Chapter 10: Acid-Base Equilibria

Acid & Base Definitions

Arrhenius Theory	An acid is a substance that releases hydrogen ions when dissolved in water. A base is a substance that releases hydroxide ions when dissolved in water.
☆ Bronsted-Lowry Theory	An acid is a proton donor. A base is a proton acceptor. – conjugate acid – base pair · differ only by 1 proton
Lewis Theory	An acid is an electron pair acceptor. A base is an electron pair donor.

Strength & concentration

Strength

- strong acids & bases dissociate fully in solution. (ie. use full arrows)
- weak acids & bases dissociate partially in solution (ie. use reversible arrows)
  - ↳ forms an equilibrium

B-L Theory

The stronger the acid / base, the weaker the conjugate base/acid.
The weaker the acid / base, the stronger the conjugate base / acid. } relative strength

⇒ weak conjugate base : negligible tendency for it to be protonated
↳ unlikely to form back the acid by taking back H+
↳ reverse reaction unlikely to take place.

⇒ strong conjugate acid : moderate tendency for it to be deprotonated
↳ likely to form back the base by releasing the H+
↳ reverse reaction will take place

} vice versa applies

pH & pOH

The pH of a solution is defined as the negative logarithm to base 10 to H^+ concentration in mol dm^{-3}.

① $pH = -\log_{10}[H^+]$ (no units)

② $[H^+] = 10^{-pH}$ (mol dm^{-3})

The pOH of a solution is defined as the negative logarithm to base 10 to OH^- concentration in mol dm^{-3}

③ $pOH = -\log_{10}[OH^-]$

④ $[OH^-] = 10^{-pOH}$

☆ 7 is the neutrality point at 25°C.

Acid dissociation constant, Ka

- only changes with temperature
- exclude concentration of water unless qn specify

$\boxed{\text{can}}$ omit water from equation

⑤ $K_a = \frac{[H^+][A^-]}{[HA]}$ (mol dm^{-3})

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

⑥ $pKa = -\log_{10} Ka$

↳ $-\log_{10}$

* The larger the Ka value, the smaller the pKa, the stronger the acid.

Base dissociation constant, K_b

- only changes with temperature
- exclude concentration of water unless question specify

$\boxed{\text{cannot}}$ omit water from equation

⑦ $K_b = \frac{[BH^+][OH^-]}{[B]}$ (mol dm^{-3})

$B + H_2O \rightleftharpoons BH^+ + OH^-$

⑧ $pK_b = -\log_{10} K_b$

* The larger the K_b value, the smaller the pK_b, the stronger the base.

Ionic product of water, K_w

⑨ $K_w = [H^+][OH^-]$ $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

$(mol^2 dm^{-6})$ $= 1 \times 10^{-14}$, at 25°C → in data booklet ↳ endothermic

- only changes with temperature
- omit concentration of water unless question specify

⑩ $pK_w = -\log_{10} K_w$

$= 14.00$ at 25°C

*point of neutrality (7) can shift. ↑ temp, K_w ↑, point of neutrality shifts. (water is still neutral at high temperatures)

⑪ $pH + pOH = pK_w$

$= 14.00$ (at 25°C)

note

For a conjugate acid-base pair:

⑫ $K_a \times K_b = K_w$

⑬ $pK_a + pK_b = pK_w$

Degree of dissociation, α

- fraction or proportion of weak acid or base molecules that are ionised in water

⑭ $$\alpha = \frac{\text{amount ionised}}{\text{initial amount}}$$

strong acid/base α close to 1

weak acid/base α << 1

Salt Hydrolysis

salt $\xrightarrow{\text{hydrolysis}}$ acidic solution : cations are strong conjugate acid

salt $\xrightarrow[\text{hydrolysis}]{\text{no}}$ neutral solution

salt $\xrightarrow{\text{hydrolysis}}$ alkaline solution : anions are strong conjugate base

* Salt hydrolysis : salt reacting with water to some extent to produce OH^- or H^+ ions

* How to know if a salt will hydrolyse?

① weak acid or weak base in the equation

⇒ the conjugate base or conjugate acid will hydrolyse

Strong acid - strong base

eg. $HCl + NaOH \rightarrow NaCl + H_2O$

Sa Sb salt

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

Na^+: weak conjugate acid

Cl^-: weak conjugate base

⇒ ∴ no reaction, salt will not hydrolyse

Strong acid - weak base

eg. $HCl + NH_3 \rightarrow NH_4Cl$

Sa Wb salt

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

NH_4^+: strong conjugate acid → reaction ✓ ∴ salt will hydrolyse

Cl^-: weak conjugate base → no reaction

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

$NH_4^+ \rightleftharpoons NH_3 + H^+$

Since $[H^+] > [OH^-]$, $pH < 7$

* All hydrolysis reactions are reversible !

Weak acid- strong base

eg. $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

Wa Sb

$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+ \rightarrow$ no reaction

strong conjugate base

weak conjugate acid

↳ reaction ✓ ∴ salt will hydrolyse

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

Since $[OH^-] > [H^+]$, pH >7

Salts with small and highly charged ions → WILL hydrolyse

* Al^{3+}, Cr^{3+}, Fe^{3+}

Al^{3+}, Cr^{3+}, Fe^{3+} has a high charge density

↳ highly polarising

↳ polarises the election cloud of H_2O

↳ O-H bond weakens

↳ release H_3O^+ ion

↳ external H_2O accepts proton

⇒ excess of H_3O^+ (H^+) ions, solution is acidic

Buffer solutions

A buffer solution is a solution capable of maintaining a fairly constant pH when a small amount of acid or base is added to it.

① weak acid buffers

$4 < pH < 6$

② weak base buffers

$8 < pH < 11$

weak acid buffers

weak acidic buffer solutions have a constant pH between 4 and 6. They are madeup of a weak acid and its salt of a strong base.

weak acid: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
salt : $CH_3COONa \rightarrow CH_3COO^- + Na^+$

By LCP, since the salt fully dissociates, CH_3COO^- producted suppresses the dissociation of weak acid.

→ weak acid
⇒ mixture contains more CH_3COOH molecules and more CH_3COO^- ions than pure weak acid
→ strong conjugate base

① Add acid

large reservoir of CH_3COO^- ions from the salt in the buffer
↓
removes the additional H^+ ions from the added acid
↓
pH remains almost constant

$\boxed{CH_3COO^- + H^+ \rightarrow CH_3COOH}$

② Add base

large reservoir of CH_3COOH molecules from the weak acid in the buffer
↓
removes the additional OH^- ions from the added base
↓
pH remains almost constant

$\boxed{CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O}$

⑮ $pH = pKa + \log_{10}\frac{[A^-]}{[HA]}$

$[A^-]$ → from the salt
$[HA]$ → initial acid

*pH of a buffer solution is not affected by dilution.
↳ [salt] and [acid]initial change by the same amount

weak base buffers

weak base buffer solutions have constant pH values between 8 and 11. They are made up of a weak base and its salt of a strong acid.

weak base : $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

salt : $NH_4Cl \rightarrow NH_4^+ + Cl^-$

By LCP, since the salt fully dissociates, NH_4^+ produced suppresses the dissociation of weak base

⇒ mixture contains $\boxed{\begin{array}{l} \text{more } \overset{\text{weak base}}{NH_3} \text{ molecules} \\ \text{more } \underset{\text{strong conjugate acid}}{NH_4^+} \text{ ions} \end{array}}$ and than pure weak base

① Add acid

large reservoir of NH_3 molecules from the weak base in the buffer

↓

removes the additional H^+ ions from the added acid

↓

pH remains almost constant

② Add base

large reservoir of NH_4^+ ions from the salt in the buffer

↓

removes the additional OH^- ions from the added base

↓

pH remains almost constant

⑯ $$pOH = pK_b + \log_{10} \frac{[BH^+]}{[B]}$$

→ from the salt

→ initial base

Buffer capacity

The buffer capacity is a measure of the amount of acid or base that the buffer can remove without a significant change in pH.

- effective buffer region : $\frac{[salt]}{[acid]/[base]}$ is between 0.1 and 10
  $\downarrow$
  $\frac{1}{10}$

→ pH range = pKa ± 1 → pOH range = $pK_b \pm 1$

- for maximum buffer capacity :

  pH = pKa pOH = pK_b

  [acid] = [salt] [base] = [salt]

Application : Blood →

$$\begin{array}{c} CO_2(g) + H_2O(l) \\ \rightleftharpoons \\ H_2CO_3(aq) \\ \rightleftharpoons \\ HCO_3^-(aq) + H^+(aq) \end{array}$$

If the blood becomes too alkaline:

from buffer

$\underline{H_2CO_3(aq)} + OH^- \rightarrow HCO_3^-(aq) + H_2O(l)$

If the blood becomes to acidic:

$\underline{HCO_3^-(aq)} + H^+ \rightarrow H_2CO_3(aq)$

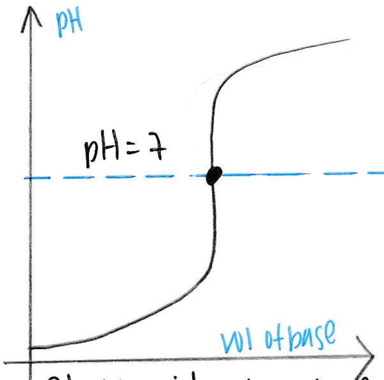
Acid- base titration

→ pH changes drastically

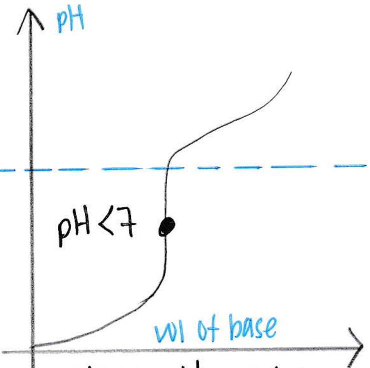
① end point : point at which the reaction is observed to be complete

② equivalence point : point at which stoichiometric amount of titrant is added

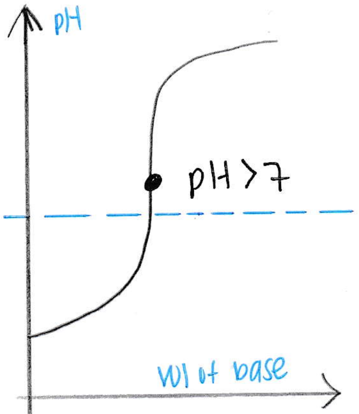
* end-point ≠ equivalence point *



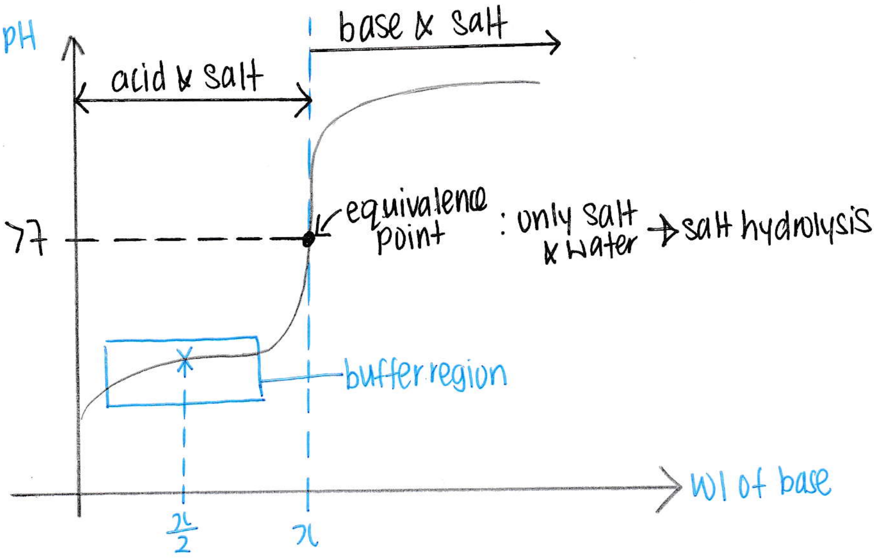
Strong acid- strong base



Strong acid- weak base



weak acid- strong base



- if buffer is before equivalence point, max buffer capacity = $\frac{x}{2}$
- if buffer is after equivalence point, max buffer capacity = $2x$

Acid- base indicators

- usually weak acids or weak bases
- colour depends on the relative concentrations of HIn (acid form) and In^- (base form)

☆ methyl orange : red in acidic, yellow in alkaline
$pK_{In} = 3.7$, pH range = 3.1 - 4.4

☆ phenolphthalein : colourless in acid, pink in alkaline
$pK_{In} = 9.4$, pH range = 8.3 - 10.0

} colour does not indicate whether a solution is basic or acidic

→ Choice of indicator

(a) Strong acid - strong base : almost any indicator
(b) strong acid - weak base : methyl orange
(c) weak acid - strong base : phenolphthalein

Polybasic acids

Acids that contain more than one dissociable proton.

- dissociate in a stepwise manner
  - ↳ each step has its own Ka

$* \; Ka_1 > Ka_2 > Ka_3$

$Ka_1 > Ka_2$: ∵ of electrostatic forces, it is more difficult to remove a positively charged proton from a negative ion than an uncharged molecule.

$Ka_2 > Ka_3$: → ∵ of electrostatic forces, it is more difficult to remove H+ from an anion with a double negative charge than an anion with a single positive charge