Chapter 7 Acids & Bases
第七章 酸與鹼

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- **What is acid? What is base?**
  何謂酸？何謂鹼？

- **Are acids and bases two classes of substances that have opposite properties, and their character could be canceled off by meeting each other?**
  酸與鹼是兩種性質相反的物質，相遇時彼此的性質就相互抵銷嗎？

Background *酸鹼的歷史*

- ***By tastes*** *感官的認識*

  - ***Acids are a class of substances that taste sour***
    酸嚐起來是「酸」的

  - ***Bases (alkalis) are a class of substances that taste bitter***
    鹼嚐起來是「苦」的

By Alchemist Experience
煉金術士對酸與鹼的認識

- ***HCl was called salt spirit*** ***HCl**稱作鹽精*
- ***Many metal containing minerals gave alkalis in water***
  許多含金屬的礦物在水中呈現鹼性
- ***Minerals without metal often give acidic solutions***
  許多不含金屬的礦物在水中呈現酸性

能舉例嗎？

***Arrhenius concept** – The First Modern Theory*

阿瑞尼士理論 1884

- ***Acids produce hydrogen ion in aqueous solutions***
  酸在水溶液中產生氫離子(H^+)

- ***Bases produce hydroxide ion in aqueous solutions***
  鹼在水溶液中產生氫氧根離子(OH^-)

The Content of Arrhenius Concept
阿瑞尼士理論的精義

- ***Theory of Ionization*** *游離說*

  $$\mathrm{HCl}_{(aq)} \longrightarrow \mathrm{H}^{+}_{(aq)} + \mathrm{Cl}^{-}_{(aq)}$$

  $$\mathrm{NaOH}_{(aq)} \longrightarrow \mathrm{Na}^{+}_{(aq)} + \mathrm{OH}^{-}_{(aq)}$$

  $$\mathrm{NaCl}_{(aq)} \longrightarrow \mathrm{Na}^{+}_{(aq)} + \mathrm{Cl}^{-}_{(aq)}$$

- ***Electrolytes & Non-electrolytes***
  電解質與非電解質

Brønsted-Lowry concept
布忍司特—羅瑞理論

- **Acid is proton donor in aqueous solution**
  酸在水溶液中是質子供給者
- **Base is proton acceptor in aqueous solution**
  鹼在水溶液中是質子接受者
- **Conjugate acid-base pair**
  共軛酸鹼對酸是相互競爭
- **Chemical equilibrium for acid-base reactions**
  酸鹼反應是共軛酸鹼對的化學平衡，反應傾向從強共軛酸鹼往弱共軛酸鹼的方向進行

Arrhenius vs Brønsted-Lowry concepts

Arrhenius

ionization
游離

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

Brønsted-Lowry

proton transfer
質子傳遞

$$HCl + H_2O \rightleftharpoons H_3O^{+} + Cl^{-}$$

conjugate acid	**conjugate base**	**conjugate acid**	**conjugate base**

Self- Ionization of Water
水的自身游離

- ***The chemistry of aqueous solution is unique***
  水溶液有獨特的化學行為
- ***Rapid proton exchange via H-bonding***
  水分子間藉由氫鍵進行快速的質子交換
- ***H_3O^+ is hydrated proton, and called hydronium ion***
  質子在水溶液中呈水合的狀態稱為鋞離子(H_3O^+)
- ***Actually, either H^+ or OH^- is hyrdated***
  事實上，大部分溶在水中的物質都是呈水合的狀態

- **Self ionization of water is in chemical equilibrium**
  水的自身游離常呈化學平衡狀態

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

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

- **$K_w = [H_3O^+][OH^-]$, *and is called ion product constant***
  $K_w = [H_3O^+][OH^-]$,稱為離子積常數

- **At 25℃, $[H_3O^+] = [OH^-] = 1.0\times10^{-7}$ M; $K_w = 1.0\times10^{-14}$**

Acid-Base in Other Solutions
其他溶液中的酸鹼平衡

- ***in ethanol*** *乙醇中*

$$2EtOH \rightleftharpoons EtO^- + EtOH_2^+$$

$$EtO^- + H_2O \rightleftharpoons EtOH + OH^-$$

$$EtOH_2^+ + H_2O \rightleftharpoons EtOH + H_3O^+$$

- ***Ethoxide is a stronger base than water, and protonated ethanol is a stronger acid than water.***
  乙烷氧離子在水中是強鹼，質子化的乙醇則是強酸

- ***Basicity:*** $EtO^- > OH^- > H_2O > EtOH > H_3O^+ > EtOH_2^+$

- ***in ammonia 氨水中***

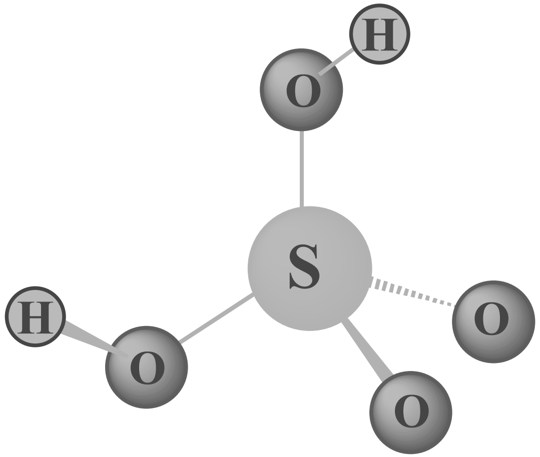
$$2NH_3 \rightleftharpoons NH_2^- + NH_4^+$$

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

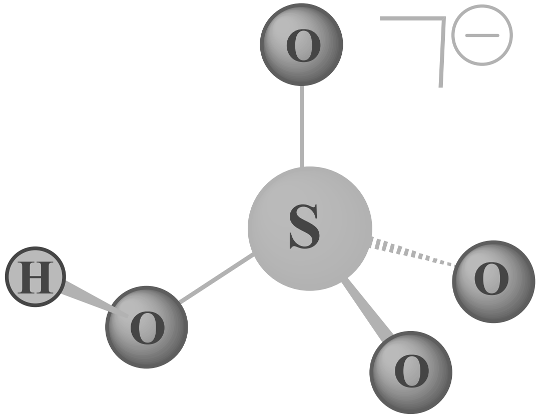
$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

- ***Bacicity:*** $NH_2^- > OH^- > NH_3 > H_2O > NH_4^+ > H_3O^+$

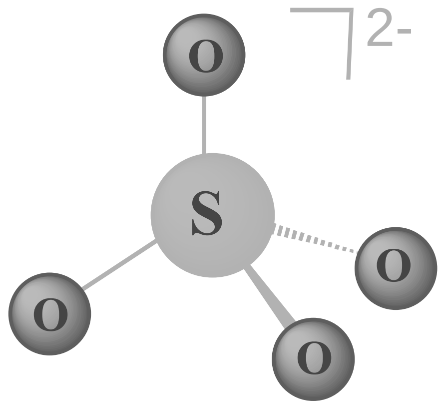
Structure of Oxyacids
常見含氧酸的分子結構



sulfuric acid
硫酸

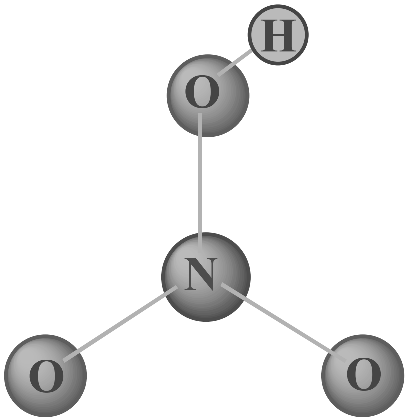


hydrogen sulfate
硫酸氫根



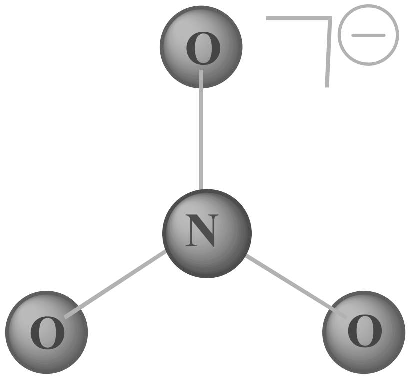
sulfate (tetrahedral)
硫酸根(正四面體)

The higher oxidation state of the central atom, the stronger acid it will be. *中央原子的氧化態越高的酸酸性愈強*



nitric acid

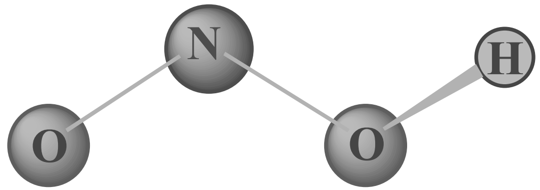
硝酸



nitrate

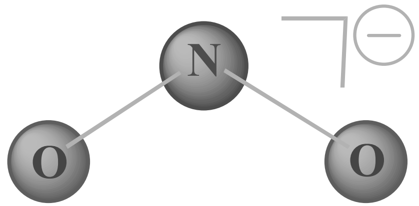
(trigonal planar)

硝酸根(平面三角形)



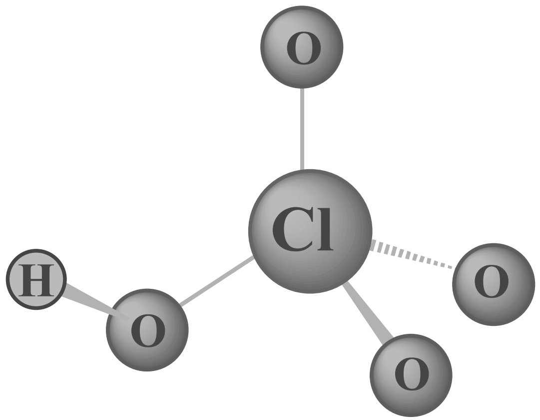
nitrous acid

亞硝酸

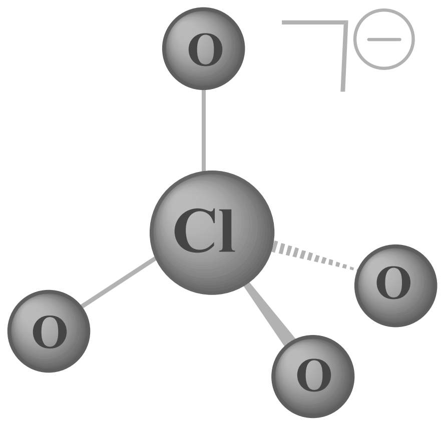


***nitrite* (angular)**

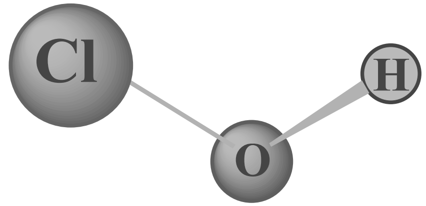
亞硝酸根(角形)



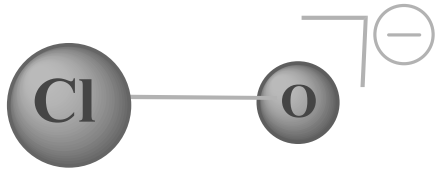
perchloric acid
過氯酸



perchlorate
(tetrahedral)
過氯酸根(正四面體)

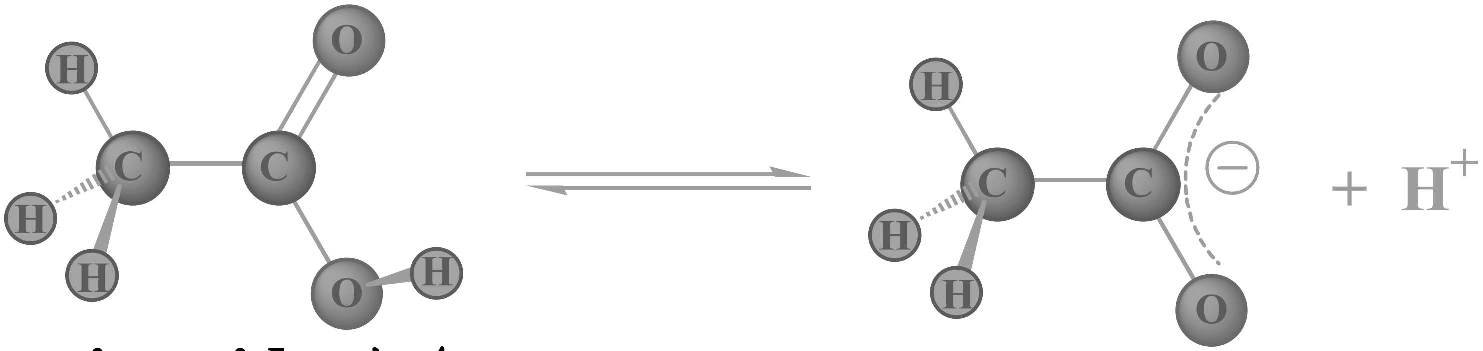


hypochlorous acid
次氯酸



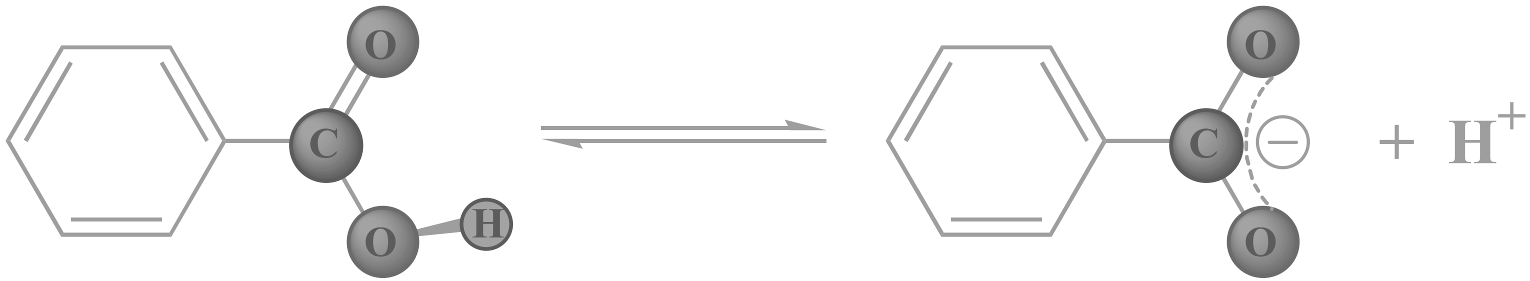
***hypochlorite* (linear)**
次氯酸根

Organic Acids 有機酸



acetic acid 醋酸

acetate
醋酸根



benzoic acid 苯酸

benzoate
苯酸根

Acid Strength 酸的強度

- ***K_a — acid dissociation constant, indicating the extent of dissociation of acids*** ***K_a***是酸的解離常數
- ***the equilibrium of strong acid goes toward its complete dissociation*** 強酸完全解離
- ***the weak acid reaches its equilibrium with partial dissociation*** 弱酸部分解離
- ***$pH = -\log [H^+]$***
- ***the pH scale of aqueous solutions is <14***
  水溶液的***pH***值範圍***<14***
- ***pH meter —Saturated Calomel Electrode (SCE)***

  $$Hg + Cl^- = \frac{1}{2} Hg_2Cl_2 + e^-$$

Acid Strength

- *pH of strong acid,* $[H^+] = [HA]_0$
- *Leveling Effect 平準效應*

$HClO_4$

H_2SO_4

HCl

HBr

HI

HNO_3

$$\xrightarrow{H_2O} H^+ + A^-$$

All strong acids or bases show the same strength in the same solvent. In aqueous solution, the strongest acid allowed is H^+, the strongest base allowed is OH^-.

水中的最強酸是H^+，最強鹼是OH^-

Acid Strength

- ***pH of weak acid,***

$$HA \rightleftharpoons H^+ + A^-$$

before	$[HA]_0$		
after	$[HA]_0 - x$	x	x

$$K_a = \frac{x^2}{[HA]_0 - x}$$

$[HA]_0 >> x$,

$x = [H^+] = (K_a[HA]_0)^{1/2}$

Percent Dissociation 解離率

$$\frac{x}{[HA]_0}\times 100\% = \frac{\sqrt{K_a[HA]_0}}{[HA]_0}\times 100\%$$

$$= \sqrt{\frac{K_a}{[HA]_0}}\times 100\%$$

Percent Dissociation 計算解離率

$$HA \rightleftharpoons H^{+} + A^{-}$$

	HA	H^+	A^-
before	C		
after	C-αC	αC	αC

,

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

$$\therefore \frac{\alpha^2}{1-\alpha} = \frac{K_{\alpha}}{C} \quad \alpha << 1 \quad \alpha = \sqrt{\frac{K_a}{C}}$$

The pH of mixture of weak acids depends on the relative acidity

Example: ***Calculate the pH of a solution that contains 1.00 M HCN (6.2×10^{-10}) and 5.00 M HNO_2 (4.0×10^{-4}) and calculate $[NO_2^-]$ and $[CN^-]$.***

$$HCN \rightleftharpoons H^+ + CN^- \qquad K_a=6.2\times10^{-10}$$

$$HNO_2 \rightleftharpoons H^+ + NO_2^- \qquad K_a=4.0\times10^{-4}$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_w=10^{-14}$$

Nitrous acid is stronger than cyanic acid to the 6th order of magnitude, it will dominate $[H^+]$.

$$4.0\times10^{-4} = \frac{[H^+][NO_2^-]}{[HNO_2]} = \frac{[H^+]^2}{5.00-[H^+]} \approx \frac{[H^+]^2}{5.00}$$

$$[H^+] = [NO_2^-] = 4.5x10^{-2}\ M \quad pH = 1.35$$

$$6.2\times10^{-10} = \frac{[H^+][CN^-]}{[HCN]} \approx \frac{(4.5\times10^{-2})[CN^-]}{1.00}$$

$$\therefore [CN^-] = 1.4\times10^{-8}\ M$$

The dissociation of cyanic acid is suppressed by nitrous acid.

The pH of very dilute acid ($[H^+] < 1.0x10^{-6}$ M)

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad ......(eq\ 1)$$

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

$$K_w = [H^+][OH^-] = 1.0x10^{-14} \quad ......(eq\ 2)$$

,

mass balance: $[HA]_0 = [HA] + [A^-]$ ......(eq 3)
質量平衡

charge balance: $[H^+] = [OH^-] + [A^-]$ ......(eq 4)
電荷平衡

Unknowns: $[H^+]$, $[OH^-]$, $[HA]$, $[A^-]$

Knowns: $[HA]_0$, K_a, K_w

- ***learn how to set up equations***
  會設定方程式
- ***learn mass and charge balance***
  會使用質量及電荷平衡的概念
- ***learn how to solve the unknowns***
  找出未知量的參數
- ***learn how to do approximation***
  使用概算法簡化計算
- ***learn the meaning of approximation***
  檢驗概算的假設

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

$$=[A^-]+\frac{K_w}{[H^+]}$$

$$\therefore [A^-]=[H^+]-\frac{K_w}{[H^+]}$$

$$[HA]=[HA]_0-[A^-]$$

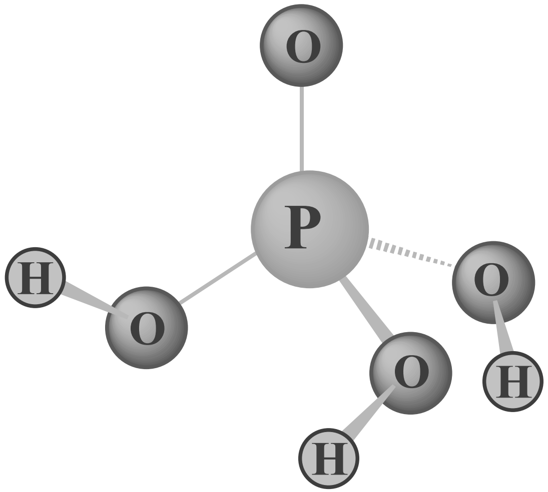
$$=[HA]_0-([H^+]-\frac{K_w}{[H^+]})$$

$$K_a=\frac{[H^+]([H^+]-\frac{K_w}{[H^+]})}{[HA]_0-([H^+]-\frac{K_w}{[H^+]})}=\frac{[H^+]^2-K_w}{[HA]_0-(\frac{[H^+]^2-K_w}{[H^+]})}$$

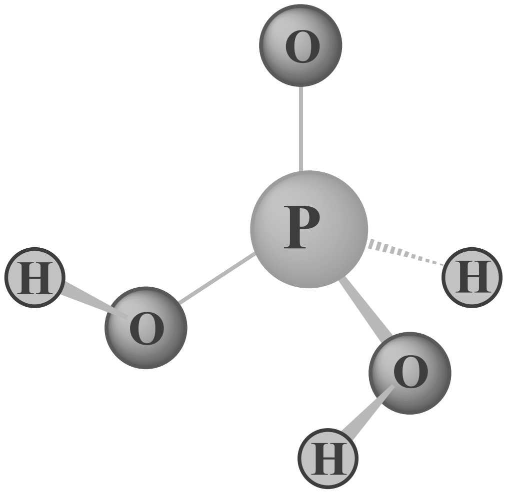
$$\text{if } [H^+]^2 >> K_w \quad K_a=\frac{[H^+]^2}{[HA]_0-[H^+]}$$

$$\text{if } [HA]_0 >> ([H^+]^2-K_w)/[H^+] \quad [H^+]=(K_a[HA]_0+K_w)^{1/2}$$

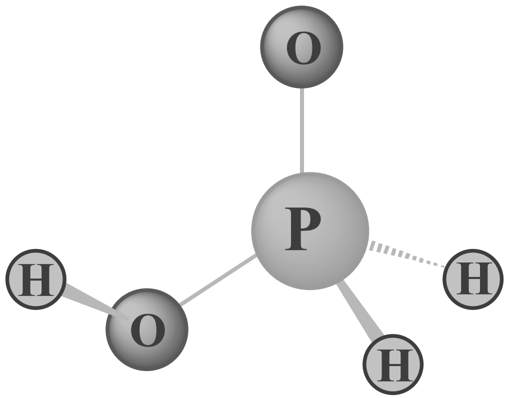
Polyprotic (Polybasic) Acids 多質子酸



phosphoric acid
(tribasic)
磷酸(三質子酸)



phosphorous acid
(dibasic)
亞磷酸(二質子酸)



hypophosphorous acid
(monobasic)
次磷酸(單質子酸)

The pH of a diprotic acid – H_2CO_3

$$H_2A + H_2O \rightleftharpoons H_3O^+ + HA^- \quad K_1 = \frac{[H_3O^+][HA^-]}{[H_2A]} \quad \text{...(eq 1)}$$

$$HA^- + H_2O \rightleftharpoons H_3O^+ + A^{-2} \quad K_2 = \frac{[H_3O^+][A^{-2}]}{[HA^-]} \quad \text{...(eq 2)}$$

mass balance:

$$C_{H_2A} = [H_2A] + [HA^-] + [A^{2-}] \text{ ......(eq 3)}$$

,

charge balance:

$$[H_3O^+] = [OH^-] + [HA^-] + 2[A^{2-}] \text{ ......(eq 4)}$$

Unknowns: $[H^+]$, $[OH^-]$, $[H_2A]$, $[HA^-]$, $[A^{2-}]$

Knowns: C_{H_2A}, K_1, K_2, K_w

if $K_1 >> K_2$ (more than 1000 fold larger)

$[HA^-] >> [A^{2-}]$

$[H_3O^+] \approx [HA^-]$

$[A^{2-}] \approx K_2$ (double checked later)

$[H_2A] = [H_2A] + [HA^-] = [H_2A] + [H_3O^+]$

$$K_1 = \frac{[H_3O^+]^2}{C_{H_2A} - [H_3O^+]}$$

if $C_{H_2A} >> [H_3O^+]$

$$[H_3O^+] = \sqrt{K_1 C_{H_2A}}$$

Calculate pH of 5.00 M H_3PO_4 and the concentrations of anions.

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$

$$K_{a_1} = 7.5\times10^{-3} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \approx \frac{x^2}{5.0}$$

$$[H^+]=1.9\times10^{-1} \quad pH=0.72$$

$$K_{a_2} = 6.2\times10^{-8} = \frac{[H^+][HPO_4^{-2}]}{[H_2PO_4^-]}$$

$$[H^+] \approx [H_2PO_4^-]$$

,

$$\therefore\ [HPO_4^{-2}] \approx K_{a_2} = 6.2\times10^{-8}$$

$$K_{a_3} = 4.8\times10^{-13} = \frac{[H^+][PO_4^{-3}]}{[HPO_4^{-2}]} = \frac{0.19[PO_4^{-3}]}{6.2\times10^{-8}}$$

$$\therefore\ [PO_4^{-3}]=1.6\times10^{-19}\ M$$

Calculate $[H_3O^+]$ for 0.0100 M H_2SO_4.

$$H_2SO_4 \xrightarrow{H_2O} HSO_4^- + H_3O^+$$

$$H_2SO_4 \underset{}{\overset{H_2O}{\rightleftharpoons}} SO_4^{-2} + H_3O^+ \qquad K_2 = 1.2\times10^{-2}$$

$[H_3O^+] \approx [HSO_4^-] = 0.0100$ M approximation

,

$$\frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} \approx [SO_4^{2-}] = 1.2\times10^{-2}\ \mathrm{M}$$

$[SO_4^{2-}] << [HSO_4^-]$ or $[SO_4^{2-}] << [H_3O^+]$ thus is not a proper assumption.

$$C_{H_2SO_4} = [HSO_4^-] + [SO_4^{2-}]$$ **…Mass balance**

$$[H_3O^+] = [HSO_4^-] + 2[SO_4^{2-}]$$ **…charge balance**

$$[H_3O^+] - C_{H_2SO_4} = [SO_4^{2-}]$$

$$[H_3O^+] = 0.0100 + [SO_4^{2-}]$$

$$[HSO_4^-] = 0.0100 - [SO_4^{2-}]$$

$$K_2 = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(0.0100 + [SO_4^{2-}])[SO_4^{2-}]}{(0.0100 - [SO_4^{2-}])}$$

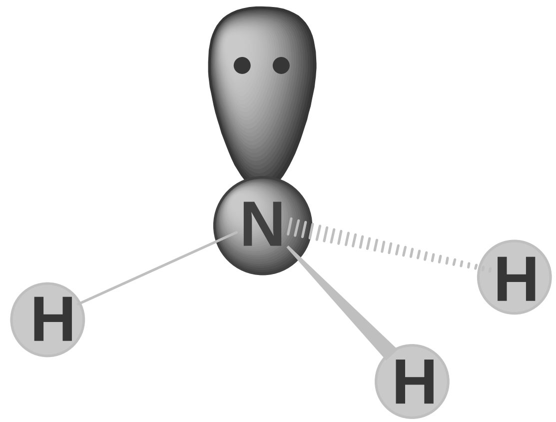
,

$$[SO_4^{2-}] = 4.5 \times 10^{-3}\ M$$

$$[H_3O^+] = 0.0145\ M$$

$$[HSO_4^-] = 0.0055\ M$$

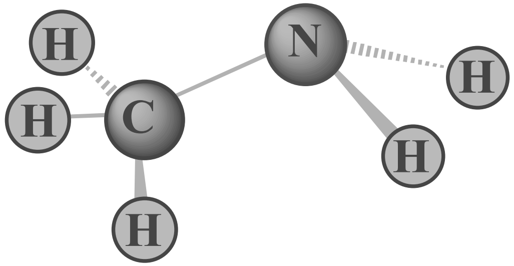
Inorganic Bases 無機鹼



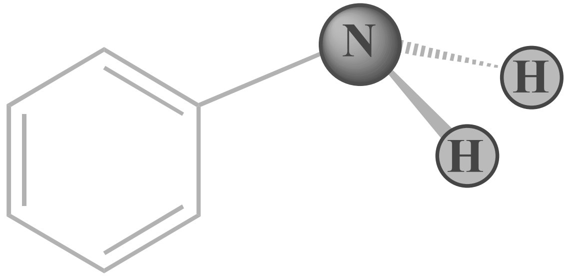
- *ammonia* 氨
- *metal hydroxides* 金屬氫氧化物: *NaOH, KOH, $Ca(OH)_2$*
- *metal oxides* 金屬氧化物: *CaO, BaO*
- *metal hydrides* 金屬氫化物: *NaH, KH*
- *metal amides* 金屬氨化物: *$NaNH_2$, $LiNMe_2$, NaOMe*
- *weak acid salts* 金屬弱酸鹽: *NaOAc, NaCN, Na_2CO_3*

Organic amines 有機鹼

primary (1º) amine 一級胺



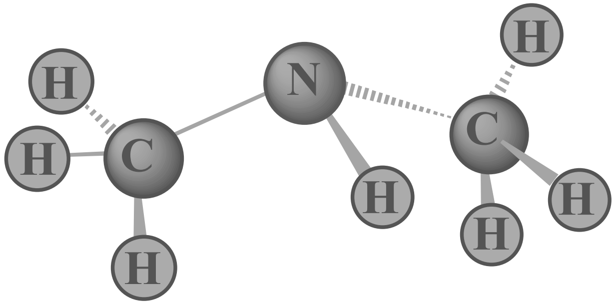
methyl amine
甲胺



aniline
苯胺

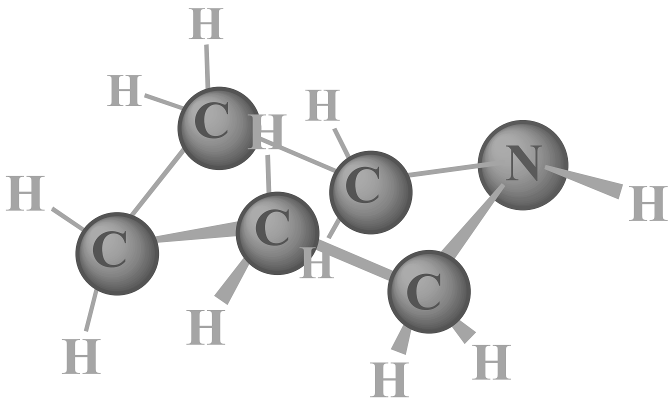
Organic amines

- *secondary (2º) amine 二級胺*



dimethyl amine

二乙胺

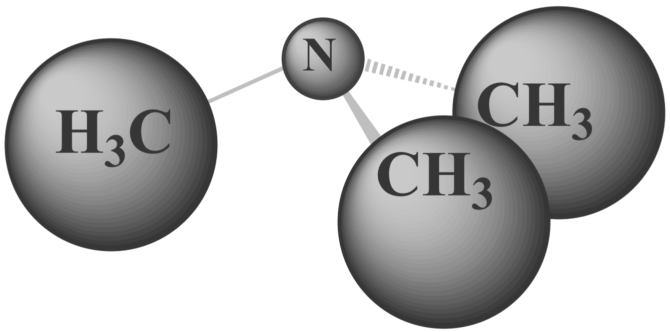


piperidine

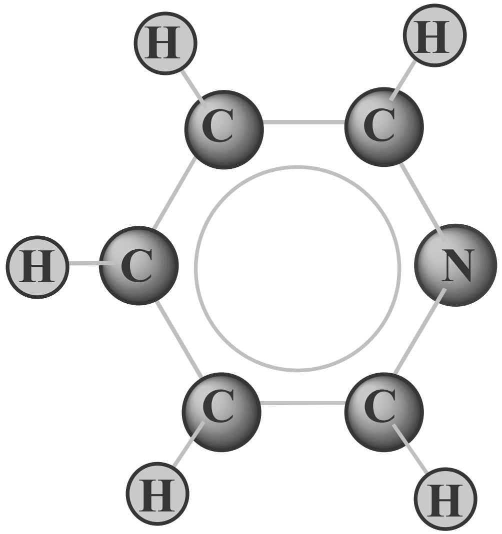
環戊胺

Organic amines

- *tertiary (3º) amine* 三級胺

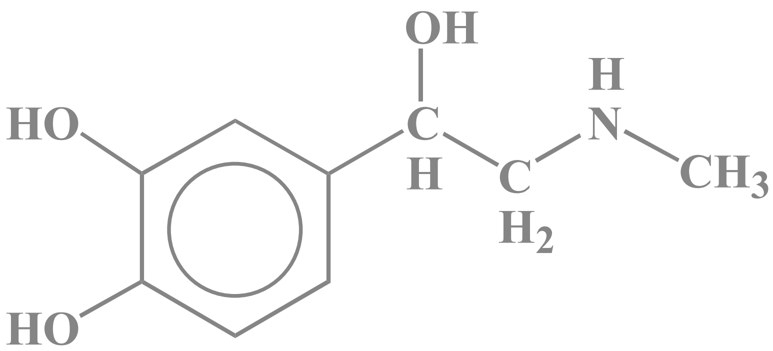


trimethyl amine
三甲胺



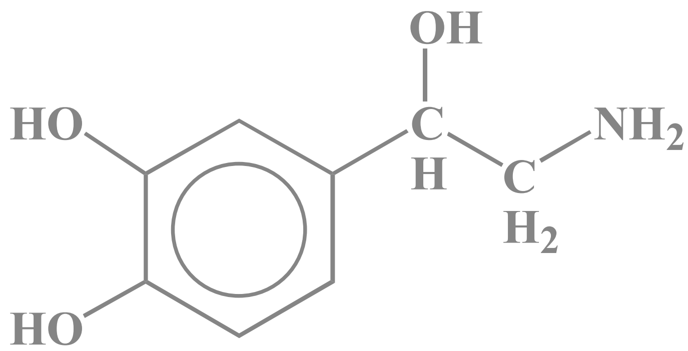
Pyridine
吡啶

Biofunctional amines 生物胺



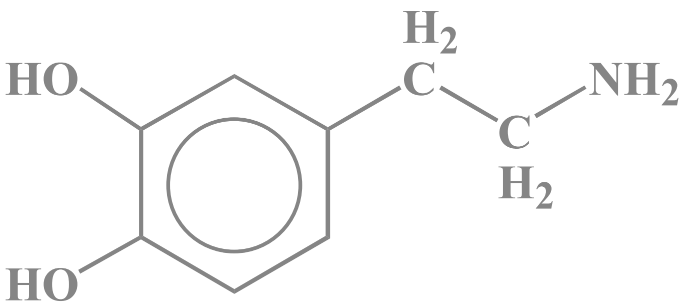
Epinephrine

肾上腺素



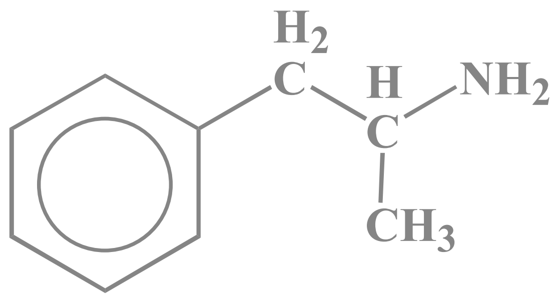
Norepinephrine

降肾上腺素



dopamine

多巴胺



amphetamine

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Salts 鹽類

- ***Neutral Salts: salts formed from strong acid & strong base are always of neutral salts, pH = 7.***
  強酸與強鹼形成的鹽為中性鹽

  Example:

  $$HCl_{(aq)} + NaOH_{(aq)} \rightleftharpoons NaCl_{(aq)} + H_2O$$

- ***Acidic Salts: salts formed from strong acid & weak base*** 強酸與弱鹼形成酸性鹽

$$HCl + NH_3 \rightleftharpoons NH_4Cl$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad K_a = 5.6\times10^{-10}$$

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \sim \frac{[H_3O^+]^2}{[NH_4^+]}$$

For 1M NH_4Cl at 25 ℃

$$[H_3O^+] = (K_a[NH_4^+])^{1/2} = (K_a[NH_4Cl])^{1/2}$$

$$= 2.4\times10^{-5}\ M$$

∴ pH=4.6 The solution is slightly acidic.

Solution of acidic salts of ampholyte 兩性鹽

$$NaHA \rightleftharpoons HA^- + Na^+$$

$$HA^- + H_2O \rightleftharpoons H_2A + OH^- \quad K_{b''} = \frac{K_w}{K_1} = \frac{[H_2A][OH^-]}{[HA^-]}$$

$$HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+ \quad K_2 = \frac{[A^{2-}][H_3O^+]}{[HA^-]}$$

Mass balance: $C_{NaHA} = [H_2A] + [HA^-] + [A^{2-}]$

Charge balance: $[Na^+] + [H_3O^+] = [OH^-] + [HA^-] + 2[A^{2-}]$

$$[H_2A] = [A^{2-}] + [OH^-] - [H_3O^+]$$

$$\frac{K_w[HA^-]}{K_1[OH^-]} = \frac{K_2[HA^-]}{[H_3O^+]} + [OH^-] - [H_3O^+]$$

$$\frac{[H_3O^+][HA^-]}{K_1} = \frac{K_2[HA^-]}{[H_3O^+]} + \frac{K_w}{[H_3O^+]} - [H_3O^+]$$

$$[H_3O^+]^2\left(\frac{[HA^-]}{K_1} + 1\right) = K_2[HA^-] + K_w$$

$$[H_3O^+] = \sqrt{\frac{K_1K_2[HA^-] + K_1K_w}{[HA^-] + K_1}}$$

if both $K_{b''}$, K_2 are small

$[HA^-] \approx C_{NaHA}$

and $K_1 << [HA^-] = C_{NaHA}$

$K_w << C_{NaHA}$

$$[H_3O^+] = \sqrt{K_1K_2}$$

$$pH = \frac{1}{2}pK_1 + \frac{1}{2}pK_2$$

Salts formed from weak acid & weak base (NH_4OAc)
弱酸與弱鹼形成的鹽

$$NH_4OAc \rightleftharpoons NH_4^+ + OAc^-$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \quad K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$OAc^- + H_2O \rightleftharpoons HOAc + OH^- \quad K_b = \frac{[HOAc][OH^-]}{[OAc^-]}$$

Mass balance:

$$C_{NH4OAc} = [NH_4^+] + [NH_3] = [HOAc] + [OAc^-]$$

Charge balance:

$$[NH_4^+] + [H_3O^+] = [OH^-] + [OAc^-]$$

$$[NH_3] - [H_3O^+] = [HOAc] - [OH^-]$$

$$\frac{[NH_4^+]}{[H_3O^+]}\frac{K_w}{K_b}-[H_3O^+]=\frac{[OAc^-][H_3O^+]}{K_a}-\frac{K_w}{[H_3O^+]}$$

$$\Downarrow$$

$$[NH_4^+]\frac{K_w}{K_b}-[H_3O^+]^2=\frac{[OAc^-][H_3O^+]^2}{K_a}-K_w$$

$$\Downarrow$$

$$(1+\frac{[OAc^-]}{K_a})[H_3O^+]^2=[NH_4^+]\frac{K_w}{K_b}+K_w$$

$$\Downarrow$$

$$[H_3O^+]=\sqrt{\frac{K_wK_a([NH_4^+]+K_b)}{K_b(K_a+[OAc^-])}}$$

K_a, K_b are small, $\therefore [NH_4^+]=[OAc^-]\approx F_{NH_4OAc}$

$$\therefore\ [H_3O^+]=\sqrt{\frac{K_wK_a}{K_b}}$$

if $K_a > K_b$ soln is acidic

$K_a < K_b$ soln is basic

$K_a = K_b$ soln is neutral

Solution of weak acid & Its Salt
弱酸及其鹽類的同離子效應

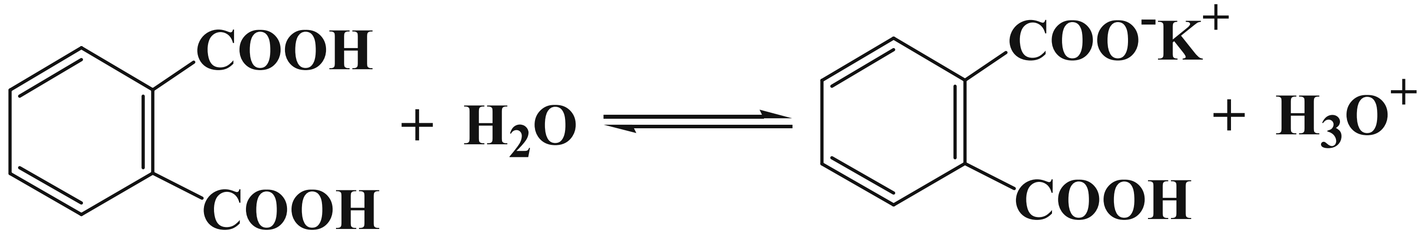
- **HA/NaA**
- **H_2A/ NaHA or H_2A/Na_2A**
- **NaHA/Na_2A**

$$H_2A + H_2O \rightleftharpoons HA^- + H_3O^+ \quad pH = pK_{a_1} + \log\frac{[HA^-]}{[H_2A]}$$

or

$$HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+ \quad pH = pK_{a_2} + \log\frac{[A^{2-}]}{[HA^-]}$$

- ***0.0100 M phthalic acid/0.200 M KHP***



$$K_1 = \frac{[HP^-][H_3O^+]}{[H_2P]} = 1.3 \times 10^{-3}$$

$$K_2 = \frac{[P^{2-}][H_3O^+]}{[HP^-]} = 3.9 \times 10^{-6} << K_1$$

$$[H_2P] = 0.100 - [H_3O^+] \approx 0.100 \text{ M}$$

$$[HP^-] = 0.200 - [H_3O^+] \approx 0.200$$

- **Method 1.**

$$\frac{0.200[H_3O^+]}{0.100} = 1.3\times10^{-3}$$

$$[H_3O^+]=6.5\times10^{-4}\ M \quad pH=3.19$$

- **Method 2.**

$$pH=pK_{a_1} + \log(\frac{[HA^-]}{[H_2P]}$$

$$=2.89+\log\frac{0.2}{0.1}$$

$$=3.19$$

總結

酸、鹼、鹽都是在水中會游離的物質，水會發生自身解離，所以酸與鹼都會和水分子競爭質子，鹽類則發生水合的行為 。

不同的物質解離程度和競爭質子的能力均不同，利用測量酸、鹼、鹽在水中的平衡的情形，可以計算各種化學成分在水溶液中的含量。

有機、無機與生化物質都可能在水中有酸鹼鹽的性質。物質的結構與組成都影響其酸或鹼的性質。