EQUILIBRI DI IDROLISI

1. SALE FORMATO DA ACIDO FORTE E BASE FORTE

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

$$Na^+ + H_2O \not\rightleftharpoons NaOH + H^+$$

$$Cl^- + H_2O \not\rightleftharpoons HCl + OH^-$$

} pH = 7

non c'è idrolisi

2. SALE FORMATO DA ACIDO DEBOLE E BASE FORTE

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

$$Na^+ + H_2O \not\rightleftharpoons NaOH + H^+$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \qquad K_i = \frac{K_w}{K_a}$$

idrolisi dell'anione – idrolisi basica; $[OH^-] = \sqrt{K_i c_s}$

3. SALE FORMATO DA ACIDO FORTE E BASE DEBOLE

$$AgNO_3 \longrightarrow Ag^+ + NO_3^-$$

$$NO_3^- + H_2O \not\rightleftharpoons HNO_3 + OH^-$$

$$Ag^+ + H_2O \rightleftharpoons Ag(OH) + H^+ \qquad K_i = \frac{K_w}{K_b}$$

idrolisi del catione – idrolisi acida; $[H^+] = \sqrt{K_i c_s}$

4. SALE FORMATO DA ACIDO DEBOLE E BASE DEBOLE

$$AB \longrightarrow A^- + B^+$$

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

idrolisi simultanea dell'anione e del catione $[H^+] = \sqrt{K_w \frac{K_a}{K_b}}$

EQUILIBRI DI IDROLISI

1. SALE FORMATOSI DA ACIDO FORTE E BASE FORTE

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

$$\left.\begin{array}{l} Na^+ + H_2O \longrightarrow \text{NO} \\ Cl^- + H_2O \longrightarrow \text{NO} \end{array}\right\} \; pH = 7$$

2. SALE FORMATO DA ACIDO DEBOLE E BASE FORTE: IDROLISI DELL' ANIONE

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

$$Na^+ + H_2O \longrightarrow \text{NO}$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$ pH basico

$$K_i = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} = \frac{K_w}{K_a}$$

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

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

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

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

$$K_i \cong \frac{[OH^-]^2}{[CH_3COO^-]} \cong \frac{[OH^-]^2}{C_s}$$

Trascurando gli OH^- che provengono da H_2O

Trascurando la quantità di anione che subisce idrolisi rispetto a quella iniziale

$$[OH^-] \cong \sqrt{K_i \cdot C_s}$$

A parità di concentrazione, se l'acido da cui si è formato il sale è più debole...:

CH_3COONa $c_s = 10^{-1}$ M
$K_a \simeq 10^{-5}$

$\alpha = 0.01\%$

$NaCN$ $c_s = 10^{-1}$ M
$K_a \simeq 10^{-9}$

$CN^- + H_2O \rightleftharpoons HCN + OH^-$

$[OH^-] = \sqrt{K_i \cdot c_s} = 10^{-3}$ M

$\alpha = \frac{[OH^-]}{c_s} = \frac{10^{-3}}{10^{-1}} = 10^{-2} = 1\%$

3. SALE FORMATO DA ACIDO FORTE E BASE DEBOLE: IDROLISI DEL CATIONE

$AgNO_3 \longrightarrow Ag^+ + NO_3^-$

$NO_3^- + H_2O \longrightarrow$ NO

$Ag^+ + H_2O \rightleftharpoons AgOH + H^+$; pH acido

$K_i = \frac{[AgOH][H^+]}{[Ag^+]} = \frac{K_w}{K_b}$

$[H^+] = \sqrt{K_i \cdot c_s}$

$AgOH \rightleftharpoons Ag^+ + OH^-$

$K_b = \frac{[Ag^+][OH^-]}{[AgOH]}$

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

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

Es. $AgNO_3$ 10^{-1} M $K_b = 10^{-3}$
$K_i = 10^{-11}$

$[H^+] = \sqrt{K_i \cdot c_s} = 10^{-6}$ M

$\alpha = \frac{[H^+]}{c_s} = 10^{-5} = 0.001\%$

$Na_2S \longrightarrow 2\,Na^+ + S^=$

$S^= + H_2O \rightleftharpoons HS^- + OH^-$

$K_{i_1} = \dfrac{[HS^-][OH^-]}{[S^=]} = \dfrac{K_w}{K_{a_2}}$

$HS^- + H_2O \rightleftharpoons H_2S + OH^-$

$K_{i_2} = \dfrac{[H_2S][OH^-]}{[HS^-]} = \dfrac{K_w}{K_{a_1}}$

$H_2S \rightleftharpoons H^+ + HS^-$

$K_{a_1} = \dfrac{[H^+][HS^-]}{[H_2S]}$

$HS^- \rightleftharpoons H^+ + S^=$

$K_{a_2} = \dfrac{[H^+][S^=]}{[HS^-]}$

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

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

GRADO DI IDROLISI

Rapporto tra n°. moli di sale idrolizzato e n°. moli iniziali.

$A^- + H_2O \rightleftharpoons HA + OH^-$

$\alpha = \dfrac{[HA]}{C_S}$

Es. CH_3COONa $C_S = 10^{-1}\,M$ $K_a \simeq 10^{-5}$

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

$[CH_3COOH] = [OH^-]$; $\alpha = \dfrac{[OH^-]}{C_S}$; $[OH^-] = \sqrt{K_i \cdot C_S} =$

$= \sqrt{\dfrac{K_w}{K_a} \cdot C_S} = \sqrt{\dfrac{10^{-14}}{10^{-5}} \cdot 10^{-1}} = \sqrt{10^{-9} \cdot 10^{-1}} = \sqrt{10^{-10}} = 10^{-5}\,M$

$\alpha = \dfrac{[OH^-]}{C_S} = \dfrac{10^{-5}}{10^{-1}} \simeq 10^{-4} \simeq 0.01\,\%$

In una soluzione più diluita ($C_S = 10^{-3}\,M$)

$[OH^-] = \sqrt{K_i \cdot C_S} = \sqrt{10^{-9} \cdot 10^{-3}} = \sqrt{10^{-12}} = 10^{-6}\,M$

$\alpha = \dfrac{[OH^-]}{C_S} = \dfrac{10^{-6}}{10^{-3}} = 10^{-3} \simeq 0.1\,\%$; IN soluz più diluite > il grado di idrolisi

$$AB \longrightarrow A^- + B^+$$

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad K_i = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{K_w}{K_b}$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

4. SALE FORMATO DA ACIDO DEBOLE E BASE DEBOLE: IDROLISI SIMULTANEA DELL'ANIONE E DEL CATIONE

$$AB \longrightarrow A^- + B^+$$

$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad K_{i,an.} = \frac{[HA][OH^-]}{[A^-]} = \frac{K_w}{K_a}$$

$$B^+ + H_2O \rightleftharpoons BOH + H^+ \qquad K_{i,cat.} = \frac{[BOH][H^+]}{[B^+]} = \frac{K_w}{K_b}$$

$$A^- + B^+ + H_2O \rightleftharpoons HA + BOH$$

$$K_{i\,TOT} = \frac{[HA][BOH]}{[A^-][B^+]} = \frac{[HA][BOH][H^+][OH^-]}{[A^-][B^+][H^+][OH^-]} = \frac{K_w}{K_a \cdot K_b}$$

$$[HA] \cong [BOH] \; ; \; [A^-] \cong [B^+]$$

$$K_{i\,TOT} = \frac{K_w}{K_a \cdot K_b} = \frac{[HA]^2}{[A^-]^2} = \frac{[HA]^2[H^+]^2}{[A^-]^2[H^+]^2} = \frac{[H^+]^2}{K_a^2}$$

$$[H^+]^2 = \frac{K_w \cdot K_a^2}{K_a \cdot K_b} = K_w \cdot \frac{K_a}{K_b} \; ; \; \boxed{[H^+] = \sqrt{K_w \cdot \frac{K_a}{K_b}}}$$

CASO PARTICOLARE: SALE FORMATO DA IONE ANFOLITA

$$NaHCO_3 \longrightarrow Na^+ + HCO_3^-$$

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

$$K_{i_2} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} = \frac{K_w}{K_{a_1}}$$

($CO_3^= + H_2O \underset{K_{i_1}}{\rightleftharpoons} HCO_3^- + OH^-$; $HCO_3^- + H_2O \underset{K_{i_2}}{\rightleftharpoons} H_2CO_3 + OH^-$)

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^=$$

$$K_{a_2} = \frac{[CO_3^=][H_3O^+]}{[HCO_3^-]}$$

$$[H^+] = \sqrt{K_w \cdot \frac{K_a}{K_b}} = \sqrt{K_w \cdot \frac{K_{a_2}}{K_{i_2}}} = \sqrt{K_w \cdot \frac{K_{a_2} \cdot K_{a_1}}{K_w}} = \sqrt{K_{a_1} K_{a_2}}$$

$$\boxed{[H^+] = \sqrt{K_{a_1} K_{a_2}}}$$

5. EFFETTO DEL pH SULL'IDROLISI

Es. CH_3COONa $\quad c_s = 10^{-1}\ M \quad K_{a_{CH_3COOH}} \cong 10^{-5}$

$\alpha_i \cong 0.01\%$

a pH = 12

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$K_a = \frac{[A^-][H^+]}{[HA]} \cong 10^{-5} = \frac{[CH_3COO^-] \cdot 10^{-12}}{[CH_3COOH]} \simeq 10^{-5}$$

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = 10^7 \Longrightarrow [CH_3COO^-] \gg [CH_3COOH] \cong 10^{-1}\ M$$

$$[CH_3COOH] = \frac{[CH_3COO^-]}{10^7} = \frac{10^{-1}}{10^7} = 10^{-8}\ M$$

$$\alpha_i = \frac{[CH_3COOH]}{C_S} = \frac{10^{-8}}{10^{-1}} = 10^{-7} = 0.00001\ \%$$

a pH = 0

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$K_a = \frac{[CH_3COO^-] \cdot 1}{[CH_3COOH]} \cong 10^{-5} \qquad \frac{[CH_3COO^-]}{[CH_3COOH]} = 10^{-5}$$

$$[CH_3COOH] \gg [CH_3COO^-] \simeq 10^{-1}\ M$$

$$[CH_3COO^-] = 10^{-5} \cdot [CH_3COOH] = 10^{-6}\ M$$

$$\alpha_i = \frac{[CH_3COOH]}{C_S} = \frac{10^{-1}}{10^{-1}} = 1 = 100\ \%$$

ESEMPI DI EQUILIBRI DI IDROLISI NELLE PROCEDURE DI ANALISI QUALITATIVA

- Ricerca degli Acetati

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$CH_3COO^- + HSO_4^- \longrightarrow CH_3COOH + SO_4^=$$

- Ricerca dei Carbonati

$$CO_3^= + H_2O \rightleftharpoons HCO_3^- + OH^-$$

$$+ H_2O \rightleftharpoons H_2CO_3 + OH^-$$

$$\uparrow\downarrow$$

$$H_2O + CO_2$$

$$CO_3^= + 2H^+ \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2$$

$$+ Ba(OH)_2 \rightarrow BaCO_3 + H_2O$$

- Ricerca dello ione Ammonio

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

- Ricerca di I^-, Br^- e Cl^- dalla solut. alcalina degli ANIONI

$$Ag^+ + H_2O \rightleftharpoons Ag(OH) + H^+$$

$$CO_3^= + 2H^+ \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2$$

- Ricerca dei SOLFATI dalla solut. alcaline degli ANIONI

$$Ba^{+2} + CO_3^= \rightleftharpoons BaCO_3 \downarrow$$

$$Ba^{+2} + SO_4^= \rightleftharpoons BaSO_4$$

$$CO_3^= + 2H^+ \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2$$