Ch 13 Acids and Bases

13-1 BrΦnsted-Lowry acid-base model
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§ 13-1 BrΦnsted-Lowry acid-base model

Acid: a proton (H^+ ion) donor
Base: a proton acceptor

conjugated acid-base

$$HB_{(aq)} + A^-_{(aq)} \rightleftharpoons HA_{(aq)} + B^-_{(aq)}$$

acid 1 base 2 acid 2 base 1

conjugated acid-base

Ex 13-1:
a) HNO_2 之 conjugated base? F^- 之 conjugated acid?
b) HCO_3^- 之 conjugated base 及之 conjugated acid?

Sol: a) NO_2^-; HF
b) CO_3^{2-}; H_2CO_3
conjugated base conjugated acid

§ 13-2 The ion product of water

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

25°C $K_w = 10^{-14}$
65°C $K_w = 10^{-13}$
100°C $K_w = 10^{-12}$

at 25°C $[H^+] > 1.0\times10^{-7}$ acidic
$[H^+] < 1.0\times10^{-7}$ basic

§ 13-3 pH and pOH

$$pH = -\log[H^+] = -\log[H_3{}^+O]$$

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

25^oC, pH < 7.0 acidic
pH = 7.0 neutral
pH > 7.0 basic

25^oC, pH + pOH =14

Ex 13-2: 25^oC,
a) $[H^+]$ and pH of a tap-water sample $[OH^-] = 2.0\times10^{-7}$
b) $[H^+]$ and $[OH^-]$ of a human body pH = 7.4
c) pOH of a solution which $[H^+] = 5.0[OH^-]$

Sol: a) 25^oC $[H^+]\cdot[OH^-] = 1.0\times10^{-14}$

$$[H^+]\cdot 2.0\times10^{-7} = 1.0\times10^{-14}$$

$$[H^+] = 5.0\times10^{-8}$$

$$pH = -\log[H^+] = 7.3$$

b) pH = 7.4 $[H^+] = 4.8\times10^{-8}$

$$[OH^-] = \frac{1.0\times10^{-14}}{4.0\times10^{-8}} = 2.5\times10^{-7}$$

c) $[H^+] = 5.0[OH^-]$

$$5.0[OH^-]\cdot[OH^-] = 1.0\times10^{-14}$$

$$[OH^-] = 4.5\times10^{-8}$$

$$pOH = -\log[OH^-] = \cancel{7.35} \rightarrow 7.4$$

§ pH for strong acids and strong bases

Strong acids: HCl, HBr, HI completely ionized
$HClO_4$, HNO_3, H_2SO_4

Strong bases: LiOH, NaOH, KOH completely ionized
$Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$

↙MM = 171.3g/mole

Ex 13-3: pH value of 1.00g $Ba(OH)_2$ dissolving in water to form 1L solution.

Sol: $Ba(OH)_{2(g)} + H_2O_{(l)} \rightarrow Ba^{2+}_{(aq)} + 2OH^-_{(aq)}$

$$n_{Ba(OH)_2} = \frac{1}{171.3} = 5.84\times10^{-3}$$

$$M_{Ba(OH)_2} = \frac{5.84\times10^{-3}}{1} = 5.84\times10^{-3}M$$

$$M_{OH^-} = 2\cdot5.84\times10^{-3} = 1.17\times10^{-2}M$$

$$pOH = -\log[OH^-] = 1.93$$

$$pH = 14.0 - 1.93 = 12.07$$

§ 13-4 Weak acids and their equilibrium constants

weak acid HB

$$HB_{(aq)} + H_2O_{(l)} \rightarrow H_3{}^+O_{(aq)} + B^-_{(aq)}$$

↳ 少於 1%解離

弱酸多爲下列二類之一

1. Molecules containing an ionizable hydrogen atom.
   ex: $HNO_{2(aq)} + H_2O \rightarrow H_3{}^+O_{(aq)} + NO_2{}^-_{(aq)}$
2. 陽離子 cations ex: $NH_4{}^+$

$$NH_4{}^+_{(aq)} + H_2O \rightarrow H_3{}^+O_{(aq)} + NH_3$$

0.1M $NH_4Cl_{(aq)}$ pH = 5

§ The equilibrium constant for a weak acid

$$HB_{(aq)} + H_2O \rightleftharpoons H_3{}^+O(aq) + B^-_{(aq)}$$

簡化 ⇒

$$HB_{(aq)} \rightleftharpoons H^+(aq) + B^-_{(aq)}$$

$$K_a = \frac{[H^+][B^-]}{[HB]}$$ Ka : acid equilibrium constant

HNO_2 $K_a = 6.0\times10^{-4}$ $pK_a = 3.22$ Ka ↑⇒酸性↑

HCN $K_a = 5.8\times10^{-10}$ $pK_a = 9.24$

$pK_a = -\log Ka$

Ex 13-4: Acetic acid $HC_2H_3O_2$ (CH_3COOH) and hydrated zinc cation $Zn(H_2O)_4^{2+}$ 四水合鋅離子

a) 解離方程式？

b) Which is the stronger acid?

c) What is the pKa of $Zn(H_2O)_4^{2+}$?

Sol:

a) $HC_2H_3O_{2(aq)} + H_2O \rightleftharpoons H_3^+O_{(aq)} + C_2H_3O_{2(aq)}^-$

$Zn(H_2O)_{4(aq)}^{2+} + H_2O \rightleftharpoons Zn(H_2O)_3(OH)_{(aq)}^+ + H_3^+O_{(aq)}$

b) $HC_2H_3O_2 \quad K_a = 1.8\times10^{-5}$

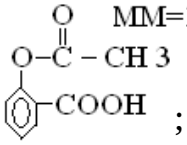
$Zn(H_2O)_4^{2+} \quad K_a = 3.3\times10^{-10}$ } Table 13-2

$\therefore HC_2H_3O_2$ is the stronger acid **Q** K_a較大

c) $pK_a = -\log K_a$

$= -\log 3.3\times10^{-10}$

$= 9.48$

Ex 13-5: Aspirin: $HC_9H_7O_4$ 

; 3.60g dissolve in water per liter pH = 2.60. Calculate K_a?

Sol:

$$M_{HC_9H_7O_4} = \frac{3.60/180.15}{1} = 2.0\times10^{-2}\,M$$

$pH = 2.60 \quad [H^+] = 2.5\times10^{-3}\,M$

$$HC_9H_7O_{4(aq)} \longrightarrow H_{(aq)}^+ + C_9H_7O_{4(aq)}^-$$

starting	0.0200M	–	–
equilibrium	$0.020 - 0.0025 = 0.0175M$	0.0025	0.0025

$$K_a = \frac{[H^+][C_9H_7O_4^-]}{[HC_9H_7O_4]} = \frac{(2.5\times10^{-3})^2}{1.75\times10^{-2}} = 3.6\times10^{-4}$$

$$\text{percent ionization} = \frac{[H^+]_{eq}}{[HB]_o}\times100$$

Ex 3-5: % ionization $= \frac{2.5\times10^{-3}}{2\times10^{-2}}\times100 = 13\%$

Ex 13-6: What is the percent ionization of the acid?
Sol: % ionization = 1/5 × 100 = 20%

§ Calculate of $[H^+]$ in a water solution of a weak acid.

由 K_a 求$[H^+]$

Ex 13-7: Nicotinic acid, $HC_6H_4O_2N$ (HNic)($Ka = 1.4\times10^{-5}$); 0.1mole of nicotinic acid dissolve in water to foam 1.0L solution, 求$[H^+]$ =?

Sol:

$$HNic_{(aq)} \rightleftharpoons H^+_{(aq)} + Nic^-_{(aq)}$$

starting	0.1	–	–
equilibrium	$0.1-x$	x	x

$$K_a = \frac{[H^+][Nic^-]}{[HNic]} = 1.4\times10^{-5}$$

$$\Rightarrow \frac{x\cdot x}{0.1-x} = 1.4\times10^{-5}$$

$$\Rightarrow \quad \frac{x^2}{0.1} = 1.4\times10^{-5}$$

$$x^2 = 1.4\times10^{-6}$$

$$x = 1.2\times10^{-3}$$

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

$$\frac{x}{a} \le 0.05 \ \ (5\%)$$

$a - x \approx a$ 才成立

Ex 13-8: Calculate $[H^+]$ in a 0.100M HNO_2, $Ka = 6.0\times10^{-4}$.

Sol:

$$HNO_{2(aq)} \longrightarrow H^+_{(aq)} + NO^-_{2(aq)}$$

starting	0.100	–	–
equilibrium	$0.100-x$	x	x

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} = 6.0\times10^{-4}$$

$$\frac{x\cdot x}{0.100-x} = 6.0\times10^{-4}$$

若 $0.100 - x \approx 0$

$$x^2 = 6.0\times10^{-5}$$

$$x = \boxed{7.7\times10^{-3}}$$

不妥 >5%

$$a = 0.1 \quad \frac{x}{a} = \frac{7.7\times10^{-3}}{0.1} = 7.75\times10^{-2} > 0.05$$

∴解法一：二次方程式法：

$$\frac{x^2}{0.100 - x} = 6.0\times10^{-4}$$

二次方程式公式： $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$$x^2 + (6.0\times10^{-4})x - 6.0\times10^{-5} = 0$$

$$x = \frac{-6.0\times10^{-4} \pm \sqrt{(6.0\times10^{-4})^2 - 4\cdot 6.0\times10^{-5}}}{2}$$

$$x = 7.4\times10^{-3}\text{M} \quad \text{or} \quad -8.0\times10^{-3}\text{M}$$

or 解法二： The method of successive approximations 連續近似值法：

$$[HNO_2] = 0.100 - \boxed{7.7\times10^{-3}}$$

$$= 0.092$$

$$\frac{x^2}{0.100 - x} = 6.0\times10^{-4}$$

$$\frac{x^2}{0.092} = 6.0\times10^{-4}$$

$$x^2 = 5.5\times10^{-5}$$

$$x = 7.4\times10^{-3}$$

§ Polyprotic weak acids 多質子弱酸

$$H_3PO_{4(aq)} \rightleftharpoons H^+_{(aq)} + H_2PO^-_{(aq)} \qquad K_{a1} = 7.1\times10^{-3}$$

$$H_2PO^-_{4(aq)} \rightleftharpoons H^+_{(aq)} + HPO^{2-}_{(aq)} \qquad K_{a2} = 6.2\times10^{-8}$$

$$HPO^{2-}_{4(aq)} \rightleftharpoons H^+_{(aq)} + PO^{3-}_{(aq)} \qquad K_{a3} = 4.5\times10^{-13}$$

$$K_{a1} > K_{a2} > K_{a3}$$

Ex 13-9: 0.0010M $H_2CO_{3(aq)}$之 pH?

Sol:

Table 13-3 $\Rightarrow$

$$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)} \quad K_{a1} = 4.4\times10^{-7}$$

$$HCO^-_{3(aq)} \rightleftharpoons H^+_{(aq)} + CO^{2-}_{3(aq)} \quad K_{a2} = 4.7\times10^{-11}$$

	$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)}$		
starting	0.0010	–	–
equilibrium	0.0010-x	x	x

$$K_{a1} = \frac{x^2}{0.0010 - x} = 4.4\times10^{-7}$$

$$0.0010 - x \approx 0.0010$$

$$x^2 = 4.4\times10^{-10}$$

$$x = 21\times10^{-5}$$

$$pH = 4.68$$

第二階段可以忽略 ∵K_a較小∴影響小

§ 13-5 Weak bases and their equilibrium constants

弱鹼分兩類

1. molecules; ex: NH_3

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

2. Anion; 爲弱酸之陰離子:

$$F^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HF_{(aq)} + OH^-_{(aq)}$$

Ex 13-10:水解方程式

a) NO_2^- b) Na_2CO_3 c) $KHCO_3$

Sol:

a) $NO^-_{2(aq)} + H_2O \rightleftharpoons HNO_{2(aq)} + OH^-_{(aq)}$

b) $CO^{2-}_{3(aq)} + H_2O \rightleftharpoons HCO^-_{3(aq)} + OH^-_{(aq)}$

c) $HCO^-_{3(aq)} + H_2O \rightleftharpoons H_2CO_{3(aq)} + OH^-_{(aq)}$

$$B^-_{(aq)} + \cancel{H_2O} \rightleftharpoons HB_{(aq)} + OH^-_{(aq)}$$

$$K_b = \frac{[HB][OH^-]}{[B^-]}$$

$$pK_b = -\log K_b$$

NH_3 $\quad K_b = 1.8\times10^{-5} \quad pK_b = 4.74$

$C_2H_3O_2^-$ $K_b = 5.6\times10^{-5} \quad pK_b = 9.25$

§ Calculation of $[OH^-]$ in water solution of a weak base

Ex 13-11: pH of 0.10M NaF K_b for F^- = 1.4×10^{-11}

Sol:

$$F^- \rightleftharpoons HF + OH^-$$

satrting	0.10	–	–
equilibrium	$0.10-x$	x	x

$$K_b = \frac{x\cdot x}{0.1-x} = 1.4\times10^{-11}$$

$0.1-x \approx 0.1$

$$x^2 = 1.4\times10^{-12}$$

$$[OH^-] = x = 1.2\times10^{-6}\,M$$

$$pOH = 5.92$$

$$pH = 14 - pOH = 8.08$$

§ Relation between K_a and K_b

$$HB_{(aq)} \rightleftharpoons H^+_{(aq)} + B^-_{(aq)} \qquad K_a$$

$$+)\ B^-_{(aq)} + H_2O \rightleftharpoons HB_{(aq)} + OH^-_{(aq)} \qquad K_b$$

$$H_2O \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \qquad K = K_a\cdot K_b = K_w$$

25^oC K = 10^{-14}

$$K_{HNO_2}\cdot K_{NO_2^-} = 6.0\times10^{-4}\cdot1.7\times10^{-11}$$

$$= 1.0\times10^{-14}$$

BrΦnsted-Lowry acid:

a) strong acid: $HClO_4$, H_2SO_4…are stronger proton donors than the H_3^+O ion

b) weak acid: HF, HI…are weaker proton donors than the H_3^+O ion

c) species, such as C_2H_5OH; which are weak proton donor than H_2O molecule.

BrΦnsted-Lowry base:

a) strong base (H^-,…), are stronger than proton acceptor than OH^- ion.

b) weak base (F^-,…),are weaker than proton acceptor than OH^- ion.

c) anions of stronger acid (ClO_4^-, NO_3^-,…) weaker proton acceptor than H_2O.

strong acid:

$$HClO_{4(aq)} + H_2O_{(l)} \longrightarrow H_3^+O_{(aq)} + ClO_{4(aq)}^-$$

$$HCl_{(aq)} + H_2O_{(l)} \longrightarrow H_3^+O_{(aq)} + F_{(aq)}^-$$

$$HNO_{3(aq)} + H_2O_{(l)} \longrightarrow H_3^+O_{(aq)} + NO_{3(aq)}^-$$

stronger base:

$$H_{(aq)}^- + H_2O_{(l)} \longrightarrow OH_{(aq)}^- + H_{2(aq)}$$

$$O_{(aq)}^{2-} + H_2O_{(l)} \longrightarrow OH_{(aq)}^- + OH_{(aq)}^-$$

$$C_2H_5O_{(aq)}^- + H_2O_{(l)} \longrightarrow OH_{(aq)}^- + C_2H_5O_{(aq)}$$

H^-, O^{2-}, $C_2H_5O^-$在水溶液中不存在

§ 13-6 Acid-base properties of salt solutions

Table 13-5 Acid-base properties of ions in water solution.

Anion	spectator Cl^-, Br^-, I^- ClO_4^-, NO_3^-	Basic $C_2H_3O_2^-$, CO_3^{2-} F^-, PO_4^{3-} many others	Acidic
Cation	Li^+, Na^+, K^+ Ca^{2+}, Sr^{2+}, Ba^2		NH_4^+, Al^{3+}, Mg^{2+} transition metal ions

Ex 13-12: Consider water solution

NH_4I, $Zn(NO_3)_2$, $KClO_4$, Na_3PO_4 爲酸鹼或中性

Sol:

Salt	Cation	Anion	Solution of salt
NH_4I	NH_4^+(acidic)	I^-(spectator)	acidic
$Zn(NO_3)_2$	Zn^{2+}(acidic)	NO_3^{2-}(spectator)	acidic
$KClO_4$	K^+(spectator)	ClO_4^-(spectator)	neutral
Na_3PO_4	Na^+(spectator)	PO_4^{3-}(basic)	basic

通則：

$K_a > K_b$ 酸性 NH_4F, $K_{a,NH_4^+} = 5.6\times10^{-10}$

$K_{b,F^-} = 1.4\times10^{-11}$

$K_a < K_b$ 鹼性 NH_4ClO $K_{a,NH_4^+} = 5.6\times10^{-10}$

$K_{b,ClO_4^-} = 3.6\times10^{-7}$