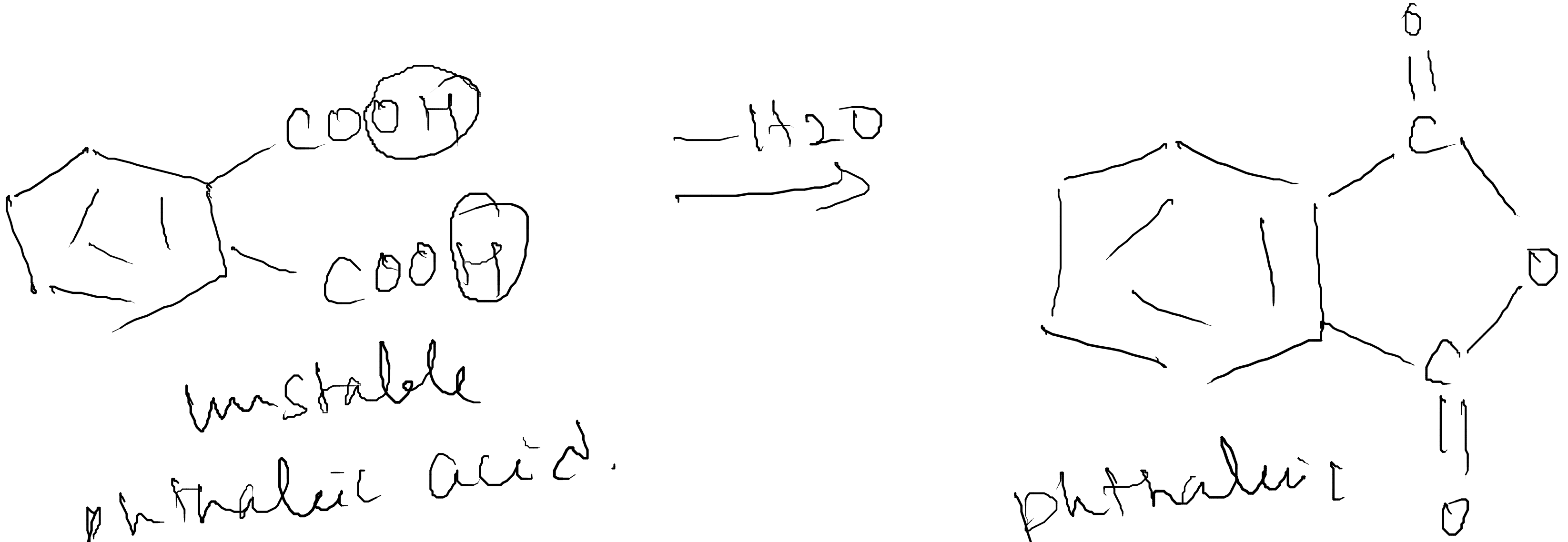
quinonoid

deep colours



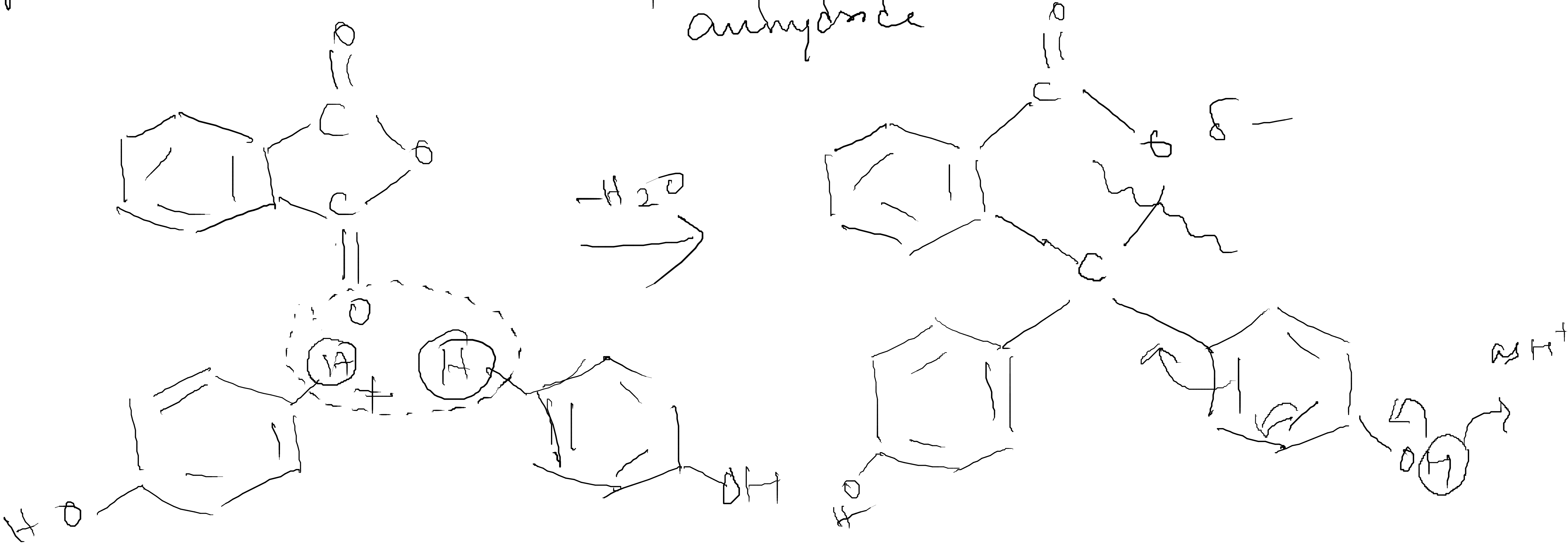
benzenoid

v. pale colour (or) colourless.

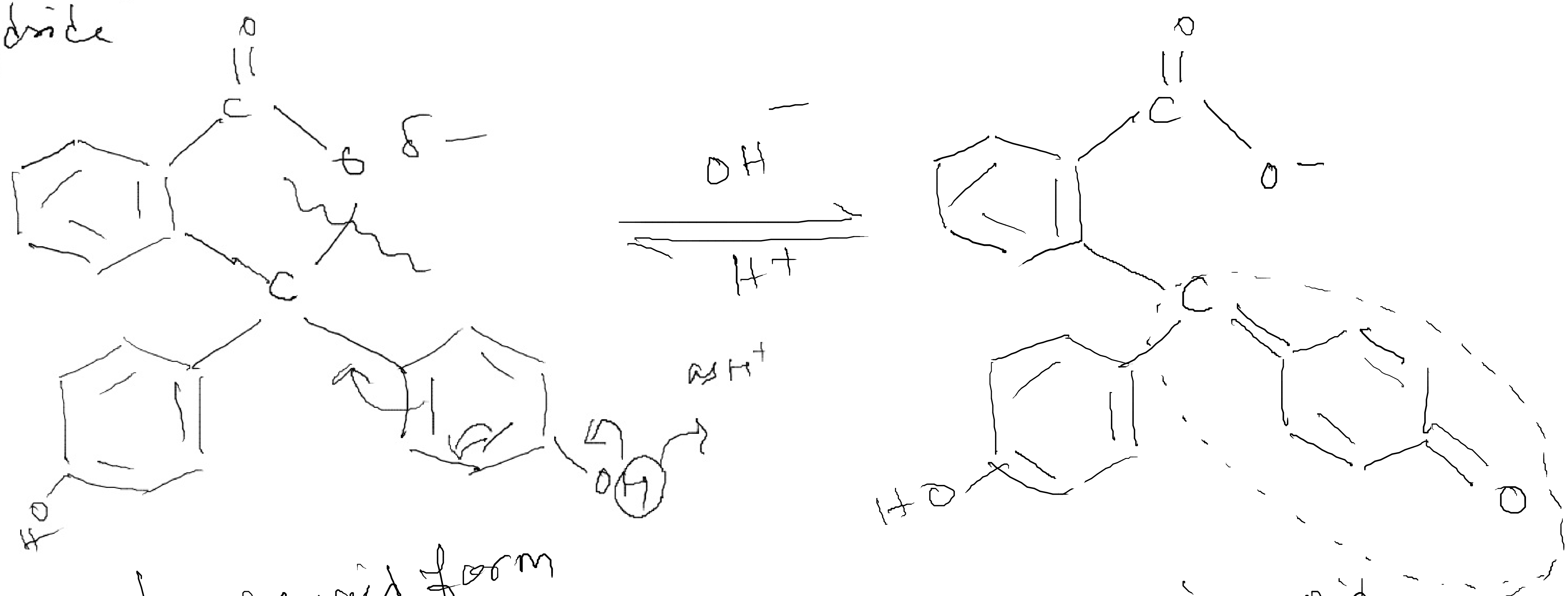


unstable
phthalic acid.

phthalic
anhydride



ydside⁻



benzenoid form

colourless

in acid

quinonoid

form

pink colour

in base

IONIC PRODUCT OF WATER

- Pure water does not conduct electric current.
- Acidulated water conducts current.

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

(or)

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

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

$[H_2O] = 1$

$$K_w = [H^+][OH^-] = 10^{-14}$$

Ionic product of water

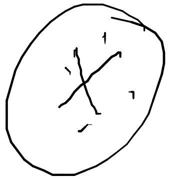
$$K_w = [H^+][OH^-] = 10^{-14}$$

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

$\times(-1)$

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

$$\boxed{pK_w = pH + pOH = 14}$$



Acidic: $[H_3O^+] > [OH^-]$

Neutral: $[H_3O^+] = [OH^-]$

Basic : $[H_3O^+] < [OH^-]$

ODL (Ostwald's Dilution Law)

weak acid

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Initial mol. of molecule	1	—	—
during diss	α	—	—
after diss.	$(1-\alpha)$	α	α
conc	$C(1-\alpha)$	$C\alpha$	$C\alpha$

Acc. to LMA

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$K_a = \frac{\cancel{C}\alpha \times C\alpha}{\cancel{C}(1-\alpha)}$$

$$K_a = \frac{C\alpha^2}{(1-\alpha)}$$

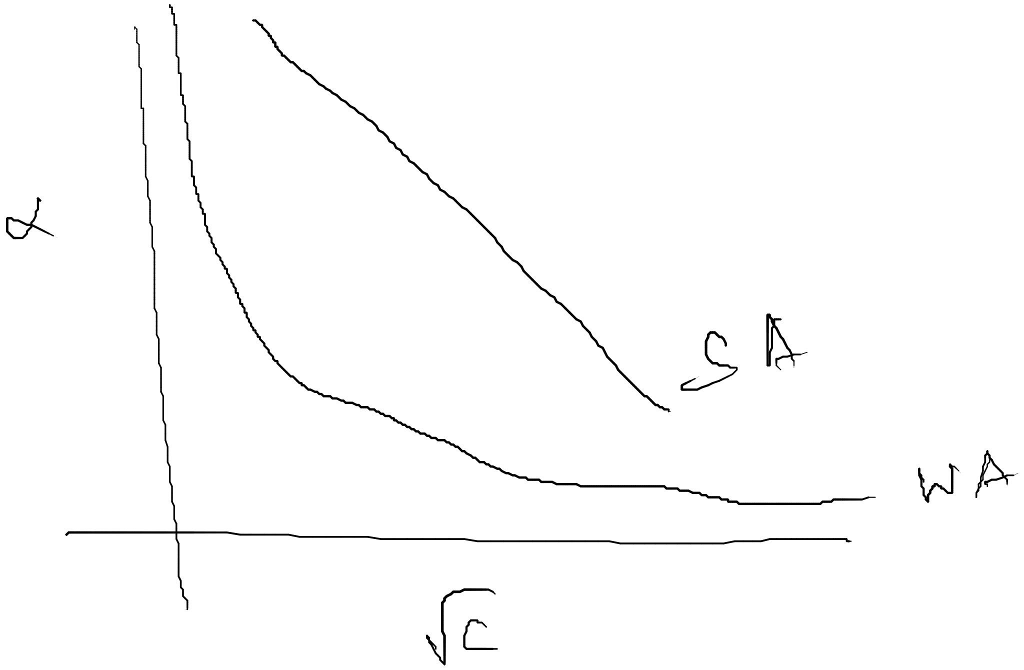
$\alpha << 1$

$$Ka = C\alpha^2$$

$$\boxed{\alpha = \sqrt{Ka/c}}$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

$$\alpha \propto \frac{1}{\sqrt{C}}$$



Weak base

$$\alpha = \sqrt{\frac{K_b}{C}}$$

dibasic acid

$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ bisulphate anion Ka_1

Sulphuric acid

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ sulphate anion Ka_2

$H_3PO_4 \rightarrow 3H^+$

tri basic acid

solubility product

$$BaSO_4(s) \xrightleftharpoons[\text{in water}]{\text{Saturated Solution}} Ba^{2+}(aq) + SO_4^{2-}(aq)$$

The equilibrium constant is given by the equation:

$K = \{[Ba^{2+}][SO_4^{2-}]\} / [BaSO_4]$

For a pure solid substance the concentration remains constant and we can write

$$K_{sp} = K[BaSO_4] = \boxed{[Ba^{2+}][SO_4^{2-}]} \qquad (7.39)$$

We call K_{sp} the *solubility product constant* or simply *solubility product*. The experimental value of K_{sp} in above equation at 298K is 1.1×10^{-10}. This means that for solid barium sulphate in equilibrium with its saturated

$NaCl$	$BaSO_4 \downarrow$	$AgCl \downarrow$
↓	↓	↓
H_2O	H_2O	H_2O
↓		
True soln.	Sparingly sol.	sp. sol.
C	S	S

$$K = \frac{\overbrace{[Ba^{2+}]\,[SO_4^{2-}]}^{s} \rightarrow s}{[BaSO_4] \rightarrow 1}$$

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

A salt may give on dissociation two or more than two anions and cations carrying different charges. For example, consider a salt like *zirconium phosphate* of molecular formula $(Zr^{4+})_3(PO_4^{3-})_4$. It dissociates into 3 zirconium cations of charge +4 and 4 phosphate anions of charge –3. If the molar solubility of zirconium phosphate is S, then it can be seen from the stoichiometry of the compound that

$[Zr^{4+}] = 3S$ and $[PO_4^{3-}] = 4S$

and $K_{sp} = (3S)^3 (4S)^4 = 6912\ (S)^7$

or $S = \{K_{sp} / (3^3\ 4^4)\}^{1/7} = (K_{sp} / 6912)^{1/7}$

$$Zr_3(PO_4)_4 \rightleftharpoons 3Zr^{4+} + 4PO_4^{3-}$$

$$S \qquad\qquad S$$

$$K = \frac{[Zr^{4+}]^3\,[PO_4^{3-}]^4}{Zr_3(PO_4)_4}$$

$$K_{sp} = (3S)^3(4S)^4$$

$$= 3^3 \cdot 4^4 \cdot S^7$$

$$K_{sp} = 6912S^7$$

Common ion effect

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \alpha_1$$

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+ \quad \alpha_2 \; ; \; \alpha_2 > \alpha_1$$

$$\underbrace{\underline{CH_3COOH} + \underline{CH_3COONa}}_{\text{buffer}} \rightleftharpoons \underline{\underline{2CH_3COO^-}} + H^+ + Na^+ \quad \alpha_3$$

$$\boxed{\alpha_3 < \alpha_1}$$