/ / التاريخ:

Analytical Chemistry

* Reaction

irreversible

$2H_2 + O_2 \rightarrow 2H_2O$

Reversible

$A + B \rightleftharpoons C + D$

at some Point the rate of Forward = rate of backward

∴ equilibrium

Ex: weak Acids & weak bases

* $aA + bB \rightleftharpoons cC + dD$

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

eq^m Constant

* $H_2 + Br_2 \rightleftharpoons 2HBr$

$$K = \frac{[HBr]^2}{[H_2][Br_2]}$$

For H_2O :

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$\cancel{K} = \frac{[OH^-][H_3O^+]}{[H_2O]^2}$$

$K[H_2O]^2 = K_w = [OH^-][H^+]$

K_w → ion Product Constant for water

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

$1\times10^{-7} \times 1\times10^{-7}$

taking -log of Both Sides:

$-\log(K_w) = -\log[OH^-] - \log(H^+)$

$pK_w = pOH + pH$

$14 = pOH + pH$

for water, $pH = pOH = \underline{\underline{7}}$

Some molecules of water dissociate into H_3O^+ (for every H_3O^+, OH^- is formed

For weak Acids

$HNO_2 + H_2O \rightleftharpoons NO_2^- + H_3O^+$

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

K_a → Constant for Acid

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* For weak bases :-

$$NH_3 + H_2O \rightleftharpoons \overset{+}{N}H_4 + OH^-$$

$$K_b = \frac{[\overset{+}{N}H_4][OH^-]}{[NH_3]}$$

Relation bet^n K_a & K_b :-

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

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

$$K_a = \frac{[H_3O][\cancel{A^-}]}{\cancel{[HA]}} \qquad K_b = \frac{[OH^-]\cancel{[HA]}}{\cancel{[A^-]}}$$

$$\cancel{K_w = K_a \cdot K_b}$$

$$K_a \cdot K_b = [H_3O^+][OH^-] = K_w = 1 \times 10^{-14}$$

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9-7

(a) $C_6H_5NH_2 \underset{}{\overset{H_2O}{\rightleftharpoons}} C_6H_5\overset{+}{N}H_4 + OH^-$

$$K_b = \frac{[C_6H_5\overset{+}{N}H_4][OH^-]}{[C_6H_5NH_2]} = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{}$$

(b) $HClO \overset{H_2O}{\rightleftharpoons} H_3O^+ + ClO^-$

$$K_a = \frac{[ClO^-][H_3O^+]}{[HClO]} = 3\times10^{-8}$$

(c) $CH_3NH_3Cl \rightleftharpoons CH_3\overset{+}{N}H_3 + Cl^-$

(d) $H_3AsO_3 \underset{Ka_1}{\overset{H_2O}{\rightleftharpoons}} H_2AsO_3^- + H_3O^+$

$H_2AsO_3 + H_2O \underset{Ka_2}{\rightleftharpoons} HAsO_3^{2-} + H_3O^+$

$HAsO_3 + H_2O \underset{Ka_3}{\rightleftharpoons} AsO_3^{5-} + H_3O^+$

$H_3AsO_3 + 3H_2O \rightleftharpoons AsO_3^{3-} + 3H_3O^+$

$$K = Ka_1 \cdot Ka_2 \cdot Ka_3 = \frac{[AsO_3][H_3O^+]^3}{[H_3AsO_3]} = \text{\_\_\_\_}$$

assumption ...

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$\frac{C_{HA}}{K_a} > 10^3$ error < 1.5%

20.

$C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$

0.0300M   zero   zero

0.0300 − x   x   x

$$K_a = \frac{[H_3O^+][C_6H_5COO^-]}{[C_6H_5COOH]}$$

$$K_a = \frac{x^2}{[0.03 - x]}$$

assume $[C_6H_5COOH] = [HA]$

$$K_a = \frac{x^2}{0.03}$$

$0.03 K_a = x^2$

$x = \sqrt{0.03 K_a}$

$K_a = \cancel{\ }$

$x = \sqrt{6.5\times10^{-5}\times0.03}$

$[H_3O^+] = x = 1.39\times10^{-3}$

$$[OH^-] = \frac{1\times10^{-14}}{1.39\times10^{-3}} \quad \frac{K_w}{[H_3O^+]}$$

$[OH^-] = 7.1\times10^{-12}$

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NO assumptions made

$$K_a = \frac{x^2}{0.03 - x}$$

$$K_a \times 0.03 - x K_a = x^2$$

$$1.95 \times 10^{-6} - x K_a = x^2$$

$$x^2 + 6.5 \times 10^{-5} x - 1.95 \times 10^{-6} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - (4 \times a \times c)}}{2a}$$

$[H_3O^+] = x = 1.3 \times 10^{-3}$ $\qquad$ $[OH^-] = 7.6 \times 10^{-12}$

$$\text{Error} = \frac{(1.39 - 1.3) \times 10^{-3}}{1.39} \times 100$$

$= \_\_\_\_ \%$

hydrazoic Acid التاريخ:

$$HN_3 + H_2O \rightleftharpoons H_3O^+ + N_3^-$$

0.06 zero zero

0.06 − x x x

$$K_a \approx \frac{[x][x]}{0.06 - x}$$

$$C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3^+ + OH^-$$

0.1 zero zero

0.1 − x x x

$$K_b \approx \frac{[x]^2}{0.1 - x}$$

$$0.1\,K_b = [x]^2 \qquad x = \sqrt{0.1\,K_b}$$

$x =$

$$C_6H_5COONa \rightleftharpoons C_6H_5COO^- + Na^+$$

$$C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + OH^-$$

0.2 zero zero

0.2 − x x x

$$K_b \approx \frac{[x]^2}{0.2 - x}$$

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$$\frac{1\times10^{-14}}{6.28\times10^{-5}} = \frac{[X]^2}{0.2 - X} \text{ ignore}$$

$$[OH^-]x = \sqrt{\frac{1\times10^{-14}}{6.28\times10^{-5}} \times 0.2} = \underline{\underline{5.64\times10^{-7}}}\ M$$

$$[H^+] = \frac{1\times10^{-14}}{5.64\times10^{-7}} = 1.77\times10^{-8}\ M$$

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* Buffer Solutions:

Are solutions that resist small changes in pH due to the addition of strong acid or strong base.

$$HB \rightleftharpoons H^+ + B^-$$

$$K_a = \frac{[H^+][B^-]}{[HB]}$$

$$[H^+] = \frac{K_a [HB]}{[B^-]}$$

$$\log[H^+] = \log[K_a] + \log[HB] - \log[B^-]$$

$$\log[H^+] = \log K_a + \log\left(\frac{HB}{B^-}\right) \quad \times -1$$

$$pH = pK_a + \log\left(\frac{B^-}{HB}\right)$$

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1.4×10^{-4}

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Example 9

$pH = pK_a + \log\left(\frac{salt}{Acid}\right)$

$= -\log(1.8 \times 10^{-4}) + \log\left(\frac{1}{0.4}\right)$

$= 4.14$ #

Lactic Acid

$K_a = 1.4 \times 10^{-4}$

$[HA] = \frac{1}{550 \times 10^{-3}} =$ $[A^-] = \frac{1}{550 \times 10^{-3}} =$

$pH = pK_a + \log\left[\frac{A^-}{HA}\right]$

$pH = -\log(1.4 \times 10^{-4}) + \log\left(\frac{1.81}{1.81}\right)$

$pH = 3.85$ $[H^+] = 1.41 \times 10^{-4}$ M

$[A^-] = \frac{34.6}{[23 + (3 \times 12) + 5 + (3 \times 16)] \times 550 \times 10^{-3}} = 0.561$ M

=

$[HA] = 1.20$ M

$pH = 3.523$ $[H^+] = 2.99 \times 10^{-4}$ M

(a) $pH = pKa + \log\left(\frac{A^-}{HA}\right)$

$pH = -\log(1.8\times10^{-5}) + \log\left(\frac{\frac{5\times10^{-3}}{200\times10^{-3}}}{0.1}\right)$

$pH = 4.34$

~~pH = -log (1.8x10^-5) + log (~~

$HOAC + NaOH \longrightarrow CH_3COONa + H_2O$

$10^{-3}\times0.175\times100$ $\quad 0.05\times100\times10^{-3}$ $\quad$ zero $\quad$ zero

0.0175 mol $\quad 5\times10^{-3}$ mol $\quad$ zero $\quad$ zero

0.0125 mol $\quad$ Zero $\quad 5\times10^{-3}$ mol $\quad 5\times$

$pH = -\log(1.8\times10^{-5}) + \log\left(\frac{\frac{5\times10^{-3}}{200}}{\frac{0.0125}{200}}\right)$

$pH = 4.346$

$CH_3COONa + HCl \longrightarrow ??$

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

0.0420

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + H_3O^+$

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(a) $pH = pK_a + \log\left(\frac{A^-}{HA}\right)$

$pH = -\log(1.8\times10^{-5}) + \log\left(\frac{\frac{8\times10^{-3}}{200\times10^{-3}}}{0.1}\right)$

$pH = 4.34$

~~pH = -log (1.8×10^-5) + log (~~

$\underline{HOAC} + NaOH \longrightarrow \underline{CH_3COONa} + H_2O$

$10^{-3}\times0.175\times100$ $\quad 0.05\times100\times10^{-3}$ $\quad$ zero $\quad$ zero

0.0175 mol $\quad 5\times10^{-3}$ mol $\quad$ zero $\quad$ zero

0.0125 mol $\quad$ zero $\quad 5\times10^{-3}$ mol $\quad 5\times10^{-3}$

$pH = -\log(1.8\times10^{-5}) + \log\left(\frac{\frac{5\times10^{-3}}{200}}{\frac{0.0125}{200}}\right)$

$pH = 4.346$

$CH_3COONa + HCl \longrightarrow ??$

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

0.0420

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + H_3O^+$