Chapter 14:

Acids and Bases

Common household substances that contain acids and bases. Vinegar is a dilute solution of acetic acid. Drain cleaners contain strong bases such as sodium hydroxide.

一些酸 & 鹼的性質

Acids	**Bases**
Sour taste	Bitter taste
React with active metals to give H_2	Slippery feeling
Change colors of indicators, e.g., litmus turns from blue to red	Change colors of indicators, e.g., litmus turns from red to blue
Produce CO_2 when added to limestone	
Neutralize bases	Neutralize acids
Some acidic substances	**Some basic substances**
Vinegar, tomatoes, citrus fruits, carbonated beverages, black coffee, gastric fluid, vitamin C, aspirin	Household ammonia, baking soda, soap, detergents, milk of magnesia, oven cleaners, lye, drain cleaners

生活中常碰到的酸

Common acids

Name	Strength	Use
Sulfuric acid	Strong	Cleaning steel, car batteries, making plastics, dyes, fertilizers
Hydrochloric acid	Strong	Cleaning metals and brick mortar
Nitric acid	Strong	Making fertilizers, explosives, plastics
Phosphoric acid	Moderate	Making fertilizers, detergents, food additives
Acetic acid	Weak	Vinegar
Propionic acid	Weak	Swiss cheese
Citric acid	Weak	Fruits
Carbonic acid	Weak	Carbonated beverages
Boric acid	Weak	Eye drops, mild antiseptic

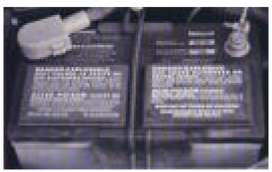
生活中常碰到的鹼

Common bases

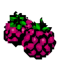
Name	Strength	Use
Sodium hydroxide	Strong	Drain cleaner, producing aluminum, rayon, soaps and detergents
Potassium hydroxide	Strong	Producing soaps, detergents, fertilizers
Calcium hydroxide	Strong	Producing bleaching powder, paper and pulp, softening water
Ammonia	Weak	Producing fertilizers, explosives, plastics, insecticides, detergents
Sodium bicarbonate	Weak	Antacid
Sodium carbonate	Weak	Detergents, glass-making

生活中常見含酸 or 鹼的東西

Many cleaning products contain bases.



Some common products that contain phosphates as additives.



14.1 The Nature of Acids and Bases

Models of Acids and Bases

Arrhenius concept:

Acids produce H^+ in aqueous solution.

Bases produce OH^- ion.

Brønsted-Lowry model:

Acids are proton (H^+) donors.

Bases are proton acceptors.

$$HCl + H_2O \rightarrow Cl^- + H_3O^+$$

acid base

Conjugate Acid / Base Pairs

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

Acid — Base — Conjugate acid — Conjugate base

conjugate base (共軛鹼): everything that remains of the acid molecule after a proton is lost. (酸失去質子後)

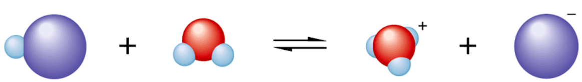
conjugate acid (共軛酸): formed when the proton is transferred to the base. (鹼得到質子後)

Acid Dissociation Constant (K_a)

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

or $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H^+][A^-]}{[HA]}$$



Sample exercise 14.1

14.2 Acid Strength

Acid Strength

酸的強度依其平衡時解離的程度決定

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

Strong Acid:

- Its equilibrium position lies far to the right. [例如: $HNO_{3(aq)} \rightarrow H^+_{(aq)} + NO_3^-{}_{(aq)}$]
- Yields a weak conjugate base. (NO_3^-)

Weak Acid:

- Its equilibrium position lies far to the left. [例如: $CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$]
- Yields a much stronger (relatively strong) conjugate base than water. (CH_3COO^-)

Fig. 14.4: Graphic representation of the behavior of acids of different strengths in aqueous solution. (a) A strong acid. (b) A weak acid.

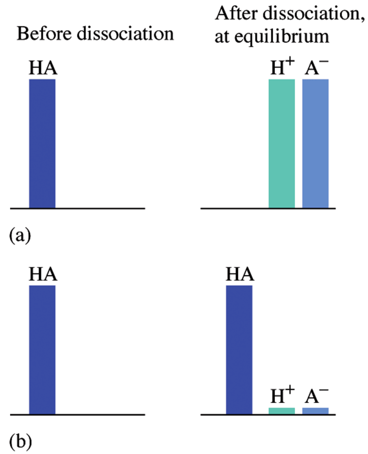


Fig. 14.5: The relationship of acid strength and conjugate base strength for the reaction:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

酸(HA)愈強，其共軛鹼

(A^-)愈弱

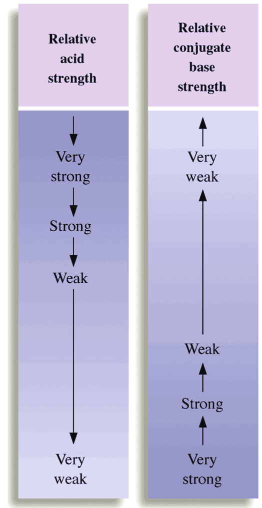


Fig. 14.6: (a) A strong acid HA is completely ionized in water. (b) A weak acid HB exists mostly as undissociated HB molecules in water. Note that the water molecules are not shown in this figure.

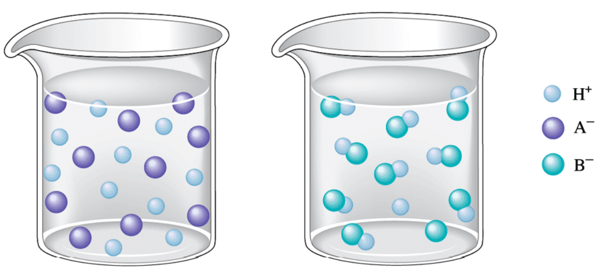


TABLE 14.1 Various Ways to Describe Acid Strength

Property	Strong Acid	Weak Acid
K_a value	K_a is large	K_a is small
Position of the dissociation (ionization) equilibrium	Far to the right	Far to the left
Equilibrium concentration of H^+ compared with original concentration of HA	$[H^+] \approx [HA]_0$	$[H^+] \ll [HA]_0$
Strength of conjugate base compared with that of water	A^- much weaker base than H_2O	A^- much stronger base than H_2O

- **monoprotic acid** (單質子酸):
  含 1 acidic proton, 如 HCl
- **diprotic acid** (雙質子酸):
  含 2 acidic proton, 如 H_2SO_4
- **triprotic acid** (三質子酸):
  含 3 acidic proton, 如 HCl

Oxyacids (含氧酸):
the acidic proton 接於氧原子上, 如 H_2SO_4

Organic acids (有機酸):
含 –COOH (carboxyl group)

TABLE 14.2 Values of K_a for Some Common Monoprotic Acids

Formula	Name	Value of K_a*
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
$HC_2H_2ClO_2$	Monochloracetic acid	1.35×10^{-3}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
$HC_2H_3O_2$	Acetic acid	1.8×10^{-5}
$[Al(H_2O)_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}
HOCl	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HOC_6H_5	Phenol	1.6×10^{-10}

↑ Increasing acid strength

Sample exercise 14.2

Water as an Acid and a Base

Water is ***amphoteric*** (it can behave either as an acid or a base).

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Ion-product constant (or dissociation constant):

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-]$$

$$K_w = 1 \times 10^{-14} \text{ at } 25\,^\circ\text{C}$$

T↑, K_w↑ ⇒ indicating an endothermic process

14.3 The pH Scale

The pH Scale

pH » -log$[H^+]$

pH in water ranges from 0 to 14

At 25 C, $K_w = 1.00 \times 10^{-14} = [H^+]\,[OH^-]$

$pK_w = 14.00 = pH + pOH$

14.4 Calculating the pH of Strong Acid Solutions

14.5 Calculating the pH of Weak Acid Solutions

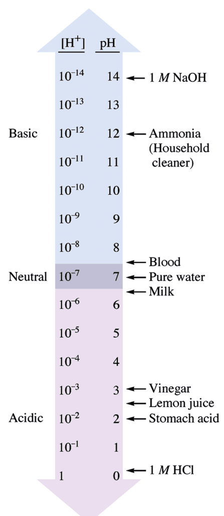


Fig. 14.8: The pH scale and pH values of some common substances.

Fig. 14.9: pH meters are used to measure acidity.

Solving Weak Acid Equilibrium Problems

1. List major species in solution.
2. Choose species that can produce H^+ and write reactions.
3. Based on *K* values, decide on dominant equilibrium.
4. Write equilibrium expression for dominant equilibrium.
5. List initial concentrations in dominant equilibrium.

6. Define change at equilibrium (as “*x*”).
7. Write equilibrium concentrations in terms of *x*.
8. Substitute equilibrium concentrations into equilibrium expression.
9. Solve for *x* the “easy way.”
10. Verify assumptions using 5% rule.
11. Calculate $[H^+]$ and pH.

Be systematic, flexible, patient, and confident.

Percent Dissociation (Ionization)

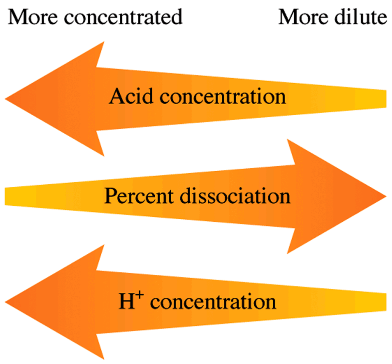
$$\%\,\text{dissociation} = \frac{\text{amount dissociated}(M)}{\text{initial concentration}(M)} \times 100\%$$

對一弱酸 HA,

當 $[HA]_0 \downarrow \Rightarrow [H^+] \downarrow$, 但 % dissociation $\uparrow$

An acetic acid solution, which is a weak electrolyte, contains only a few ions and does not conduct as much current as a strong electrolyte. The bulb is only dimly lit.

Figure 14.10: The effect of dilution on the percent dissociation and $[H^+]$ of a weak acid solution.



14.6 Bases

Bases (鹼)

- "Strong" and "weak" are used in the same sense for bases as for acids.

- strong = complete dissociation (hydroxide ion supplied to solution)

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

- weak = very little dissociation (or reaction with water)

$$H_3CNH_2(aq) + H_2O(l) \leftrightarrow H_3CNH_3^+(aq) + OH^-(aq)$$

$Ca(OH)_2$: slaked lime 熟石灰

- 可用於除去工業煙囪所排放之SO_2

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$$

$$Ca(OH)_2(aq) + H_2SO_3(aq) \rightleftharpoons CaSO_3(s) + 2H_2O(l)$$

- 可用於使硬水軟化

lime-soda process: 於水中加入 $CaO + Na_2CO_3$

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)}$$

$$Ca(OH)_{2(aq)} + Ca^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)} \rightarrow 2CaCO_{3(s)} + 2H_2O_{(l)}$$

from hard water

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

Base — Acid — Conjugate acid — Conjugate base

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

TABLE 14.3 Values of K_b for Some Common Weak Bases

Name	Formula	Conjugate Acid	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	$CH_3NH_3^+$	4.38×10^{-4}
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^+$	5.6×10^{-4}
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^+$	3.8×10^{-10}
Pyridine	C_5H_5N	$C_5H_5NH^+$	1.7×10^{-9}

14.7 Polyprotic Acids

Polyprotic Acids (多質子酸)

- can furnish more than one H^+ to the solution
- dissociate in a stepwise manner

例如:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (K_{a_1})$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad (K_{a_2})$$

For a typical weak polyprotic acid,

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

TABLE 14.4 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid*	H_2S	1.0×10^{-7}	$\sim 10^{-19}$	
Oxalic acid	$H_2C_2O_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}	

14.8 Acid-Base Properties of Salts

Type	Cation (陽離子)	Anion (陰離子)	Acidic or Basic	Example
強酸強鹼鹽	neutral	neutral	neutral	NaCl
弱酸強鹼鹽	neutral	conj base of weak acid	basic	NaF
強酸弱鹼鹽	conj acid of weak base	neutral	acidic	NH_4Cl
弱酸弱鹼鹽	conj acid of weak base	conj base of weak acid	depends on K_a & K_b values	NH_4CN

Qualitative Prediction of pH for Solutions of Salts for Which Both Cation and Anion Have Acidic or Basic Properties

$K_a > K_b$	pH < 7 (acidic)
$K_b > K_a$	pH > 7 (basic)
$K_a = K_b$	pH = 7 (neutral)

TABLE 14.6 Acid–Base Properties of Various Types of Salts

Type of Salt	Examples	Comment	pH of Solution
Cation is from strong base; anion is from strong acid	KCl, KNO_3, NaCl, $NaNO_3$	Neither acts as an acid or a base	Neutral
Cation is from strong base; anion is from weak acid	$NaC_2H_3O_2$, KCN, NaF	Anion acts as a base; cation has no effect on pH	Basic
Cation is conjugate acid of weak base; anion is from strong acid	NH_4Cl, NH_4NO_3	Cation acts as acid; anion has no effect on pH	Acidic
Cation is conjugate acid of weak base; anion is conjugate base of weak acid	$NH_4C_2H_3O_2$, NH_4CN	Cation acts as an acid; anion acts as a base	Acidic if $K_a > K_b$, basic if $K_b > K_a$, neutral if $K_a = K_b$
Cation is highly charged metal ion; anion is from strong acid	$Al(NO_3)_3$, $FeCl_3$	Hydrated cation acts as an acid; anion has no effect on pH	Acidic

14.9 The Effect of Structure on Acid-Base Properties

Structure and Acid-Base Properties

Two factors for acidity in binary compounds:

- Bond Polarity (high is good)
- Bond Strength (low is good)

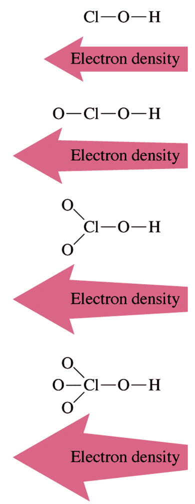
TABLE 14.7
Bond Strengths and Acid Strengths for Hydrogen Halides

H—X Bond	Bond Strength (kJ/mol)	Acid Strength in Water
H—F	565	Weak
H—Cl	427	Strong
H—Br	363	Strong
H—I	295	Strong

Bond polarity: H–F > H–Cl > H–Br > H–I

Bond strength: H–F > H–Cl H–Br > H–I

Fig. 14.11: The effect of the number of attached oxygens on the O—H bond in a series of chlorine oxyacids.



As the # of O atoms -

Þ the acid strength -

TABLE 14.8 Several Series of Oxyacids and Their K_a Values

Oxyacid	Structure	K_a Value
$HClO_4$	$H—O—Cl(=O)_3$	Large (~10^7)
$HClO_3$	$H—O—Cl(=O)_2$	~1
$HClO_2$	H—O—Cl—O	1.2×10^{-2}
HClO	H—O—Cl	3.5×10^{-8}
H_2SO_4	$H—O—S(—O—H)(=O)_2$	Large
H_2SO_3	$H—O—S(—O—H)(=O)$	1.5×10^{-2}
HNO_3	$H—O—N(=O)_2$	Large
HNO_2	H—O—N—O	4.0×10^{-4}

TABLE 14.9 Comparison of Electronegativity of X and K_a Value for a Series of Oxyacids

Acid	X	Electronegativity of X	K_a for Acid
HOCl	Cl	3.0	4×10^{-8}
HOBr	Br	2.8	2×10^{-9}
HOI	I	2.5	2×10^{-11}
$HOCH_3$	CH_3	2.3 (for carbon in CH_3)	$\sim 10^{-15}$

電負度: Cl > Br > I > C (in $–CH_3$)

K_a: HOCl > HOBr > HOI > $HOCH_3$

14.10 Acid-Base Properties of Oxides

Oxides

- Acidic Oxides (Acid Anhydrides):
  - O–X bond is strong and covalent.

    例如: SO_2, NO_2, CO_2

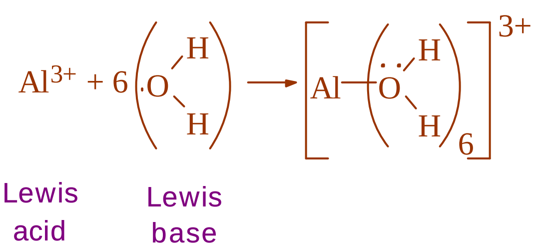
- Basic Oxides (Basic Anhydrides):
  - O–X bond is ionic.

    例如: K_2O, CaO

14.11 The Lewis Acid-Base Model

Lewis Acids and Bases

- Lewis Acid: electron pair acceptor
- Lewis Base: electron pair donor



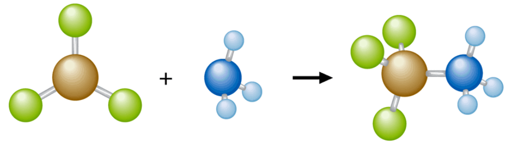


Fig. 14.12: Reaction of BF_3 with NH_3.

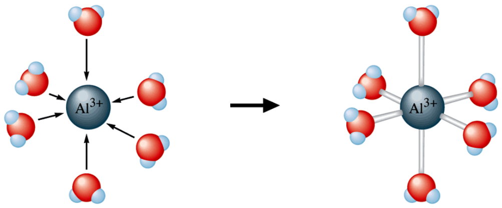


Fig. 14.13: The $Al(H_2O)_6^{3+}$ ion.

TABLE 14.10 Three Models for Acids and Bases

Model	Definition of Acid	Definition of Base
Arrhenius	H^+ producer	OH^- producer
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	Electron-pair acceptor	Electron-pair donor

14.12 Strategy for Solving Acid-Base Problems: A Summary

1. List the major species in solution.
2. Look for reactions that can be assumed to go to completion—for example, a strong acid dissociating or H^+ reacting with OH^-.
3. For a reaction that can be assumed to go to completion:
   - **a.** Determine the concentration of the products.
   - **b.** Write down the major species in solution after the reaction.
4. Look at each major component of the solution and decide if it is an acid or a base.
5. Pick the equilibrium that will control the pH. Use known values of the dissociation constants for the various species to help decide on the dominant equilibrium.
   - **a.** Write the equation for the reaction and the equilibrium expression.
   - **b.** Compute the initial concentrations (assuming the dominant equilibrium has not yet occurred, that is, no acid dissociation, and so on).
   - **c.** Define x.
   - **d.** Compute the equilibrium concentrations in terms of x.
   - **e.** Substitute the concentrations into the equilibrium expression, and solve for x.
   - **f.** Check the validity of the approximation.
   - **g.** Calculate the pH and other concentrations as required.

Although these steps may seem somewhat cumbersome, especially for simpler problems, they will become increasingly helpful as the aqueous solutions become more complicated. If you develop the habit of approaching acid–base problems systematically, the more complex cases will be much easier to manage.

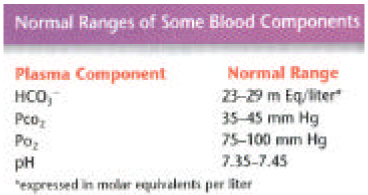
酸鹼與健康 – 血液

Blood buffer: dissolved CO_2 (血液中CO_2的量影響血液之pH值)

$CO_2(g) + H_2O(l)$ ® $H_2CO_3(aq)$

added OH^-: $H_2CO_3(aq) + OH^-(aq)$ ® $HCO_3^-(aq) + H_2O(l)$

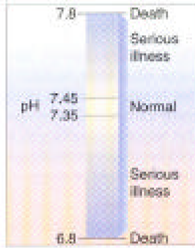
added H^+: $HCO_3^-(aq) + H^+(aq)$ ® $H_2CO_3(aq)$



Normal Ranges of Some Blood Components

Plasma Component	Normal Range
HCO_3^-	23–29 m Eq/liter*
Pco_2	35–45 mm Hg
Po_2	75–100 mm Hg
pH	7.35–7.45

*expressed in molar equivalents per liter



pH > 7.45 alkalosis (e.g. hyperventilation)

pH < 7.35 acidosis (e.g. breathe with a bag covering one's nose & mouth)

人體中的強酸 – 胃酸

胃酸 (gastric juice): HCl [pH of the stomach: 0.9 – 1.5]

胃酸分泌過多會造成消化不良 (acid indigestion or heartburn) 或甚至於胃潰瘍 (ulcer)，可以制酸劑 (antacids)中和胃酸。

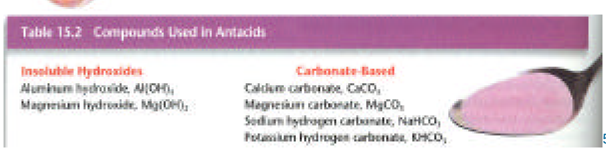


Table 15.2 Compounds Used in Antacids

Insoluble Hydroxides	Carbonate-Based
Aluminum hydroxide, $Al(OH)_3$	Calcium carbonate, $CaCO_3$
Magnesium hydroxide, $Mg(OH)_2$	Magnesium carbonate, $MgCO_3$
	Sodium hydrogen carbonate, $NaHCO_3$
	Potassium hydrogen carbonate, $KHCO_3$

環境中的酸鹼 – 酸雨

Examples:

$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$

$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$