

CHEM 3.6

Standard 91392 Demonstrate understanding of equilibrium principles in aqueous systems

This standard can be divided into two parts

1. Equilibrium and reaction quotient
 - a. Solubility of ionic compounds in aqueous system
 - i. Saturated solution, ionic products, K_s and calculation
 - ii. Common ion effects, formation of complex ions and pH in solubility system
2. Acids and bases
 - a. K_w , K_a and K_b
 - b. Weak acid and weak base calculation
 - c. Species in solution
 - d. Buffer solutions concept and calculation
 - e. Titration curve concept and calculation

Please read [this document](#)

Useful equations (equations will not be provided in the examination)

$$n = c v \quad m = n \times M$$

Solubility of ionic compounds

- For AB ionic salts

$$K_s = [A^+][B^-] \quad s = \sqrt{K_s}$$

- For A_2B ionic salts

$$K_s = [A^+]^2[B^{2-}] \quad s = \sqrt[3]{\frac{K_s}{4}}$$

Acid and bases

$$\begin{aligned} K_w &= [H_3O^+][OH^-] & K_w &= 10^{-14} & K_w &= K_a K_b \\ -\log[K_a] &= pK_a & 10^{-pK_a} &= K_a & 14 - pK_a &= pK_b & 10^{-pK_b} \\ &= K_b \\ -\log[H_3O^+] &= pH & 10^{-pH} &= [H_3O^+] \end{aligned}$$

For weak acid calculation

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

Assumptions

- Since K_a is small, therefore $c HA = [HA]$
- Since K_w is small, therefore $[H_3O^+] = [A^-]$

$$[H_3O^+] = \sqrt{K_a \times cHA}$$

For weak base calculation

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

Assumptions

- Since K_b is small, therefore the origin concentration $c B = [B]$
- Since K_w is small, therefore the $[OH^-] = [HB^+]$

$$[OH^-] = \sqrt{K_b \times cB}$$

Equilibrium and solubility

This part of the standard focuses on the equilibrium system of saturated ionic solutions.

1. Equilibrium constant and reaction quotient
2. Solubility of ionic compounds in aqueous system
 - a. Saturated solution, ionic products, K_s and calculations
 - b. Common ion effects, formation of complex ions and pH in solubility system

Equilibrium constant and reaction quotient

- Equilibrium constant (K) is the concentration ratio of species when the system is at equilibrium.
- Reaction quotient (Q) is the concentration ratio of species in any given moment.
- When $Q \neq K$, changes will be made until $Q = K$.
- In a closed system, for a reversible reaction, only three possible situations.
 - System at equilibrium ($Q = K$)
 - Forward reaction toward the equilibrium ($Q < K$)
 - Reverse reaction toward the equilibrium ($Q > K$)

Solubility of ionic compounds in aqueous system

- When an ionic solution is oversaturated, the solution is in an equilibrium system between the left over solids and the dissolved ions.
- This equilibrium constant is called solubility constant (K_s)
- For AB ionic salts
 - $AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$
 - $K_s = [A^+][B^-]$
- For A_2B ionic salts
 - $A_2B(s) \rightleftharpoons 2A^+(aq) + B^-(aq)$
 - $K_s = [A^+]^2[B^{2-}]$

Saturated solution, ionic products, K_s and calculations

- The Q_s of solubility system is also called *ionic products (IP)*
 - When the $IP > K_s$, the solution is oversaturated and precipitate will be formed.
- Solubility (s) is the maximum concentration of the substance at particular temperature.
 - For AB salt
 - $AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$
 - Since the ratio of $AB : A^+ : B^-$ is 1:1:1, therefore $[A^+] = [B^-] = s$
 - $K_s = [A^+][B^-] = s^2$
 - Therefore the relationship between K_s and solubility for AB salt would be

$$s = \sqrt{K_s}$$

- For A_2B salt
 - The $[A^+]$ is twice the amount of $[B^{2-}]$
 - $A_2B(s) \rightleftharpoons 2A^+(aq) + B^-(aq)$
 - Since the ratio between $A_2B : A^+ : B^{2-}$ is 2:1:1, therefore $2[A^+] = [B^{2-}] = s$
 - $K_s = [A^+]^2[B^{2-}] = (2s)^2s = 4s^3$
 - Therefore the relationship between K_s and solubility for A_2B salt would be

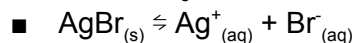
$$K_s = [A^+]^2[B^{2-}] \quad s = \sqrt[3]{\frac{K_s}{4}}$$

Common ion effects, formation of complex ions and pH in solubility system

- When a solution contains an ion that is common to the saturated solution, the solubility decreases.
- This is called the common ion effects.

○ For example

40.0 mL of 0.150 mol L⁻¹ HBr solution was added to 25.0 mL of a saturated silver bromide, AgBr, solution. $K_s(\text{AgBr}) = 5.00 \times 10^{-13}$



- $K_s = [\text{Ag}^+][\text{Br}^-]$

- Since the K_s is very small

- Therefore an assumption is made that the Br⁻ from the AgBr is insignificant.

- $[\text{Ag}^+] = \text{solubility } (s)$

- The amount of Br⁻ would be

$$0.150 \text{ mol L}^{-1} \times 0.0400 \text{ L} = 0.00600 \text{ mol}$$

- The concentration of Br⁻ would be

$$[\text{Br}^-] = \frac{0.00600 \text{ mol}}{(0.04 + 0.025) \text{ L}} = 0.0923 \dots \text{ mol L}^{-1}$$

- Substitute the values into the K_s expression

$$5.00 \times 10^{-13} = s \times 0.923 \dots$$

$$s = \frac{5.00 \times 10^{-13}}{0.923} = 5.42 \times 10^{-13} \text{ mol L}^{-1}$$

- When complex ions is formed with one of the species, the concentration of the ion decreases, therefore the solubility increases as a result.
 - For example
 - In the reaction above, if ammonia (NH₃) is added to the system, NH₃ is going to form a complex ion with Ag⁺ forming the complex ion $[\text{Ag}(\text{NH}_3)_2]^+$.
 - Complex ions from **CHEM 2.2** will be assumed.
 - Since the product is removed, therefore it gives the reaction forward and the solubility of the substance increases.
- If the ionic compound contains hydroxide, the concentration of the hydroxide can be calculated by the *pH* of the solution.
 - If *pH* decreases (by adding acid), the solubility of the substance increases
 - Similarly if the *pH* increases, the solubility of the substance decreases.

Exercise for equilibrium and solubility

- 1) Write the K_s expression and calculate the solubility of the following salts when it dissolves in water:
 - a) BaSO_4 $K_s = 1.1 \times 10^{-10}$

 - b) CaCO_3 $K_s = 3.3 \times 10^{-9}$

 - c) Ag_2CrO_4 $K_s = 2.6 \times 10^{-12}$

- 2) Calculate the K_s of the following solutions:
 - a) Solubility of PbI_2 is $0.00125 \text{ mol L}^{-1}$

 - b) Solubility of Ag_2SO_4 is $1.55 \times 10^{-2} \text{ mol L}^{-1}$

- 3) Predict will precipitate form in the following mixtures
 - a) 200 mL of $0.0010 \text{ mol L}^{-1}$ of NaSO_4 is mixed with 200 mL of $0.0010 \text{ mol L}^{-1}$ of BaCl_2 .
 $K_s(\text{BaSO}_4) = 1.1 \times 10^{-10}$

 - b) 30 mL of 0.100 mol L^{-1} $\text{Pb}(\text{NO}_3)_2$ is mixed with 20 mL of 0.100 mol L^{-1} of K_2CrO_4
 $K_s(\text{PbCrO}_4) = 2.5 \times 10^{-13}$

- 4) Calculate the concentration of Fe^{2+} in a saturated solution of $\text{Fe}(\text{OH})_2$
 $K_s(\text{Fe}(\text{OH})_2) = 4.1 \times 10^{-15}$

- 5) Calculate the pH in the saturated solution of $\text{Fe}(\text{OH})_2$

- 6) Calculate the solubility of $\text{Fe}(\text{OH})_2$ when the $pH = 5$

Acids and bases

This standard is continuation of CHEM 2.6 with a particular focus on the equilibrium system of weak acids and weak bases in aqueous solutions

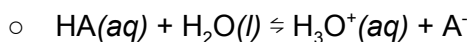
This part of the standard can be divided into five themes

1. K_w , K_a and K_b
 2. Weak acid and weak base calculations
 3. Species in solution
 4. Buffer solutions concept and calculations
 5. Titration curve concepts and calculations
- Below is the list of common acid and common base that applies to this standard

| Acid | Strength | Base | Strength |
|--|----------|--|----------|
| HCl | strong | NaOH | strong |
| HNO ₃ | strong | KOH | strong |
| H ₂ SO ₄ | strong | Ammonia | weak |
| HBr | strong | Amines | weak |
| HF | weak | Conjugate base of weak acid eg CH ₃ COO ⁻ | weak |
| Carboxylic acids | weak | | |
| Conjugate acid of weak base eg NH ₄ ⁺ | weak | | |

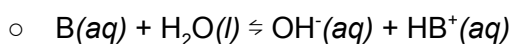
K_w , K_a and K_b

- In CHEM 2.6, the description of a weak acids or weak bases are acids and bases which partially dissociate forming an equilibrium mixture.
- Since it is an equilibrium mixture, therefore an equilibrium expression.
- For weak acid HA



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

- For weak base B



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

- The relationship between K_a and K_b is¹

$$K_w = K_a K_b$$

- Similar to $[H_3O^+]$ is often expressed as pH , K_a is often expressed as pK_a

$$- \log[K_a] = pK_a \quad 10^{-pK_a} = K_a$$

Weak acid and weak base calculations

- There are two assumptions involve for the calculation for pH of the weak acids and bases solutions
- In order to do that, the K_a or pK_a values need to be given (or able to determine)

- Since K_a is small, therefore $c HA = [HA]$

- Vice versa for weak base $c B = [B]$

- Since K_w is small, therefore $[H_3O^+] = [A^-]$

- Vice versa for weak base $[OH^-] = [HB^+]$

- The equilibrium expression is

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

- Applying assumption

$$K_a = \frac{[H_3O^+]^2}{cHA}$$

- Rearrange

$$[H_3O^+] = \sqrt{K_a \times cHA}$$

- This can also be applied to weak base

$$[OH^-] = \sqrt{K_b \times cB}$$

- In the examination, it is expected to show the steps (from K_a expression) and list the assumptions.

¹ See appendix for the mathematics

Species in solution

- The concentration of species can be compared with each other.
- The species of the highest concentration is obviously water.
- It is a useful tools to compare and contrasts the conductivity of the solution.
 - Electrolytes means solution that contains ions which can conduct electricity.
 - The higher the concentration of ions, the higher the electroconductivity.
- **For neutral salts**
 - 1:1 ratio (NaCl)
 - $\text{Na}^+ = \text{Cl}^- > \text{H}_3\text{O}^+ = \text{OH}^-$
 - 1:2 ratio (such as CaCl_2)
 - $\text{Cl}^- > \text{Ca}^{2+} > \text{H}_3\text{O}^+ = \text{OH}^-$
- **For strong acids**
 - Monoprotic acids (HCl)
 - $\text{H}_3\text{O}^+ =^* \text{Cl}^- > \text{OH}^-$
 - Diprotic acids (H_2SO_4)
 - $\text{H}_3\text{O}^+ > \text{SO}_4^{2-} > \text{OH}^-$
- **For weak acids**
 - For molecular acids (CH_3COOH)
 - $\text{CH}_3\text{COOH} > \text{H}_3\text{O}^+ =^* \text{CH}_3\text{COO}^- > \text{OH}^-$
 - For acidic salts (NH_4Cl)
 - $\text{Cl}^- > \text{NH}_4^+ > \text{H}_3\text{O}^+ =^* \text{NH}_3 > \text{OH}^-$
- **For weak bases**
 - For molecular bases (NH_3)
 - $\text{NH}_3 > \text{OH}^- =^* \text{NH}_4^+ > \text{H}_3\text{O}^+$
 - For basic salts (CH_3COONa)
 - $\text{Na}^+ > \text{CH}_3\text{COO}^- > \text{OH}^- =^* \text{CH}_3\text{COOH} > \text{H}_3\text{O}^+$

* Slightly higher due to water dissociation.

Buffer solutions concepts and calculations

- A buffer solution is a mixture of weak acids and weak bases.
- It can be produced by
 - mixing a weak acid solution (or salt) with a weak base solution (or salt)
 - Or neutralise partially a weak acid or a weak base solution with a strong acid or base.
- A buffer able to maintain pH because
 - When a small amount of H_3O^+ is added into a buffer, it will be neutralised by the weak bases
 - Similarly, when a small amount of OH^- is added, it will be neutralised by the weak acids.
- A buffer calculation can be easily done with the K_a expression
 - (some of the teacher will introduce the formula

$$pH = pK_a + \log \frac{B}{A}$$

- It is mathematically the same as the K_a expression²
- For example

An aqueous solution containing a mixture of HF and sodium fluoride, NaF, can act as a buffer solution.

Calculate the mass of NaF that must be added to 150 mL of 0.0500 mol L⁻¹ HF to give a buffer solution with a pH of 4.02. Assume there is no change in volume.

$$M(\text{NaF}) = 42.0 \text{ g mol}^{-1} \quad pK_a(\text{HF}) = 3.17$$

1. Write the K_a expression

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

2. Substitute the known values

$$10^{-3.17} = \frac{10^{-4.02}[F^-]}{0.05}$$

3. Rearrange to determine $[F^-]$ needed in this pH

$$[F^-] = \frac{10^{-3.17} \times 0.05}{10^{-4.02}} = 0.354... \text{ mol L}^{-1}$$

4. Find the amount of F^- needed

$$0.354... \text{ mol L}^{-1} \times 0.150 \text{ L} = 0.0531... \text{ mol}$$

5. Find the mass of NaF needed

$$0.0531 \text{ mol} \times 42.0 \text{ g mol}^{-1} = 2.23 \text{ g (3s.f.)}$$

² See appendix for the mathematics

Titration curve concepts and calculations

- Titration curve is a graphic expression between pH and volume of standard added during a titration.
 - y-axis *pH*
 - x-axis volume in mL
- Below are the titration curves for strong acid vs strong base and strong base vs strong acid.

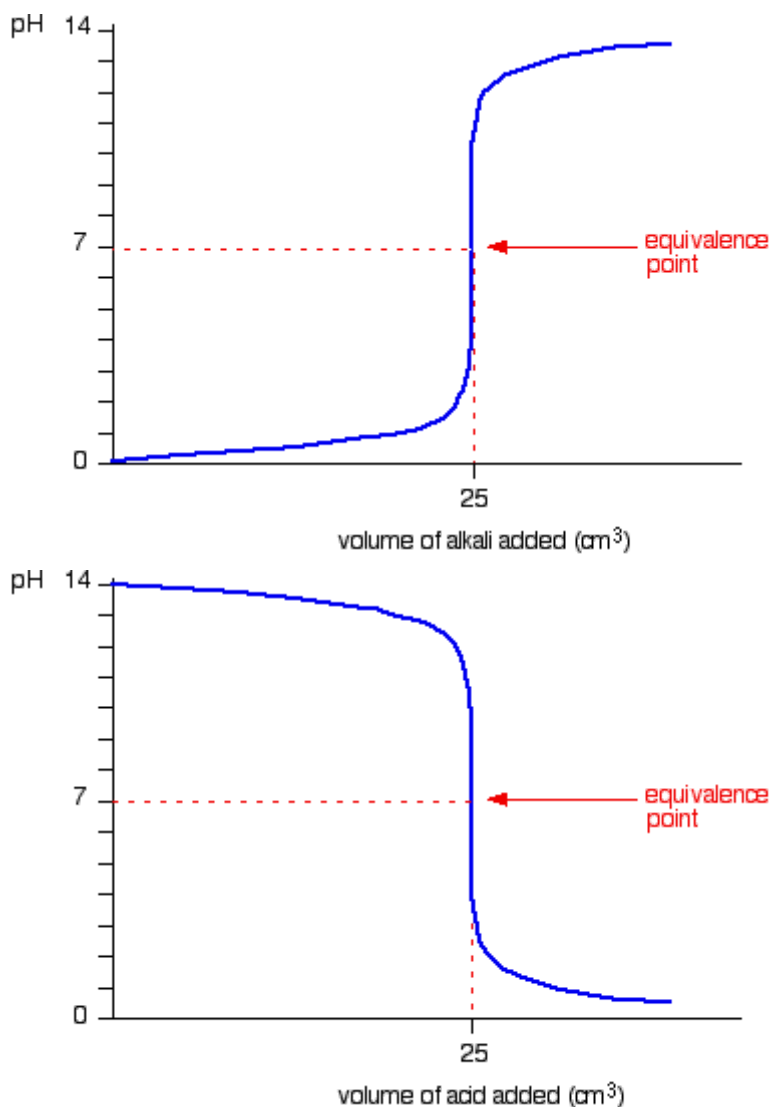


Figure 2.1- Titration curves (top) strong acid - strong base, (bottom) strong base - strong acid.³

- In both cases, the equivalence point $pH = 7$ as it contains a neutral salt.
- However for weak acid vs strong base or weak base vs strong acid, the curves will be different.

³ <https://www.chemguide.co.uk/physical/acidbaseeqia/phcurves.html> accessed on 21/11/2017

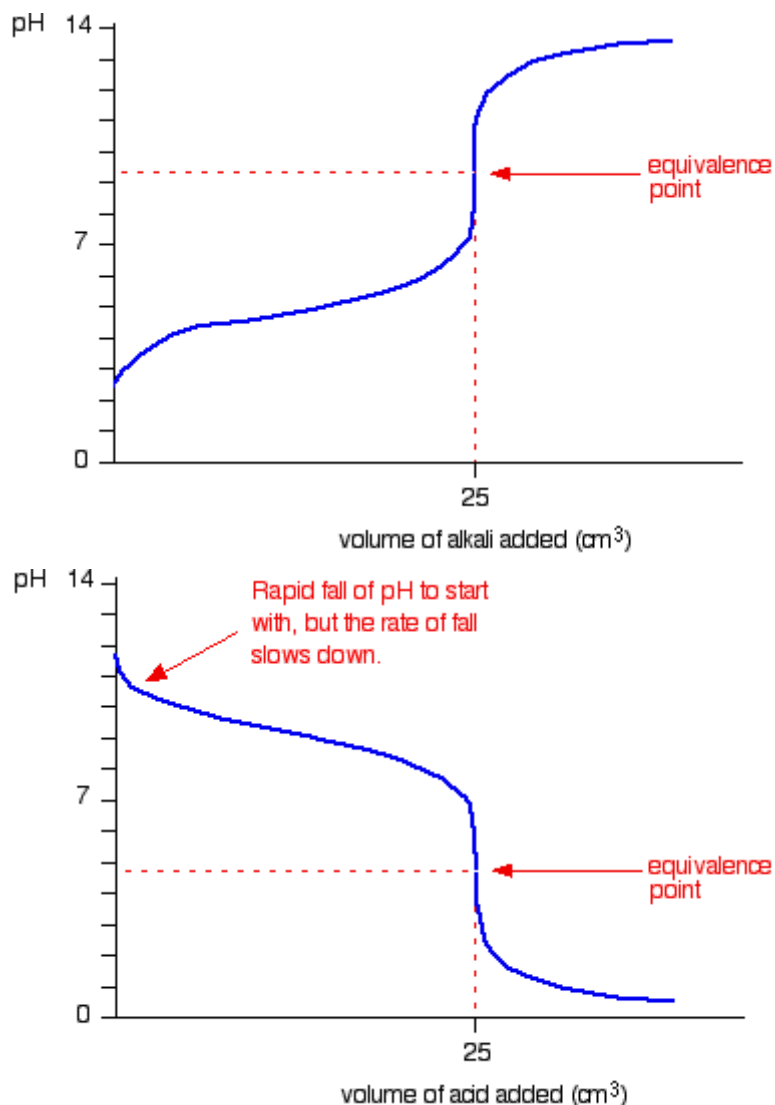


Figure 2.2- Titration curves for (top) weak acid vs strong base, (bottom) weak base vs strong acid.⁴

- There are three important points for weak vs strong titration curves for *pH* calculations.
 - Initial point
 - Buffer zone
 - Equivalence point
 - For weak acid vs strong base
 - The initial point is the weak acid, simple weak acid calculation
 - Buffer zone, use buffer calculations
 - The region between the initial point and equivalence point.
 - It contain both weak acid and its conjugate as it is being neutralised.
 - Note half way between equivalence point is called the half equivalence point.
 - At this point the concentration of the weak acid species is the same as its conjugate.
- $$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad K_a = [H_3O^+] \quad pK_a = pH$$
- Equivalence point
 - All the weak acid is neutralised leaving a conjugate base salt solution
 - Weak base calculation
 - With the amount of acid in the initial point and the **total volume** both equivalence point and the initial volume.
- Vice versa for weak base vs strong acid.

⁴ <https://www.chemguide.co.uk/physical/acidbaseeqia/phcurves.html> accessed 21/11/2017

Exercises for acids and bases

1. Calculate the pH of the following solutions

a. 0.125 mol L^{-1} of sodium ethanoate

$$K_a(\text{CH}_3\text{COOH}) = 1.74 \times 10^{-5}$$

b. 0.500 mol L^{-1} of ammonia

$$K_a(\text{NH}_4^+) = 5.75 \times 10^{-10}$$

c. $0.00250 \text{ mol L}^{-1}$ propanoic acid

$$K_a(\text{C}_2\text{H}_5\text{COOH}) = 1.35 \times 10^{-5}$$

d. 0.050 mol L^{-1} of F^-

$$K_a(\text{HF}) = 6.76 \times 10^{-4}$$

e. 25.0 mL of 0.500 mol L^{-1} ammonia is mixed with 30.0 mL of 0.200 mol L^{-1} of ammonium chloride.

f. 10.0 mL of 0.100 mol L^{-1} propanoic acid is mixed with 15.0 mL of 0.100 mol L^{-1} of sodium propanoate.

g. 10.0 mL of 0.100 mol L^{-1} of hydrogen fluoride of is mixed with 5.00 mL of 0.125 mol L^{-1} of sodium hydroxide.

2. 15.0 mL of 0.100 mol L^{-1} of ammonia is titration against 0.200 mol L^{-1} hydrochloric acid.

a. Calculate the volume of equivalence point

b. Calculate the pH at the initial point

c. Calculate the pH after 5 mL of hydrochloric acid was added

d. Calculate the pH at the equivalence point

Appendix

Reasons for

$$K_w = K_a K_b$$

- Since

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

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

- Canceling all the species

$$\therefore [H_3O^+][OH^-] = K_w = K_a K_b$$

Reason for

$$pH = pK_a + \log \frac{B}{A}$$

- B = [A⁻] or nA⁻
- A = [HA] or nHA

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

- Rearrange making [H₃O⁺] the subject

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

- -log both side

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

- Expand the log on the right hand side

$$pH = -\log K_a - \log \frac{[HA]}{[A^-]}$$

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