CHAPTER 22: Ionic Equilibria

22.1 pH, K_a, pK_a and K_w
22.2 Acid-base Titrations
22.3 Buffer Solutions
22.4 Solubility Equilibria

*Learning outcomes:*

(a) explain the terms pH, K_a, pK_a, K_w and use them in calculations.
(b) calculate $[H^+(aq)]$ and pH values for strong and weak acids and strong bases.
(c) explain the choice of suitable indicators for acid-base titrations, given appropriate data.
(d) describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases.
(e) (i) explain how buffer solutions control pH.
　　(ii) describe and explain their uses, including the role of HCO^{3-} in controlling pH in blood.
(f) calculate the pH of buffer solutions, given appropriate data.
(g) show understanding of, and use, the concept of solubility product, K_{sp}.
(h) calculate K_{sp} from concentrations and vice versa.
(r) show understanding of the common ion effect.

22.1 pH, K_a, pK_a and K_w

The ionic product of water, K_w

1) Water is able to act as an acid as well as a base. Therefore whenever liquid water is present, the following equilibrium occurs.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

This water molecule acts as a base . . .   . . . and this one acts as an acid.
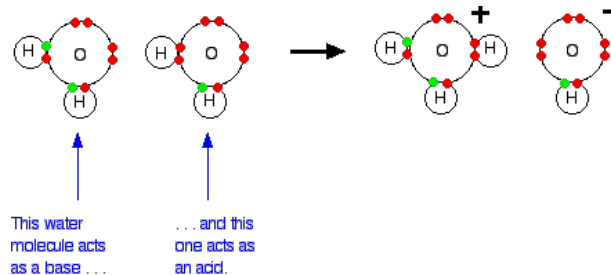
Or the more simplified version(Note that $H^+ \equiv H_3O^+$):

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

2) Therefore the ionic product of water is defined as:

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

3) It means that the product of hydrogen and hydroxide concentrations at a certain temperature is constant, this is true no matter the water is pure or impure.

4) At 25 °C, the value of K_w is **1.00×10^{-14} mol² dm⁻⁶**.

5) Since the above reaction is an endothermic reaction, the value of K_w increases with increasing temperature. At 100 °C, the value is 5.13×10^{-13} mol² dm⁻⁶.

pH of a substance

1) pH of a substance is defined as:

$$pH = -\log_{10}[H^+]$$

2) To calculate the pH of pure water at 25 °C:
   i. Since the water is pure, the hydrogen ion concentration must be equal to the hydroxide ion concentration. For every hydrogen ion formed, there is a

hydroxide ion formed as well.

   ii. So, the expression for K_w can be simplified to:
$$[H^+]^2 = 1.00 \times 10^{-14} \quad ; \text{ since } [H^+] = [OH^-]$$
$$\Rightarrow \quad [H^+] = 1.00 \times 10^{-7}$$

   iii. Therefore the pH of water is given by
$$pH = -\log(1.00 \times 10^{-7})$$
$$pH = 7.00$$

   iv. This implies that at 24 °C, pH 7.00 is the neutral point of water, equal amounts of hydrogen and hydroxide ions are present.

3) i. At 100 °C, the pH of pure water is 6.14. **This does not mean the water is more acidic at higher temperature**.

   ii. pH of 6.14 is the neutral point of water at 100 °C, there are still equal amounts of hydrogen and hydroxide ions present.

<u>Strong and weak acids</u>

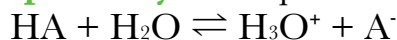1) i. A strong acid **ionises completely** in the presence of water.
$$HA + H_2O \rightarrow H_3O^+ + A^-$$
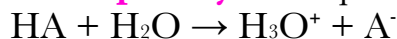
   ii. Therefore the pH of strong monoprotic acid can be calculated using:
$$pH = -\log[H_3O^+]$$
Since the acid ionises completely, $[H_3O^+] = [HA]$
$$pH = -\log[HA]$$

2) i. A weak acid **ionises partially** in the presence of water.
$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

   ii. The pH of a weak acid is calculated using the acid dissociation constant, K_a.

<u>Acid dissociation constant, K_a</u>

1) i. For the dissociation of a weak acid, K_c can be written as:
$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

   ii. However, the concentration of water is fairly constant. This is because at any one time, only about 1 % of the HA has reacted.

   iii. Therefore a new equilibrium constant, K_a is defined as:
$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

2) i. K_a can be used **to measure the strength of weak acids**.
ii. **A stronger acid** has the position of equilibrium further to the right,
   therefore **a higher K_a value**.
iii. **A weaker acid** has the position of equilibrium further to the right, therefore
   a lower K_a value.

acid	K_a (mol dm^{-3})
hydrofluoric acid	5.6×10^{-4}
methanoic acid	1.6×10^{-4}
ethanoic acid	1.7×10^{-5}
hydrogen sulphide	8.9×10^{-8}

3) To make the comparison easier to see, the strength of acids is measured on the
   pK_a scale. Just like pH, pK_a is defined as:
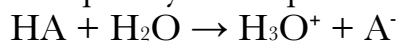
$$pK_a = - \log_{10} K_a$$

4) The numbers now become:

acid	K_a (mol dm^{-3})	pK_a
hydrofluoric acid	5.6×10^{-4}	3.3
methanoic acid	1.6×10^{-4}	3.8
ethanoic acid	1.7×10^{-5}	4.8
hydrogen sulphide	8.9×10^{-8}	7.1

5) Conclusion:
   i. **The stronger the acid, the higher the K_a and the lower the pK_a.**
   ii. **The weaker the acid, the lower the K_a and the higher the pK_a.**

Calculations on pH

1) **To calculate the pH of a strong acid**:
   i. A strong acid ionises completely in the presence of water.
$$HA + H_2O \rightarrow H_3O^+ + A^-$$
   ii. Therefore the pH of a strong monoprotic acid can be calculated using:
$$pH = -\log[H_3O^+]$$
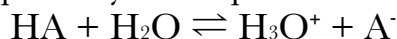
Since the acid ionises completely, $[H_3O^+] = [HA]$
$$pH = -\log[HA] \quad \text{; if [HA] is given}$$
iii. For a diprotic acid, $[H_2A] = 2[H_3O^+]$
iv. For a triprotic acid, $[H_3A] = 3[H_3O^+]$

2) **To calculate pH of a weak acid**:

i. A weak acid ionises partially in the presence of water.
$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

ii. For example, if you have c mol dm^{-3} of weak acid, HA. Do a calculation to find the concentration of H_3O^+ and A^- at equilibrium.

	[HA]	[H$_3$O$^+$]	[A$^-$]
Initial concentration	c	0	0
Change	-x	+x	+x
Equilibrium concentration	c-x	x	x

iii. Important approximations when calculating pH of a weak acid:
   - So little acid has ionised that the concentration of HA at equilibrium is the same as the initial concentration. That is, **$c - x \approx c$**.
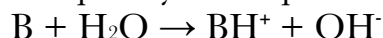   - If the acid is pure, then the concentration of hydrogen ions and the negative ions are the same. That is, **$[H_3O^+] = [A^-] = x$**.
iv. Then use the formula for K_a to obtain the concentration of hydrogen ions, given the value of K_a.
v. Then use the pH formula to calculate the pH.

3) **To calculate the pH of a strong base**:

i. A strong base ionises completely in the presence of water.
$$B + H_2O \rightarrow BH^+ + OH^-$$
ii. Since the base ionises completely, $[OH^-] = [B]$; if [B] is given
iii. Obtain the concentration of hydrogen ions from the expression of K_w. This is valid because the product of $[H^+]$ and $[OH^-]$ is constant at constant temperature.
iv. Then use the pH formula to calculate its pH.
v. Alternatively, a quantity known as pOH can be calculated where
$$pOH = -\log[OH^-]$$
Then use the fact that $pH + pOH = 14$ to calculate its pH.

[Note: Calculation involving weak bases is not required.]

22.2 Acid-base Titrations
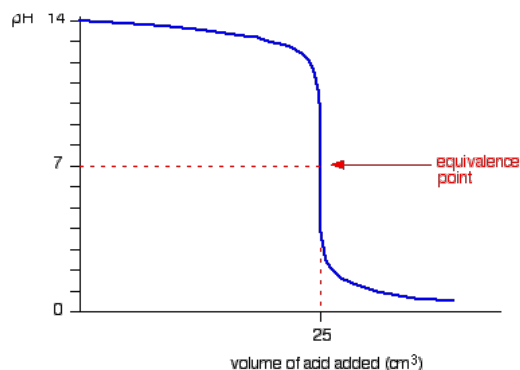
Titration curves

1) Titration curves or pH curves are curves that **show the pH changes during an acid-base titration**.

2) Titration curve of a **strong acid and strong base titration**, take hydrochloric acid and sodium hydroxide as an example:
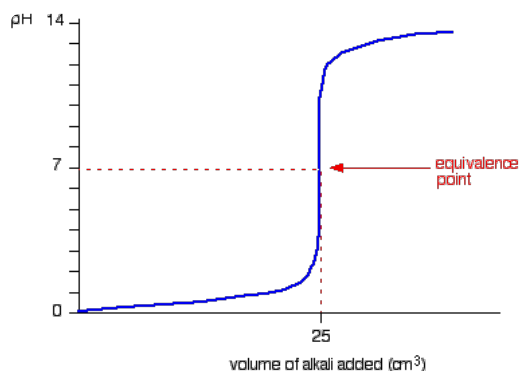   i. *Running the acid into alkali:*
   - pH changes by a small amount until the **equivalence point**, that is, the point where the solutions have been mixed in exactly the right proportions according to the equation.
   - This is followed by a sharp decrease in pH when small amount of acid is added.

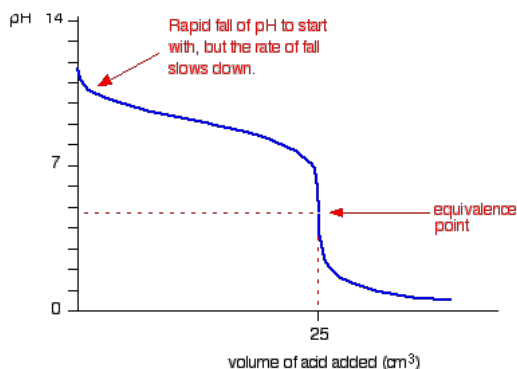   ii. *Running the alkali into acid:*
   - This is the same as above except the curves starts at pH 0, because the curve shows the pH in the conical flask.

3) Titration curve of a **strong acid and weak base titration**, take hydrochloric acid and ammonia as an example:
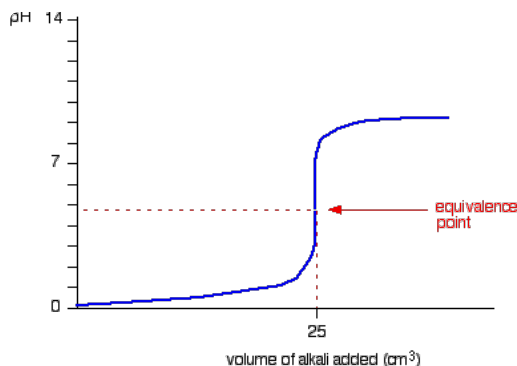
i. *Running the acid into alkali:*
   - The curve starts at pH 12 because a weak base is present.
   - Initially, the pH falls rapidly. As more acid is added, the curve becomes less steep because a buffer solution composed of excess ammonia and ammonium chloride is set up. Buffer solutions resist changes pH when small amount of acid is added.
   - The equivalence point now is a bit acidic.
   - When excess acid is added, the curve is the same as before.

ii. *Running the alkali into acid:*
   - The beginning of curve is the same as before.
   - After the equivalence point(which is also a bit acidic), the pH changes by a small amount. This is because a buffer solution composed of excess ammonia and ammonium chloride is set up. Buffer solutions resist changes in pH when small amount of alkali is added.
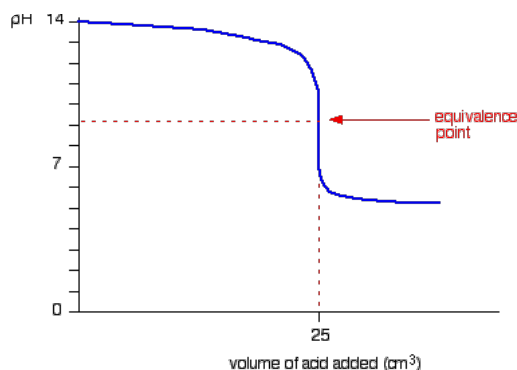

4) Titration curve of a **weak acid and strong base titration**, take ethanoic acid and sodium hydroxide as an example:
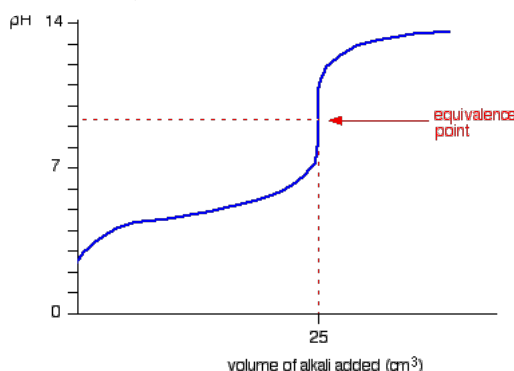   i. *Running the acid into alkali:*
      - The beginning of curve is the same as before.
      - After the equivalence point(which is a bit alkaline), the pH changes by a small amount. This is because a buffer solution composed of excess sodium

ethanoate and ethanoic acid is set up. Buffer solutions resists pH changes when small amount of acid is added.

pH 14

equivalence
point

7

0

25
volume of acid added (cm^3)

ii. *Running the alkali into acid:*
   - The curve starts at pH 3 because a weak acid is present.
   - Initially, the pH increases rapidly. As more alkali is added, the curve becomes less steep because a buffer solution composed of excess sodium ethanoate and ethanoic acid is set up. Buffer solutions resist changes pH when small amount of alkali is added.
   - The equivalence point now is a bit alkaline.
   - When excess alkali is added, the curve is the same as before.

pH 14

equivalence
point

7

0

25
volume of alkali added (cm^3)

5) Titration curve of a **weak acid and weak base titration**, take ethanoic acid and ammonia as an example:
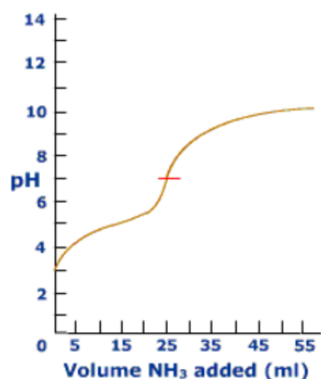   i. *Running the acid into alkali*
      - The curve starts at pH 12 because a weak base is present.
      - Initially, the pH falls rapidly. As more acid is added, the curve becomes less steep because a buffer solution composed of excess ammonia and ammonium ethanoate is set up. Buffer solutions resist changes pH when small amount of acid is added.
      - There is no sharp decrease in pH at any volume.
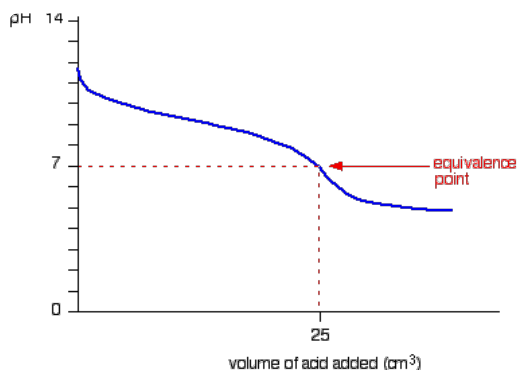
ii. _Running the alkali into acid_
- The curve starts at pH 3 because a weak acid is present.
- Initially, the pH increases rapidly. As more alkali is added, the curve becomes less steep because a buffer solution composed of excess ammonium ethanoate and ethanoic acid is set up. Buffer solutions resist changes pH when small amount of alkali is added.
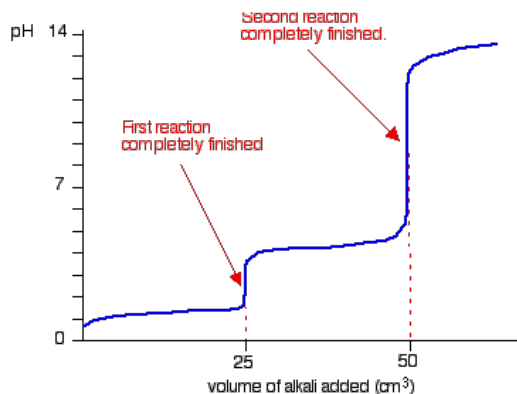

6) Titration curve of a **polyprotic acid and base titration**, take ethanedioic acid and sodium hydroxide as an example:
i. _Running the alkali into acid:_
- Ethanedioic acid is a diprotic acid, it donates the two protons in two stages. This is because one proton is more easier to remove than the other.
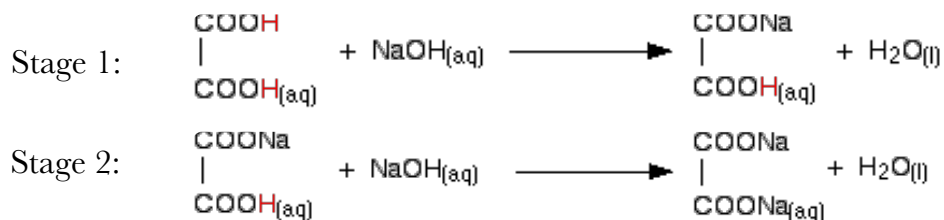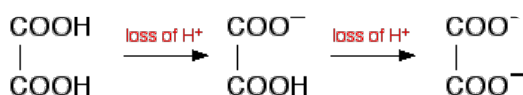
- The curve will therefore show two sharp increase in pH.

Acid-base indicator

1) An *indicator* is a substance that changes colour as the pH of the solution which it dissolves changes.

2) In an acid-base titration, an indicator is used to mark the **end point** of the titration, that is, the point where the indicator changes colour.

3) Most indicators are **weak acids**. They have an acid colour and a base colour.

4) Consider a general indicator with the formula HIn. HIn has a different colour from In$^-$. The colour of HIn is called the acid colour while the colour of In$^-$ is called the base colour.

$$HIn \rightleftharpoons H^+ + In^-$$
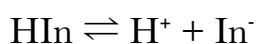
   i. When acid is added, the equilibrium position shifts to the left due to the increasing concentration of H$^+$ ions. The indicator exists predominantly as HIn. Hence, the solution shows the acid colour.
   ii. When base is added, the equilibrium position shifts to the right due to the removal of H$^+$ ions. The indicator exists predominantly as In$^-$. Hence, the solution shows the base colour.

5) Take methyl orange as an example, it has an acid colour of red and a base colour of yellow.

$$H\text{-}Meor_{(aq)} \rightleftharpoons H^+_{(aq)} + Meor^-_{(aq)}$$

   i. When acid is added, the equilibrium position shifts to the left and the solution looks red.
   ii. When base is added, the equilibrium position shifts to the right and the solution looks yellow

Importance of pK_{In}

1) Since the indicator is a weak acid, an expression of K_a can be written for it. However, the K_a now is called K_{In}.

$$K_{ind} = \frac{[H^+]\,[Ind^-]}{[HInd]}$$

2) As acid/base is added, the colour changes. At half-way through the colour changes, there will be equal amount of HIn and In⁻ present. The equilibrium expression now becomes:

$$K_{ind} = \frac{[H^+]\,\cancel{[Ind^-]}}{\cancel{[HInd]}}$$

$$K_{ind} = [H^+]$$

$$pH = pK_{ind}$$

3) This means that the end point depends entirely on the pK_{In} of the indicator. At pH = pK_{In}, the indicator is changing its colour.

4) However, the indicator usually changes its colour over a range of pH, usually around **pK_{In} ± 1**, this is called the **pH range** of am indicator.

4) Some common examples:

Indicator	pK_{In}	acid colour	alkaline colour	pH range
methyl orange	3.7	red	yellow	3.1 – 4.4
methyl red	5.1	red	yellow	4.2 – 6.3
litmus		red	blue	5.0 – 8.0
bromothymol blue	7.0	yellow	blue	6.0 – 7.6
phenolphthalein	9.3	colourless	red	8.3 – 10.0

Selecting a suitable indicator for titration

1) An indicator should be chosen such that it changes colour close to the equivalence point of the titration to give an accurate titration result.

2) The indicator therefore should have a pH range close to the equivalence point of the titration.

3) A guide to choose a suitable indicator:

Titration	Marked pH change	Indicator
strong acid – strong base	4 – 10	almost *any* indicator, e.g. methyl orange (3.1 – 4.4) litmus (5.0 – 8.0) phenolphthalein (8.3 – 10.0)
weak acid – strong base	7.5 – 10.5	phenolphthalein (8.3 – 10.0)
strong acid – weak base	3.5 – 6.5	methyl red (4.2 – 6.3) methyl orange (3.1 – 4.4)
weak acid – weak base	no marked pH change	end-point *cannot* be detected accurately by any indicator.

Finding pK$_a$ from titration curves

1) Suppose during an acid-base titration, 25 cm³ of alkali is required to neutralise a weak acid. Therefore at half-neutralisation, half-volume of the alkali has been added, that is 12.5 cm³.

$$HA_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)} + A^-_{(aq)}$$

2) Half of the acid has been neutralised and half of the salt has been formed. Therefore, [HA] = [A⁻].

3) According to the formula, log([HA]/[A⁻]) = 1 and pK$_a$ = pH.

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

4) Conclusion is, **pK$_a$ is the pH of the solution at half-neutralisation**.

22.3 Buffer Solutions

What is a buffer solution?

1) A *buffer solution* is a solution whose pH does not change significantly when small amount of acid or base is added to it.

2) Buffer solutions should therefore contain:
   i. **large amount of acid** to react with the base added.

ii. **large amount of base** to react with the acid added.

3) Since the added acid and base can be removed, the pH does not change significantly.

4) These conditions can be achieved if the solution contains **a mixture of a weak acid and its conjugate base**, or **a weak base with its conjugate acid**.

5) There are two types of buffer solutions, named acidic buffer solution and alkaline buffer solution.
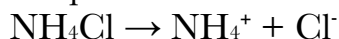
<u>Acidic buffer solution</u>

1) An acidic buffer solution is acidic and can be made **by mixing a weak acid and its conjugate base together**. Take ethanoic acid and ethanoate ion as an example.

2) Sodium ethanoate is added to ethanoic acid. Sodium ethanoate dissociates completely according to the equation:
$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$
...while ethanoic acid dissociates partially according to the equation:
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

3) The presence of ethanoate ions causes the equilibrium position to shift to the left. The solution now contains:
  i. **large reservoir of ethanoic acid molecules**.
  ii. **large reservoir of ethanoate ions**.
 iii. enough hydrogen ions to make the solution acidic.

4) **<u>When acid is added</u>**:
  i. The hydrogen ions from the acid added will **react with the large reservoir of ethanoate ions**.
$$H^+ + CH_3COO^- \rightarrow CH_3COOH$$
  ii. The extra hydrogen ions are removed, and the pH drops very little.

5) **<u>When base is added</u>**:
  i. The hydroxide ions from the base added **will react with the large reservoir of ethanoic acid molecules**.
$$OH^- + CH_3COOH \rightarrow CH_3COO^- + H_2O$$

ii. The extra hydroxide ions are removed, and the pH increases very little.

<u>Alkaline buffer solution</u>

1) An alkaline buffer solution is alkaline and can be made **by mixing a weak base and its conjugate acid together**. Take ammonia and ammonium ion as an example.

2) Ammonium chloride is added to ammonia. Ammonium chloride dissociates completely according to the equation:
$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$
...while ammonia ionises partially according to the equation:
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
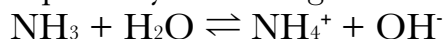
3) The presence of ammonium ions causes the equilibrium position to shift to the left. The solution now contains:
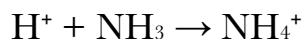   i. **large reservoir of ammonia molecules**.
   ii. **large reservoir of ammonium ions**.
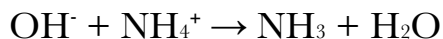   iii. enough hydroxide ions to make the solution alkaline.

4) **When acid is added**:
   i. The hydrogen ions from the acid added **will react with the large reservoir of ammonia molecules**.
$$H^+ + NH_3 \rightarrow NH_4^+$$
   ii. The extra hydrogen ions are removed, and the pH drops very little.

5) **When base is added**:
   i. The hydroxide ions from the base added **will react with the large reservoir of ammonium ions**.
$$OH^- + NH_4^+ \rightarrow NH_3 + H_2O$$
   ii. The extra hydroxide ions are removed, and the pH increases very little.

<u>Calculating the pH of buffer solutions</u>

1) For an acidic buffer solution:
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
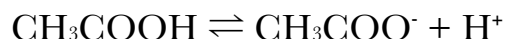
   i. Make the following assumptions:
      - **Concentration of ethanoate ions is equal to the concentration of sodium ethanoate added**. This is done by ignoring the negligible amount of ethanoate ions coming from the dissociation of ethanoic acid.

- **Concentration of ethanoic acid is equal to its original concentration**. This is done by ignoring the negligible amount of ethanoic acid dissociated.

ii. The K_a expression of ethanoic acid now becomes:

Assume this is the same as the
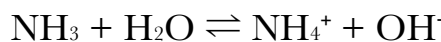concentration of the sodium ethanoate

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Assume this is the same as the
concentration of the original acid.

iii. Given the value of K_a of ethanoic acid, concentration of hydrogen ions and hence the pH of the buffer solution can be found.

2) For an alkaline buffer solution:
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

   i. **Adjust the point view to the ammonium ion rather than ammonia**. This is possible because ammonium ions are weak acids. Therefore:
$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

   ii. Make the following assumptions:
   - **Concentration of ammonium ions is equal to the concentration of ammonium chloride added**. This is done by ignoring the negligible amount of ammonium ions coming from the ionisation of ammonia.
   - **Concentration of ammonia is equal to its original concentration**. This is done by ignoring the negligible amount of ammonia ionised.

   iii. The K_a expression of ammonium ion now becomes:

Assume this is the same as the concentration
of the original ammonia solution.

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

Assume this is the same as the concentration
of the ammonium chloride.

   iv. Given the value of K_a of ammonium ion, concentration of hydrogen ions and hence the pH of the buffer solution can be found.
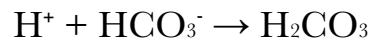
<u>Importance of buffer solutions in biological systems</u>

1) Most biological reactions(especially those involving enzymes) are very sensitive to pH, since enzymes can only function within a narrow range of pH.

2) For example, if the pH of human blood(pH 7.4) is changed by as little as 0.4 unit, it could prove fatal.

3) There are two important buffer systems in the human blood:
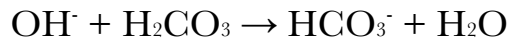   i. The carbonic acid/hydrogen carbonate system.
   ii. The phosphate system.

4) The carbonic acid/hydrogen carbonate system:
   i. The following equilibrium is involved:
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

   ii. When a little acid is added:
$$H^+ + HCO_3^- \rightarrow H_2CO_3$$
   iii. When a little base is added:
$$OH^- + H_2CO_3 \rightarrow HCO_3^- + H_2O$$

5) The phosphate system:
   i. The following equilibrium is involved:
$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$$

   ii. When a little acid is added:
$$H^+ + HPO_4^{2-} \rightarrow H_2PO_4^-$$
   iii. When a little base is added:
$$OH^- + H_2PO_4^- \rightarrow HPO_4^{2-} + H_2O$$
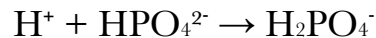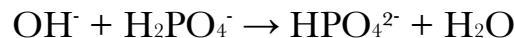
22.4 Solubility Equilibria

<u>Solubility product, K_{sp}</u>

1) *Solubility product, K_{sp}* is the product of the concentrations of each ion in a saturated solution of a sparingly soluble salt at 298 K, raised to the power of their relative concentrations.
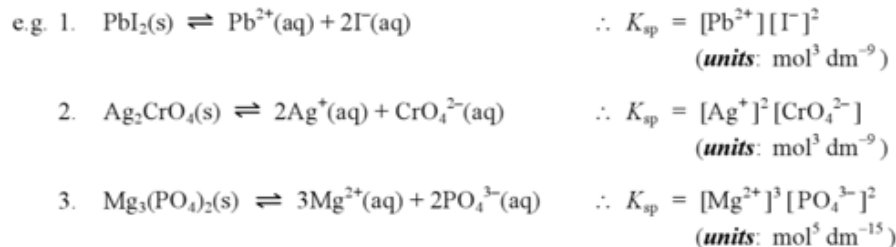
e.g. 1. $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$ $\therefore K_{sp} = [Pb^{2+}][I^-]^2$
(*units*: $mol^3\ dm^{-9}$)

2. $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$ $\therefore K_{sp} = [Ag^+]^2[CrO_4^{2-}]$
(*units*: $mol^3\ dm^{-9}$)

3. $Mg_3(PO_4)_2(s) \rightleftharpoons 3Mg^{2+}(aq) + 2PO_4^{3-}(aq)$ $\therefore K_{sp} = [Mg^{2+}]^3[PO_4^{3-}]^2$
(*units*: $mol^5\ dm^{-15}$)

2) For any so called 'insoluble salt', a tiny amount of it do dissolve in water.

3) i. Solubility product only apply if the solution is in equilibrium with its solid, in other words, **the solution is saturated**.
 ii. It means that in a saturated solution at 298 K, when the concentrations of the ions are multiplied together, the value is the solubility product.

4) **The higher the value of K_{sp}, the more soluble the salt is**.

5) Solubility product can be used **to predict precipitation**:
 i. If the product of the concentrations of ions is less than the solubility product, the solution is not saturated, **no precipitate will be formed**.
 ii. If the product of the concentrations of ions is equal to the solubility product, the solution is saturated, **no precipitate is formed yet**.
 iii. If the product of the concentrations of ions is more than the solubility product, the solution is saturated, **precipitation occurs** to reduce the concentrations to a value equal to the solubility product.

Calculations on solubility product

1) To calculate solubility product from solubility of ions:

The solubility of calcium phosphate, $Ca_3(PO_4)_2$, is 7.7×10^{-4} g dm^{-3} at 25 °C. Calculate its solubility product at this temperature. (O = 16; P = 31; Ca = 40)

First, you will have to convert the concentration into mol dm^{-3}. 1 mole of calcium phosphate weighs 310 g. The concentration in mol dm^{-3} is therefore

$$\frac{7.7 \times 10^{-4}}{310} = 2.48 \times 10^{-6} \text{ mol dm}^{-3}$$

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO_4^{3-}_{(aq)}$$
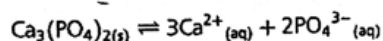
Each mole of calcium phosphate that dissolves produces 3 moles of calcium ions in solution and 2 moles of phosphate ions.

$$[Ca^{2+}] = 3 \times 2.48 \times 10^{-6}$$
$$= 7.44 \times 10^{-6} \text{ mol dm}^{-3}$$

$$[PO_4^{3-}] = 2 \times 2.48 \times 10^{-6}$$
$$= 4.96 \times 10^{-6} \text{ mol dm}^{-3}$$

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$
$$= (7.44 \times 10^{-6})^3 \times (4.96 \times 10^{-6})^2$$
$$= 1.0 \times 10^{-26} \text{ mol}^5 \text{ dm}^{-15}$$

2) To calculate the solubility of ions from the solubility product

Q6. Silver carbonate has a solubility product of 8.0×10^{-12} mol^3 dm^{-9}. What is its solubility in g dm^{-3}? [M_r of Ag_2CO_3 = 276]

S. Let the solubility of Ag_2CO_3 be x.

$$Ag_2CO_3 \text{ (s)} \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$$
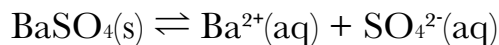$$\quad\quad x \quad\quad\quad\quad\quad 2x \quad\quad\quad\quad x$$
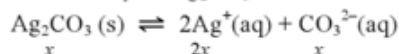
$$K_{sp} = [Ag^+]^2[CO_3^{2-}] = (2x)^2(x) = 4x^3$$

$$\therefore x = \sqrt[3]{\tfrac{1}{4}K_{sp}} = \sqrt[3]{\tfrac{1}{4}(8.0 \times 10^{-12})} = 1.26 \times 10^{-4} \text{ mol dm}^{-3}$$

Hence, solubility of $Ag_2CO_3 = nM_r = (1.26 \times 10^{-4} \times 276) = 0.0348$ g dm^{-3} *(ans)*

Common ion effect

1) Consider the equilibrium of barium sulfate and its ions:

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

If sulfuric acid, H_2SO_4 is added, the concentration of sulfate ions increases and the position of equilibrium shifts to the left. More precipitate is formed and barium sulfate becomes less soluble.

2) The common ion effect is therefore the reduction in the solubility of a dissolved salt by adding a solution of a compound which has an ion in common with the dissolved salt, this often results in precipitation.

3) The solubility of an ionic compound in aqueous solution containing a common ion is less than its solubility in water.
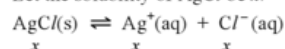
Calculations on common ion effect

1) To calculate the solubility of an ionic compound in different solvents:

To calculate the solubility of silver chloride in the following solutions:
[Solubility product of silver chloride $= 2.0 \times 10^{-10}$ mol^2 dm^{-6}]
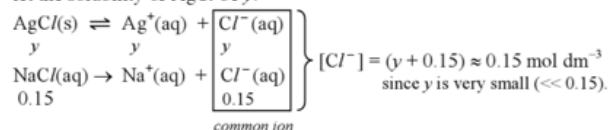
(i) water

- Let the solubility of AgCl be x.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
$$\quad\quad x \quad\quad\quad x \quad\quad\quad x$$

$$K_{sp}(AgCl) = [Ag^+][Cl^-] = x^2$$

$$\therefore x = \sqrt{K_{sp}}$$
$$= \sqrt{2.0 \times 10^{-10}} = 1.41 \times 10^{-5} \text{ mol dm}^{-3}$$

(ii) 0.15 mol dm^{-3} sodium chloride

- When AgCl is dissolved in 0.15 mol dm^{-3} NaCl(aq), let the solubility of AgCl be y.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
$$\quad\quad y \quad\quad\quad y \quad\quad\quad y$$
$$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$$
$$\quad 0.15 \quad\quad\quad\quad\quad 0.15$$

$$[Cl^-] = (y + 0.15) \approx 0.15 \text{ mol dm}^{-3}$$
since y is very small ($\ll 0.15$).

common ion

$$K_{sp}(AgCl) = [Ag^+][Cl^-]$$
$$2.0 \times 10^{-10} = (y)(0.15)$$
$$\therefore y = \frac{2.0 \times 10^{-10}}{0.15} = 1.33 \times 10^{-9} \text{ mol dm}^{-3}$$

2) To predict precipitation on mixing two solutions:

Will a precipitate of lead(II) chloride be formed if 10 cm^3 of 0.10 mol dm^{-3} lead(II) nitrate solution, Pb(NO$_3$)$_2$, is mixed with 10 cm^3 of 0.20 mol dm^{-3} hydrochloric acid, HCl? K_{sp}(PbCl$_2$) $= 1.6 \times 10^{-5}$ mol^3 dm^{-9} at 298 K.

The first thing to notice is that when you mix the solutions, all the ion concentrations will decrease. In this case each solution is being diluted from 10 cm^3 to a total volume of 20 cm^3 – so each is diluted by a factor of 2.

Before any reaction takes place, the important ion concentrations are:

$[Pb^{2+}] = 0.050$ mol dm^{-3} $[Cl^-] = 0.10$ mol dm^{-3}

The solubility product expression for lead(II) chloride is given by:

$K_{sp} = [Pb^{2+}][Cl^-]^2 = 1.6 \times 10^{-5}$ mol^3 dm^{-9}

If you multiply our ion concentrations together in the same way you get:

$[Pb^{2+}][Cl^-]^2 = 0.050 \times (0.10)^2$
$= 5.0 \times 10^{-4}$ mol^3 dm^{-9}

This answer is bigger than the solubility product. This is not allowed! You will therefore get a precipitate in order to reduce the ion concentrations in solution until $[Pb^{2+}][Cl^-]^2 = 1.6 \times 10^{-5}$ mol^3 dm^{-9}.