Equilibrium in solution

Ionization of a weak acid

A weak acid is one that is partially ionized in water. For instance a weak acid HA will ionize in water as follow

$$HA\ (aq) + H_2O(l) \leftrightarrow H^+(aq) + A^-(aq)$$

$$K_c = \frac{[H^+][A^-]}{[HA][H_2O]}$$

The concentration of H_2O is almost constant such that it can be incorporated in K_c ti give another constant Ka

thus, $K_a = K_c[H_2O] = \frac{[H^+][A^-]}{[HA]}$

The greater the extent of dissociation, the greater are [H$^+$] and [A-] in solution; the greater the Ka, and the stronger is the acid.

Alternatively, the strength of the acid is expressed in terms of pH. The 'p' in pH comes from the German word 'potenz' meaning power and 'H' from [H$^+$]. The pH of solution is the negative logarithm to base ten of the molar concentration of hydrogen ions.
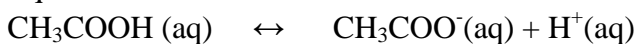i.e., $pH = -\log_{10}[H^+]$

Example 1
The pH of 0.1M ethanoic (acetic) acid, CH_3COOH, is 3.40 at 25^0C. What is the dissociation constant of ethanoic acid at this temperature?

solution

Equation
$$CH_3COOH\ (aq) \leftrightarrow CH_3COO^-(aq) + H^+(aq)$$

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

Since the concentration of H+ ions form water is much smaller that the concentration of those from acid; $[H+] \approx [CH_3COO^-] = $ antilog-3.4
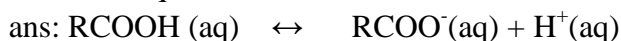
$$= 4.0 \times 10^{-4} \text{moldm}^{-3}$$

and $[CH_3COOH] = 0.01 - [H^+] \approx 0.01$

Thus, $K_a = \dfrac{[4 \times 10^{-4}][4 \times 10^{-4}]}{[0.01]}$

$$= 1.6 \times 10^{-5} \text{moldm}^{-3}$$

Example 2

RCO_2H is a weak acid

(a) Write the equation for the ionization of the weak acid RCOOH in water (1mark)

ans: $RCOOH \text{ (aq)} \longleftrightarrow RCOO^-\text{(aq)} + H^+\text{(aq)}$

(b) Write the expression for the ionization constant Ka, for the acid.

$$K_a = \frac{[H^+][RCOO^-]}{[RCOOH]}$$

(c) Calculate the hydrogen ion concentration of 0.25M solution for the acid ($K_a = 1.8 \times 10^{-5}$) (4marks)

Solution

Let $[H^+] = x$

Also, $[H^+] = [RCOO^-] = x$

$[RCOOH] = [0.25 - x) \approx 0.25 \text{ moldm}^{-3}$, since the concentration of H+ is very small.

$\Rightarrow$ 1.8 x 10-5 $= \dfrac{x^2}{0.25}$

$\Rightarrow$ $x = 2.12 \times 10^{-3} \text{ moldm}^{-3}$.

$\therefore$ Concentration of $H^+ = 2.12 \times 10^{-3} \text{ moldm}^{-3}$

Trial 1

Calculate the hydrogen ions concentration and pH of 0.01M solution of ethanoic acid, CH_3COOH (Ka = $1.8 \times 10^{-5} \text{moldm}^{-3}$)

Trial 2

The pH of s 0.001Molar solution of benzoic acid C_6H_5COOH is 3.59. Calculate

(i) the dissociation constant of the acid
(ii) The pK_a value of the acid
(iii) the degree of dissociation at concentration given

Trial 3

(a) Write an expression for the acid dissociation constant (K_a) of ethanoic acid in the following equilibrium

$$CH_3COOH \text{ (aq)} \leftrightarrow CH_3COO^-\text{(aq)} + H^+\text{(aq)}$$

(b) State the relationship between pK_a and K_a

(c) Given that the approximate value of K_a for ethanoic acid is $1.8 \times 10^{-5} \text{moldm}^{-3}$, calculate

    (i) The pK_a

    (ii) the percentage ionization of acid in a 1M aqueous solution

(d) The pK_a values of $(CH_3)_3CCOOH$ and Cl_3COOH at 20^0C are 5.50 and 0.65 respectively. Which is a stronger acid?

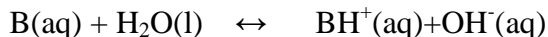## Trial 4

Chloric (I) (hypochlorous) acid HClO, is a weak acid; $K_a[HClO] = 3.2 \times 10^{-8} \text{ moledm}^{-3}$.

(a) Calculate the $[H^+]$ and $[^-OH]$ in $1.25 \times 10^{-2}M$ HClO.

(b) What is the pH of $1.25 \times 10^{-2}M$ HClO

Ionization of weak base

A base is a substance that abstracts a proton from water or dissociates in water to produce hydroxyl ion. Like weak acid, weak base are only partially dissociated in water.

$$B\text{(aq)} + H_2O\text{(l)} \leftrightarrow BH^+\text{(aq)} + OH^-\text{(aq)}$$

$$K_c = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

The concentration of H_2O is almost constant such that it can be incorporated in K_c ti give another constant K_b

thus, $K_b = K_c[H_2O] = \dfrac{[BH^+][OH^-]}{[B]}$

Like K_a, K_b, is a function of temperature, and the higher the K_b the stronger the base.

Example 3

(a) At 250C ammonia has a base ionization constant $K_b = 1.8 \times 10^{-5} \text{moldm}^3$.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

(b) Calculate the concentration of $[^-OH]$ in 0.1M ammonia solution at 25^0C. state any assumption

Lee [OH-] be x

Assumption: OH^- ions from ionization of water are negligible compared to those from ionization of ammonia

$[OH^-] = [NH_4^+] = x$

$[NH_3] = (0.1 - x) \cong 0.1$ since x is very small

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.1} = 1.8 \text{ x } 10\text{-}5$$

$\Rightarrow \quad x = 1.34 \; x \; 10^{-3}$ moldm^{-3}

Trial 5

Calculate the concentration of hydroxide ion in 0.1M NH_4OH (Kb = 1.75x 10^{-5}moldm^{-3})

Dissociation of water

Water ionizes as follows

$H_2O(l) \quad \leftrightarrow \quad H^+(aq) + OH^-(aq)$

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

The concentration of H_2O is constant and is incorporated in the value of K_c to give a new constant K_w.

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

K_w is ionic product for water, at 25^0C pure water has Kw = 1 x 10^{-14} mol^{2}dm^{-6}.

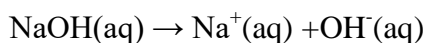## Application of K_w
It is used to determine the pH of bases

Where [H+] $= \frac{K_w}{[OH^-]}$ or $\frac{1 \; x \; 10^{-14}]}{[OH^-]}$

Example 4

Calculate the pH of 0.1M NaOH solution

Solution

Sodium hydroxide dissociate in water as follows

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

$[OH^-] = [NaOH] = 0.1$moles

$[H+] = \frac{10^{-14}}{0.1} = 10^{-13}$

pH = -log[H$^+$] = log[10^{-13}] = 13

Trial 6

Calculate the pH of 1M NH$_4$OH ($K_b = 1.7x\ 10^{-5}$moldm^{-3})

Trial 7

Calculate the basic constant $\frac{[NH_4^+][OH^-]}{[NH_3]}$ for ammonia, given that the pH of $\frac{M}{20}$ is 10.6 (kw = 10^{-14} mol^{2}dm^{-3})

Trial 8

A 0.01M solution of ammonia is 4.0% ionized
 (a) Calculate the pH of the solution, ($K_{w\ =\ 10^{-14}}$ mol^{2}dm^{-3})   (3marks)
 (b) Determine the base dissociation constant (3marks)

Trial 9

 (a) Write an expression of pH
 (b) Calculate the pH of a0.05M sodium hydroxide solution, ($K_{w\ =\ 10^{-14}}$ mol^{2}dm^{-3}) (2marks)
 (c) State the effect of dilution on pH of sodium hydroxide solution? give a reason for your answer

Trial 10

The second dissociation constant of a dibasic acid is 4.39 x 10^{-5} mol^{2}dm^{-3} at 25^{0}C.
 (a) Calculate the degree of ionization of 0.01M solution of the acid
 (b) Sketch a graph to show the degree of dissociation varies with dilution.

Trial 11

A solution containing 2.3 x 10^{-6} moldm^{-3} of aluminium hydroxide completely ionizes in water, (Kw =10^{-14}mol^{2}dm^{-3}).
(a)Write equation for the reaction of aluminium hydroxide (1 ½ mark)
(b)   Calculate the pH of the resultant solution (3marks)

Buffers

These are solutions that resist changes in pH on addition of small amounts of either the acid or base.

Buffers are usually made of either a mixture of a weak acid and its salt with strong base (e.g. $CH_3COOH + CH_3COO^-Na^+$) or a mixture of a weak base and its salt with a strong acid (e.g. $NH_3 + NH_4Cl$)

Mechanism of buffers
Consider a hypothetical weak acid, HA, in a solution with it salt MA. In this solution, HA, will be very slightly dissociated whilst MA is fully dissociated into ions;

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

MA(aq) $\rightarrow$ M$^+$(aq) + A$^-$(aq)

Hence the mixture contains a relatively high concentration of un-ionized HA (acid) and relatively high concentration of A⁻ (base)

If an acid is added to this system, the H^+ ions in the acid will combine with A⁻ions to form HA thus removing nearly all the added H+ ions and keeping the pH relatively unchanged.
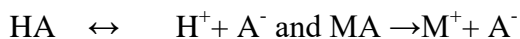
$H^+(aq) + A^-(aq) \rightarrow HA(aq)$
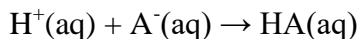
When an alkali is added to a system, the added
⁻OH ions combine with the acid to produce water

$HA(aq) + {}^-OH(aq) \rightarrow H_2O(l) + A^-(aq)$
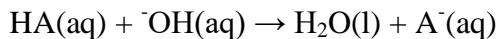
By having the reserves of HA and A- in buffer changes resulting from the addition of acid or alkali are minimized.

Calculating the pH of buffer solution

In a buffer composed of a weak acid HA and its salt MA

$HA \quad \leftrightarrow \quad H^+ + A^-$ and $MA \rightarrow M^+ + A^-$

The expression for dissociation constant of HA is written as

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

In the buffer mixture [HA] $\cong$ [acid] since the acid will be very slightly dissociated in presence of its salt and [A-] $\approx$ [salt] since the salt is fully dissociated

$\Rightarrow \quad [H+] = \frac{K_a[acid]}{[salt]}$

Introducing logarithms

$log_{10}[H^+] = log_{10}K_a + log_{10}\frac{[acid]}{[salt]}$

$Multiplying\ by - 1\ on\ both\ sides$

$-log_{10}[H^+] = -log_{10}K_a - log_{10}\frac{[acid]}{[salt]}$

or $pH = p^{K_a} + log_{10}\frac{[salt]}{[acid]}$

Similarly, a buffer composed of a weak base (e.g. NH_3) and its salt with a strong acid (e.g. NH_4Cl)

$p^{OH} = p^{K_b} + log_{10}\frac{[salt]}{[base]}$

$Also. p^{OH} + p^H = p^{K_w} = 14$

Example 5

Calculate the pH of the buffer made by adding 3.28g of sodium ethanoate to $1dm^3$ of 0.01Methanoic acid.

K_a(CH_3COOH =1.75 x 10^{-5}moldm^{-3})

Solution

[Acid] = [CH_3COOH] = 0.01M

[Salt] = [CH_3COONa] = $\frac{3.28}{82}$ = 0.04M

$[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COONa]}$ = 1.7 x 10^{-5} x $\frac{0.04}{0.01}$

$\qquad\qquad\qquad$ = 6.8x 10^{-5} moldm^{-3}

pH = -log$_{10}$[H^+] $\qquad$ = 4.17

Trial 12

a) Define the term a 'buffer' solution
b) Calculate the mass of sodium ethanoate that should be added to 1 litre of 0.1M ethanoic acid in order to produce a solution of pH = 4.0. (Ka = 1.8 x 10^{-5} moldm^{-3})
c) State what would happen to the pH of the solution in (b) if small amount of the following were added:
   i. sodium hydroxide solution
   ii. hydrochloric acid
d) State one biological application of a buffer solution

Trial 13

(a) Ethanoic is a weak acid
   (i) Explain what is meant by a 'weak acid'. (2marks)
   (ii) Calculate the pH of a 0.05M ethanoic acid solution (Ka = 1.8 x 10^{-5} moldm^{-3}). State any assumption you make
(b) (i) Explain what is meant by a 'buffer solution'
   (ii)   Discuss the action of a buffer solution (5marks)
(c) A solution was made by dissolving7.2g of ethanoic acid and 12.0g of sodium ethanoate to make 1 liter of solution. To the solution was added 0.8cm^3 of 1M HCl. Calculate the pH of the solution. State any assumption you make.

Trial 14

(a) What is meant by the term buffer solution?
(b) Calculate the mass of sodium ethanoate that should be added to 1dm^3 of 0.1M ethanoic acid in order to give a solution whose pH is 4. State any assumption made.
   K_a(CH_3COOH =1.75 x 10^{-5}moldm^{-3}) (4marks)

Hydrolysis of salts

It is the reaction of a salt with water to produce either acid or alkaline solution. The type of hydrolysis depends on the nature of salt.

(i) A salt formed by reacting a weak acid and a strong base hydrolyzes to give an alkaline solution. for example, sodium ethanoate is highly dissociated while water is very slightly ionized. The reaction occurs in solution as follows:

$CH_3COO^-Na^+ \rightarrow CH_3COO^- + Na^+$

then,

$CH_3COO^-(aq) + H_2O \leftrightarrow CH_3COOH(aq) + {^-}OH(aq)$
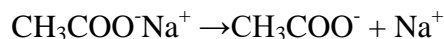
$K_c = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-][H_2O]}$

but $[H_2O]$ is almost constant

Thus, $K_c(H_2O) = K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$

K_h is called hydrolysis constant of a salt, the higher the K_h the more hydrolyzed the salt.

Expression of K_h in terms of Kw and Ka

Multiplying $[H^+]$ through the numerator and denominator give;

$K_h = \frac{[CH_3COOH]}{[CH_3COO^-][H^+]} \; x \; [H^+][OH^-] = \frac{K_w}{K_a}$

(ii) A salt of a weak base and a strong acid hydrolyzes in water to give acid solution e.g. NH4Cl dissociate in water as follows
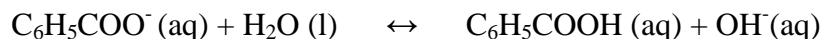
$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+$
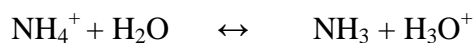
$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$ or $\frac{K_w}{K_b}$

Example 6

Sodium benzoate undergoes hydrolysis when dissolved in water

(a) Write an equation for hydrolysis of sodium benzoate

$C_6H_5COO^-(aq) + H_2O (l) \leftrightarrow C_6H_5COOH (aq) + OH^-(aq)$

(b) Write an expression for the hydrolysis constant K_h.

$K_h = \frac{[C_6H_5COOH][OH^-]}{[C_6H_5COO^-]}$

(c) The hydrolysis constant of sodium benzoate is 1.6 x 10^{-5}moll^{-1}.

(i) Calculate the concentration of the hydroxide ions in a 0.10M sodium benzoate at 25^{0}C
($Kw = 1 \times 10^{-14}$ mol^{2}dm^{-6})   (4marks)

Solution

Let the concentration of OH⁻ ions be x

$$1.6 \times 10^{-5} = \frac{x^2}{0.1}$$

$\Rightarrow$ x = 1.265 x 10⁻³moldm⁻³

(ii) $[H^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{1.265 \times 10^{-3}} = 7.9 \times 10^{-12}$moldm⁻³

$\Rightarrow$ pH = 11.1

(iii) State any assumption made in c(i) above

Hydrogen ions or hydroxyl ions from ionization of water are negligible

Trial 15

Phenylamine hydrochloride, undergoes

hydrolysis when dissolved in water. Write equation for the reaction

(b)   A 0.2M solution of phenylamine hydrochloride has a pH of 3.5. Calculate
   (i)   The molar concentration of hydrogen ions in solution (2marks)
   (ii)   The hydrolysis constant K_h of phenyl hydrochloride.

Trial 16

Ammonia chloride undergoes hydrolysis when dissolved in water according to the equation

NH_4^+ (aq) $\leftrightarrow$ NH_3(aq) + H^+(aq)

If the hydrolysis constant for ammonia hydrochloride, K_h is 5.6 x 10⁻¹⁰, calculate

(i) The pH of 0.1M solution of ammonium chloride
(ii) The percentage hydrolysis of 0.1M solution of ammonium chloride

Solubility of sparingly soluble ionic solid in water

When a sparingly soluble salt such as silver chloride or barium sulphate, is added to water, a little dissolves and produces ions in solution. Equilibrium is established between the ions and the solid salt when the rate at which ions leave the crystal frame work of the solid is equal to the rate at which they are deposited again. Since the solubility is very small, the ions present in the liquid are few in number and are so far apart that they are free from mutual interference. We can therefore say that in the very dilute saturated solution the solution is completely dissociated.

With a solution of a sparingly soluble electrolyte AxBy in contact with the solid the dissociation can be expressed as follows

$$AxBy + aq \leftrightarrow xA^{y+} + yB^{x-}$$
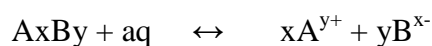
$$K_c = \frac{[A^{y+}]^x[B^{x-}]^y}{[A_xB_y][aq]}$$

Since the salt is only slightly dissociated in water, the $[A_xB_y]$ and $[aq]$ are constant

thus, $K_c[A_xB_y][aq] = K_{sp} = [A^{y+}]^x[B^{x-}]^y$

The constant K_{sp}/K_s is the solubility product of the electrolyte, AxBy. The solubility product of a sparingly soluble electrolyte is the product of the concentration of ions in a saturated solution raised to corresponding Stoichiometric ration in the salt. The higher the K_{sp} is the higher the solubility of the salt.

Example 7
The solubility of silver chloride at 18^0C is $1.46 \times 10^{-3} gdm^{-3}$. What is the solubility product (Ag =108, Cl = 35.5)

Solution

Note that in the calculation of solubility products the concentrations are expressed in **moledm^{-3} or moll^{-1}**

Mass of 1mole of AgCl = 108 + 35.5 = 143.5g

Solubility of AgCl = $\frac{1.46 \times 10^{-3}}{143.5}$ = $1.0 \times 10^{-5} moldm^{-3}$

Since one 'molecule' of silver chloride furnishes on dissociation one Ag^+ ion and one Cl^- ion, and since the dissolved silver chloride is completely dissociated in ions

$K_{sp} = [Ag^+][Cl^-] = (1 \times 10^{-5})(1 \times 10^{-5})$
$\qquad = 1 \times 10^{-10} mol^2 dm^{-6}$

Example 8
The solubility of calcium hydroxide in water at 20^0C is $2.78 gdm^{-3}$. What is the solubility product? (Ca = 40, O = 16, H = 1)

Solution

Molarity of $Ca(OH)_2 = \frac{2.78}{[40+2(16+1)]}$ = $0.0376 moldm^{-3}$

$[Ca^{2+}] = 0.0376 moldm^{-3}$
$[OH^-] = 2 \times 0.0376 = 0.0752 moldm^{-3}$
$K_{sp} = [Ca^{2+}][OH^-]^2 = 0.0376 \times (0.0752)^2$
$\qquad = 2.13 \times 10^{-4} mol^3 dm^{-9}$

Limitation to the solubility product concept

1. Salts like potassium nitrate of relatively high solubility, do not possess solubility products because the law of mass action does not hold in their case. The solubility product concept is only valid for saturated solution in which the total concentration of ions is no more than about 0.01M

2. The solubility product constant, like all other equilibrium constants change with temperature; consequently, the temperature at which solubility product is measured should always be specified unless it relates to the standard temperature of 298K or 25^0C.

Application of solubility product concept

(a) The common ion effect

This is the reduction in the solubility of a sparingly soluble salt in a solution in which it has a common ion.

Although the solubility product of a particular salt is constant at a constant temperature, the concentrations of the individual ions may vary over a very wide range. When a saturated solution is obtained by dissolving the pure salt in water the concentration of the ions produced are in the ratio determined by the stoichiometry of the compound. E.g. concentration of Ag^+ and CrO_4^{2-} ions in pure saturated silver chromate solution must be in ration 2:1. However, when a saturated solution is obtained by mixing two solutions containing a common ion (such as Ag_2CrO_4 and $AgNO_3$) there may be a big difference in the concentration of ions of any sparingly soluble electrolyte. In this case, the solubility product is used to determine the concentration of the ions in solution.

Example 9

Calculate the solubility of $BaSO_4$ in

(i) Water?

(ii) in 0.1M sodium sulphate solution?

$(K_{sp} = 1 \times 10^{-10} mol^2 dm^{-6})$

Solution

(i) $BaSO_4$ dissociate as follows

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

Let the solubility be x

$[Ba^{2+}] = [SO_4^{2-}] = x$

$K_{sp} = [Ba^{2+}][SO_4^{2-}] = x^2 = 1 \times 10^{-10}$

$\Rightarrow \quad x = 1 \times 10^{-5} moldm^{-3}$.

$\therefore$ Solubility of $BaSO_4$ in water $= 1 \times 10^{-5} moldm^{-3}$

(ii) Let the solubility of $BaSO_4$ in 0.1M Na_2SO_4 be y

$Na_2SO_4(s)$ dissociates as follows

$Na_2SO_4(aq) \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$
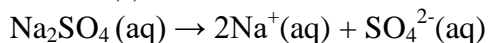
$[Ba^{2+}] = y$

$[SO_4^{2-}] = (0.1 + y)$

$K_1 = y(0.1+y) = 1 \times 10^{-10}$

y is very small that $(0.1+y) \cong 0.1$

thus $0.1y = 1 \times 10^{-10}$

$y = 1 \times 10^{-9} moldm^{-3}$

$\therefore$ Solubility of $BaSO_4$ in 0.1M Na_2SO_4
$$= 1 \times 10^{-5} moldm^{-3}$$

This example illustrate that BaSO4 is more soluble in water than in NaSO4 solution that contains a common ion (i.e. SO_4^{2-})

Trial 17

(a) Describe how the solubility product of magnesium hydroxide in water can be determined
(6marks)

(b) (i) A saturated solution of magnesium hydroxide in water contains 1.44×10^{-4} moles of magnesium hydroxide per liter of solution at 25^0C. Calculate the value of the solubility product, K_{sp}, of magnesium hydroxide at 25^0C. (3marks)

(ii) Solid magnesium hydroxide was shaken with a 0.1Msolutionof magnesium nitrate until equilibrium was attained at 25^0C. Calculate the amounts of magnesium hydroxide, in grams per liter that dissolved.

(c) Equations of some reaction are given below

$AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$ $K_1 = 1.7 \times 10^{-10}$
$Ag^+(aq) + 2NH_3(aq) \leftrightarrow Ag(NH_3)^{2+}$ $K_2 = 1.7 \times 10^7$

(i) Derive an expression in terms of K_1 and K_2 for the equilibrium constant for the following reaction:

$AgCl(s) + 2NH_3(aq) \leftrightarrow Ag(NH_3)_2^+(aq) + Cl^-(aq)$
(3marks)

(ii) Calculate the value of equilibrium constant in (i) (2marks)

Trial 18

Lead (II) sulphate is sparingly soluble in water.

(a) Write expression for the solubility product of lead (II) sulphate (1mark)

(b) 5g of lead sulphate was shaken with $1dm^3$ of water. Determine the percentage of lead (II) sulphate that dissolved. ($K_{sp} = 1.6 \times 10^{-8}$, Pb = 207, S= 32, O=16) (4marks)

(c) If 0.05M sulphuric acid was used instead of water in (b), calculate the percentage of Lead (II) sulphate that dissolved and state any assumption you make (4marks)

Trial 19

(a) Write equation for solubility of silver bromide in water at 25^0C

(b) If the solubility product of silver bromide at 25^0C is 5.0×10^{-13} mol^2dm^{-6}, calculate the solubility in gdm^{-3} at 25^0C of silver bromide in:

(i) water   (3marks)

(ii) 0.1M hydrobromic acid. (State any assumption made)   (3marks)

(c) State two methods that can be used to determine the solubility product (2marks)

(b) Prediction of Precipitation

The solubility product is used to predict the maximum concentration of ions in solution at a given temperature and hence whether or not precipitation will occur.

Suppose we mix 0.001M $CaCl_2$ solution (which contains 0.001M Ca^{2+} ions) with equal volume of 0.001M Na_2SO_4 (i.e. 0.001M SO_4^{2-} ions) solution at 25^0C. Will a precipitate of $CaSO_4$ formed? (K_{sp} CaSO4 = $2 \times 10^{-5} mol^2dm^{-6}$)

Immediately after mixing equal volumes of the two ions and before any precipitation

$[Ca^{2+}] = [SO_4^{2-}] = 5 \times 10^{-4}M$

(i.e. the concentration of each ion is halved since each solution is diluted by mixing with the other). Hence the ionic product for $CaSO_4$ immediately after mixing

$[Ca^{2+}][SO_4^{2-}]$ $= 5 \times 10^{-4} \times 5 \times 10^{-4}$
$\qquad\qquad = 2.5 \times 10^{-7} mol^2dm^{-6}$

This ionic product is less than the value of K_{sp} for $CaSO_4$ and so no precipitation occurs.

Let ionic now suppose that we mix equal volumes of 0.01M solution of each. Immediately after mixing

$[Ca^{2+}] = [SO_4^{2-}] = 5 \times 10^{-3}M$ and ionic product
$[Ca^{2+}][SO_4^{2-}]$ $= 5 \times 10^{-3} \times 5 \times 10^{-3}$
$\qquad\qquad = 2.5 \times 10^{-5} mol^2dm^{-6}$

In this case, the ionic product is greater than the solubility product and therefore precipitation of $CaSO_4$ occurs. The concentration of aqueous Ca^{2+} and SO_4^{2-} ions are lowered by the reaction.
Ca^{2+} (aq) + SO_4^{2-}(aq) $\rightarrow$ $CaSO_4$ (s)
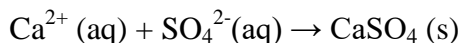
Coral reef, stalagmite and stalactites are result of slow precipitation of $CaCO_3$ from water when concentration of Ca^{2+} and CO_3^{2-} exceed the K_{sp} of $CaCO_3$.

(c) Selective precipitation

This is used to separate salts with different solubility,. e.g. Ca^{2+}, Mg^{2+} and Ba^{2+} can be separated by adding $K_2Cr_2O_4$(aq), which precipitate out $BaCrO_4$ (which is the least soluble) and removed by filtration. The remaining solution that contain Mg^{2+} and Ca^{2+} is then separated by adding Na_2SO_4 that precipitate out $CaSO_4$ ($CaSO_4$ in less soluble than $MgSO_4$) leaving Mg^{2+} in solution

Note that the order in which reagents are added is important. If we had added Na_2SO_4 solution before adding K_2CrO_4 solution a mixture of $BaSO_4$ and $CaSO_4$ would have been precipitated.

On the other hand, if Na_2CO_3 solution had been added to the mixture of the three cations; $MgCO_3$, $CaCO_3$ and $BaCO_3$ would all have been precipitated. Thus, both the precipitating reagent and the order of addition must be selected with great care.

(d) Use of potassium chromate (VI) in silver nitrate titration

When silver nitrate solution is titrated with sodium chloride solution containing a little potassium chromate (VI) only silver chloride is precipitated as long as there are any chloride ion in solution.

Only when all chloride ions have reacted doe a red precipitate of silver chromate (VI) appear. This is explained by the solubility products of the two silver salts; i.e. $(Ag^+)(Cl^-) = 1 \times 10^{-10} mol^2 dm^{-6}$ while $(Ag^+)_2(CrO_4^{2-}) = 2.5 \times 10^{-12} mol^3 dm^{-9}$. Suppose the concentration of Cl^- and CrO_4^{2-} ions in the liquid are both 0.1M. Then

$[Ag^+]$ needed to precipitate silver chloride

$$= \frac{1 \times 10^{-10}}{0.1} = 1 x 10^{-9} mol dm^{-3}$$

$[Ag^+]$ needed to precipitate silver chromate

$$= \sqrt{\frac{2.5 \times 10^{-12}}{0.1}} = 5 \times 10^{-6} mol dm^{-3}$$

Thus even if the concentration of the Cl^- ions and CrO_4^{2-} ions in the liquid are equal, it is easier by adding Ag^+ ions to reach the solubility product of the chloride than that of the chromate (VI) in spite of the lower solubility product of the latter. In practice $[Cl^-]$ is much larger than $[CrO_4^{2-}]$. Hence silver chloride I precipitated even more readily.

Trial 20
(a) State
    (i) how the solubility product of a sparingly soluble salt may be determined (2marks)
    (ii) how the solubility of sparingly soluble salt can be affected by adding a common ion (1mark)
(b) Calcium fluoride is sparingly soluble in water, write
    (i) an equation for the solubility of calcium fluoride (1mark)
    (ii) an expression for solubility product, K_{sp}, of calcium fluoride (1mark)
(c) Calculate the solubility of calcium fluoride in a solution containing 0.35moll^{-1} of fluoride ions at 25^0C, $K_{sp} = 1.7 \times 10^{-10}$ at25^0C) (3marks)
(d) State one application of solubility products (1marks)

Trial 21

The solubility product of lead (II) chloride is $1.6 \times 10^{-5} \, mol^3 l^3$ at 25^0C.

(a) Write an expression for the solubility product of lead (II) chloride (1marks)

(b) Calculate

(i) The concentration of the chloride ions in $moll^{-1}$ in a saturated solution of lead (II) chloride at 25^0C (3 ½ marks)

(ii) The solubility of lead (II) chloride in grams per liter at 25^0C (2 ½ marks)

(c)(i) State what would be observed if a saturated solution of lead (II) ethanoate was added to a solution of lead (II) chloride at at 25^0C (1mark)

(ii) Give a reason for your answer in (c)(i) (1mark)

Trial 22

(a)(i) Write an equation for solubility of silver sulphate

(ii) Determine the molar concentration of silver and sulphate ions in a saturated solution of silver sulphate at 25^0C. (The solubility product, K_{sp}, of silver sulphate is $1.7 \times 10^{-5} \, mol^3 dm^{-9}$ at 25^0C)

(b) State how the solubility of silver sulphate would be affected if the following substances were added

(i) sodium sulphate solution

(ii) ammonia

(c) Explain your answer in (b)

Trial 23

(a) Describe how the solubility product of magnesium hydroxide in water can be determined (6marks)

(b) A saturated solution of magnesium hydroxide in water contains 1.44×10^{-4} moles of magnesium per liter of solution at 25^0C.

(i) Calculate the value of solubility product, K_{sp} of magnesium hydroxide at 25^0C (3marks)

(ii) Solid magnesium hydroxide was shaken with a 0.1M solution of magnesium nitrate until equilibrium was attained at 25^0C. Calculate the amount of magnesium hydroxide in gram per liter that dissolved. (3marks)
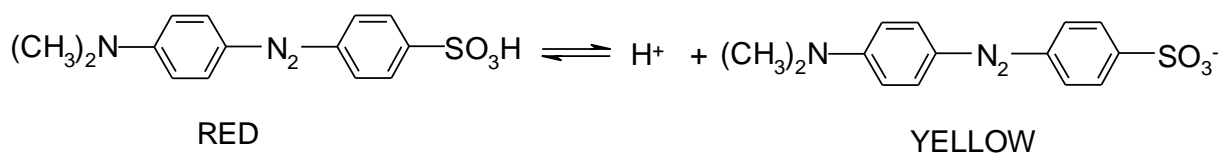
Trial 24

Barium sulphate is sparingly soluble in water

(a) Write

(i) an equation for solubility of barium sulphate in water (1mark)

(ii) The expression for the solubility product of barium sulphate (½ mark)

(b) A saturated solution of Barium sulphate contains 1.1×10^{-5} moles per liter of salts. Calculate the solubility product of barium sulphate (3marks)

(c) Calculate the solubility of barium sulphate in a liter of 0.1M barium chloride solution, in moles per liter.

Indicators

Acid-base indicators are substances which change color according to the hydrogen ions concentration of the liquid in which they are placed. They are either weak acids or weak bases, and are therefore slightly dissociated when dissolved in water. The color of the indicator depends on the color of the un-dissociated molecules and the color of the ions produced. Taking methyl orange as an example, dissociation occurs as follows:

More precisely

$$(CH_3)_2N \text{—}\underset{\text{RED}}{\bigcirc}\text{—}N_2\text{—}\bigcirc\text{—}SO_3H \rightleftharpoons H^+ + (CH_3)_2N\text{—}\bigcirc\text{—}N_2\text{—}\underset{\text{YELLOW}}{\bigcirc}\text{—}SO_3^-$$

When a drop of methyl orange is added to water, the resultant color is orange. if now an acid is added, the hydrogen ions of the acid drive back the ionization of methyl orange, very few Me$^-$ ion remain, and the indicator becomes pink. Alternatively, addition of a base provides a large concentration of hydroxyl ions which combine with the H$^+$ of the indicator to form water. More of the indicator ionizes and a large concentration of Me$^-$ ions are produced, giving a yellow color. similarly, litmus has red HA and blue A$^-$ ions.

Neutrality/ End point of indicator

The aim of any titration is to determine the volume of two solutions that just react with each other. Thus, the end point which is the point at which the titration is stopped, must coincide with equivalence point for the two reacting solutions.

In order to achieve this, the indicator should change color sharply at equivalent point on addition of a single drop of either acid or alkali. At the exact end point of the titration, the color of the indicator will be midway between the acid color HIn and the color of In$^-$. If the dissociation constant of the indicator is represented by K_I, then $K_I = \frac{[H^+][In^-]}{[HIn]}$, or $[H^+] = K_I \frac{[HIn]}{[In^-]}$

When the color of HIn and In- are equal,

$\qquad$ [HIn] = [In$^-$] so [H$^+$] = K_I

$\qquad$ or pH = -logK_I = pK_I

Range of an indicator

Every indicator has a definite range of pH over which it changes color given by

$\qquad\qquad$ pH range = pK_I ± 1

The colors and pH ranges of some common indicators are given in the table below:

Indicator	pH range	acid	alkali
Thymol blue	1.2-2.8	red	yellow
Methyl orange	2.9-4.6	pink	yellow
Congo red	3.0-5.0	blue	
Methyl red	4.2-6.3	pink	yellow
Litmus	5.0-8.0	red	blue
Phenolphthalein	7.4-9.0	colorless	red

PH change during titration

During a titration, there is a change in pH as alkali is added to acid or vice versa. At the equivalent point, the pH must change sharply by several units for it to be identifiable using an indicator.

The change in ph during the course of a titration depends largely upon the strength of the acid and alkali used.

The figure shows the effect on pH value of adding to $50cm^3$ molar HCl (strong acid) increasing quantities of molar solution of NaOH and secondary, a solution of NH_3 (a weak base)
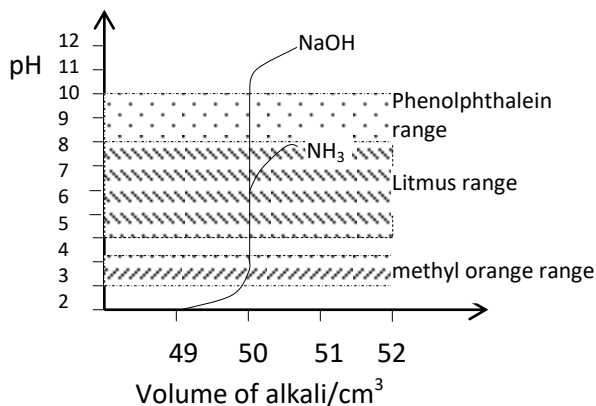
Figure 1

Note that, with NaOH addition of a very small volume of the base near the end point provides a very large change in the hydrogen ions concentration almost completely covering the pH ranges of methyl orange, litmus and phenolphthalein; In practice any of these indicator may be used during a titration of a strong acid with a strong base.

With ammonia solution adding a small amount of base near end point produces a small change in hydrogen ion concentration, and the end point is less sharp, no matter what indicator is used; although methyl orange provides the best choice.

The effect on pH value of adding tocm3 of molar ethanoic acid (weak acid) increasing quantities of first molar NaOH solution (strong base and secondly, molar ammonia (weak base) is illustrated in figure below
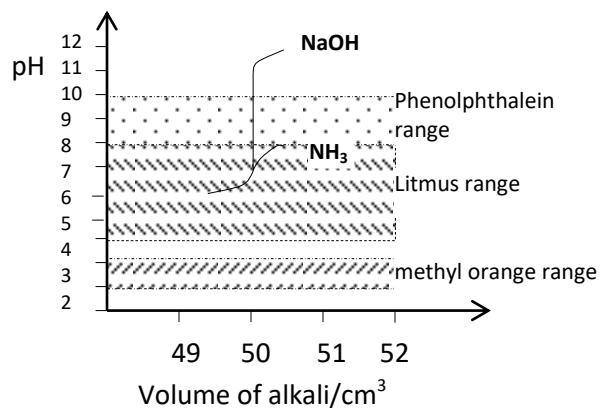
Figure 2

In the first case a less sharp end point that with a strong acid and strong base is again obtained with phenolphthalein as the best indicator for this titration. When the acid and the base are both weak, the end point is so indefinite that in practice a weak acid and weak base are never titrated against each other.

Choice of indicator

The true end point of neutralization in any titration occurs when the amount of acid and base added together are chemically equivalent to each other. The solution may not have a pH (i.e. neutral) equal to that of water at this point. With strong acids and strong base the final pH is about 7. In other cases hydrolysis of salt takes place, producing a pH greater or less than 7. Thus according to figure 1, the pH is about 5 for 0.5M NH4Cl solution and from figure 2 about 9 for a 0.5M solution of sodium ethanoate (CH_3COONa).

For a strong acid and a strong base the theoretically correct indicator is litmus, but in practice both methyl orange and phenolphthalein can be used. Similarly, methyl orange (or more accurately methyl red) is the correct indicator for titrating aqueous ammonia and hydrochloric acid, and phenolphthalein for sodium hydroxide and ethanoic acid. The general rules for indicators can be summarized as follows:
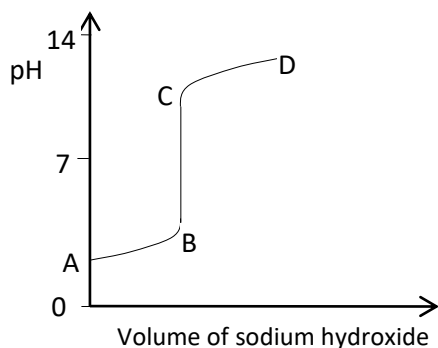
Strong acid and strong base – any indicator

Strong acid and weak base – methyl orange

Weak acid and strong base – phenolphthalein

Weak acid and weak base are not titrated.

Trial 26

(a) The curve below was obtained when hydrochloric acid was titrated with sodium hydroxide

Explain what happens to pH in the regions (6marks) (4lines each)

(i) AB

(ii) BC

(iii) CD

(b) Name one indicator that can be used in the titration in (a) (1mark)

(c) Using the above axes, sketch a graph that would be obtained if hydrochloric acid is titrated with ammonia solution (2marks)

Trial 5.37.2(2003/2/5)

(a) Draw diagrams to show the change in pH when a 0.1M sodium hydroxide solution is added in portions to

(i) 20 cm^3 of a 0.1M hydrochloric acid   (02marks)

(ii) 20cm^3 of a 0.1M ethanoic acid   (02marks)

(b) Explain the shapes of the curves in (a) (13marks)

(c) 20cm^3 of a 0.1M sodium hydroxide solution was added to 100cm^3 of a 0.1Methanoic acid. Calculate the pH of the resultant solution (Ka for ethanoic is 1.75x 10^{-5})   (03marks)

Solutions to the trials

Trial 1
Let the [H+] = x

$$CH_3COOH(aq) \leftrightarrow CH_3COO^-(aq) + H^+(aq)$$

Initial concentration:	0.01	0	0
Concentration at equilibrium	0.01-x	x	x

Since x is very small; $0.01-x \approx 0.01$

$Ka = \dfrac{x^2}{0.01} = 1.8 \times 10^{-5} moldm^{-3} \therefore x = 4.2 \times 10^{-4} Moldm^{-3}$

$pH = -log[H^+] = -log4.$

$[H^+] = 4.2$, $pH = 3.38$

Trail 2
  (i) 6.60×10^{-5} moldm^{-3}
  (ii) 4.18 ($pK_a = -logK_a$)
  (iii) 0.26 (degree of ionization is a fraction of acid that ionized) or 26%

Trail 3
  (a) (i) 4.745 (ii) 0.42%
  (b) Cl_3COOH is a stronger acid because it has a bigger K_a value

Trail 4
  (a) $[H^+] = 2 \times 10^{-5}$ moldm^{-3}
  $[^-OH] = \dfrac{K_w}{[H^+]} = \dfrac{1 \times 10^{-14}}{2 \times 10^{-5}} = 5 \times 10^{-10}$ moldm^{-3}
  (b) 4.7

Trial 5
$[OH^-] = 0.32$ modm^{-3}

Trial 6
Let the concentration of OH$^-$ be x

$$NH_4OH\ (aq) \leftrightarrow NH_4^+(aq) + OH^-(aq)$$

originally	1	0	0

At equilibrium	$(1-x) \approx 1$	x	x

$K_b = \dfrac{[NH_4^+][OH^-]}{[NH_4OH]} = \dfrac{x^2}{1} = 1.7 \times 10^{-5} moldm^{-3}$

$x = 4.123 \times 10^{-3} moldm^{-3}$

$[H^+] = \dfrac{K_w}{[OH^-]} = \dfrac{10^{-14}}{4.123 \times 10^{-3}} = 2.425 \times 10^{-12} moldm^{-3}$

$pH = -\log[H^+] = -\log[2.425 \times 10^{-12}] = 11.6$

Trial 7

$[H^+] = 10^{-10.6} = 2.5 \times 10^{-11}$

$[OH^-] = \dfrac{K_w}{[H^+]} = \dfrac{10^{-14}}{[2.5 \times 10^{-11}]} = 0.0004\,moldm^{-3}$

$[NH_3] = \dfrac{1}{20} - 0.0004 \approx \dfrac{1}{20}\,moldm^{-3}$

$K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]} = \dfrac{0.0004 \times 0.0004}{0.05}$

$$= 3.2 \times 10^{-6}\,moldm^{-3}$$

Trial 8

(a) $[OH^-] = \dfrac{4 \times 0.01}{100} = 0.0004\,moldm^{-3}$

$[H^+] = \dfrac{1 \times 10^{-14}}{0.0004} = 2.5 \times 10^{-11}\,moldm^{-3}$

$pH = -\log(2.5 \times 10^{-11}) = 10.6$

(b) $[NH_3] = 0.01 - 0.0004 \cong 0.01\,moldm^{-3}$

$K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]} = \dfrac{0.0004 \times 0.0004}{0.01}$

$$= 1.6 \times 10^{-5}\,moldm^{-3}$$

Trial 9

(a) $pH = -\log[H^+]$

(b) $[OH^-] = [NaOH] = 0.05\,moldm^{-3}$

$[H^+] = \dfrac{1 \times 10^{-14}}{0.05} = 2 \times 10^{-13}\,moldm^{-3}$

$pH = -\log(2 \times 10^{-13}) = 12.7$

(c) dilution lowers pH because it reduces $[OH^-]$

Trial 10

(a) $K_a = \propto^2 C$

$\propto$ is the degree of dissociation, C is the concentration in $moldm^{-3}$.

$1.39 \times 10^{-5} = \propto^2(0.01)$

$\propto\ = 0.066$ or 6.6%

(b)

Trial 11

(a) $Al(OH)_3(aq) \rightarrow Al^{3+}(aq) + 3OH^-(aq)$
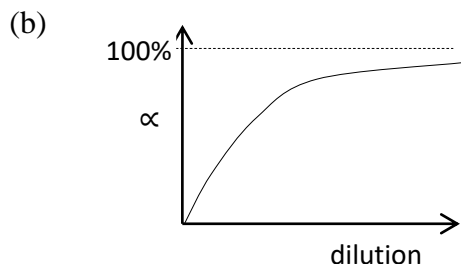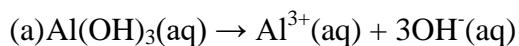
(b) 1mole of $Al(OH)_3$ produces 3 moles of OH^- ions

∴ $[OH^-] = 3 \times 2.3 \times 10^{-6} = 6.9 \times 10^{-6}$ moldm^{-3}

$[H^+] = \dfrac{K_w}{[OH^-]} = \dfrac{1 \times 10^{-14}}{6.9 \times 10^{-6}} = 1.4 \times 10^{-9}$ moldm^{-3}

pH = 8.8

Trial 12

(a) A buffer is a solution that resist changes in pH when small amounts of the acid or base are added

(b) pH = $pK_a + log_{10}\dfrac{[salt]}{[acid]}$

$1.0 = -log_{10}1.8 \times 10^{-5} + log_{10}\dfrac{[salt]}{[0.1]}$

⇨ [salt] = 0.18moldm^{-3} or (0.18 x 82)gdm^{-3}

= 14.76gdm^{-3}

(c) (i) pH remain constant

(ii) pH remain almost constant

(d) - pH of body fluids like blood are buffered for proper functioning of the enzymes.

- Preserved foods are buffered for palatability.

Trial 13

(a) (ii) 3.02

Assumption: the $[H^+]$ from ionization of water is negligible.

(c) pH = $-log_{10}1.8 \times 10^{-5} + log_{10}\dfrac{[^{12}/_{82}]}{[^{7.2}/_{60}]}$

= 4.66

Assumption: the salt is fully dissociated that [salt) = [sodium ethanoate] also, the acid is very slightly ionized that [acid] = [ethanoic acid]

Trial 14

(b) 14.76g

Trial 15

(a)
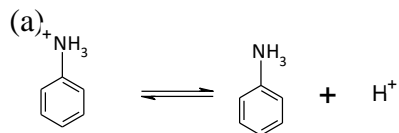
(b) (i) $[H^+] = 10^{-3.5} = 3.1 \times 10^{-4}$ moldm^{-3}

(ii) $K_h = \dfrac{[H^+]^2}{[Ph-N^+H_3]} = \dfrac{[3.1 \times 10^{-3}]^2}{0.2}$

$\qquad\qquad = 5.0 \times 10^{-7}$ moll^{-1}

Trial 16

(i) 5.13 (ii) 7.48 x 10^{-3}%

Trial 17

(a) The principle is to determine the mass of magnesium hydroxide that saturate 1000cm^3 of solution. For magnesium hydroxide this can be done in two ways: by titration or by evaporation of a given volume of saturated solution to dryness and weighing the residual mass of magnesium hydroxide.

Procedure

- To a given volume of water add a large excess of magnesium hydroxide in a stoppered container and shake until a mixture reaches equilibrium or leave overnight.
- Filter and titrate a portion of the filtrate with standard HCl using a suitable indicator of phenolphthalein.
- Calculate the concentration the concentration of OH$^-$ ion and Mg^{2+} ions in moldm^{-3}.

$[Mg^{2+}] = \frac{1}{2} [^-OH]$

$K_{sp} = [Mg^{2+}][^-OH]^2$

(b)(i) $[Mg^{2+}] = 1.44 \times 10^{-4}$ moll^{-1}

$[OH^-] = 2 \times 1.44 \times 10^{-4}$ moll^{-1}

$K_{sp} = (1.44 \times 10^{-4})(2 \times 1.44 \times 10^{-4})2$

$= 1.19 \times 10^{-11}$ mol^{3}l^{-3}

(ii) Let the solubility of Mg(OH)$_2$ be x

$[Mg^{2+}] = (0.1 + x) \approx 0.1$ i.e. x is very small that all magnesium ions come from Mg(NO$_3$)$_2$

$[^-OH] = 2x$

From $K_{sp} = [Mg^{2+}][^-OH]^2$

$\Rightarrow \quad 0.1 (2x)^2 = 1.19 \times 10^{-11}$

$\Rightarrow \quad x = 5.45 \times 10^{-6}$ moldm^{-3}.

Mass of Mg(OH)$_2 = 5.45 \times 10^{-6} \times 58$

$\qquad\qquad = 3.16 \times 10^{-4}$ gdm^{-3}

(c)(i) $K_1 = [[Ag^+][Cl^-]$

$\qquad K_2 = \dfrac{[Ag(NH_3^+]^2}{[Ag^+][NH_3]^2}$

$$K = \frac{[Ag(NH_3^+)]^2[Cl^-]}{[NH_3]^2}$$

$\Rightarrow$ $K = K_1 \times K_2$

(ii) $K = 1.7 \times 10^{-10} \times 1.7 \times 10^7$

$= 2.89 \times 10^{-3}$ moldm^{-3}

Trial 18

(a) $K_{sp} = [Pb^{2+}][SO_4^{2-}]$

(b) Let the mass of $PbSO_4$ that dissolved be x

$[Pb^{2+}] = [SO_4^{2-}] = \frac{x}{(207+32+16 \times 4)}$ or $\frac{x}{303}$

$K_{sp} = [\frac{x}{303}]^2 = 1.6 \times 10^{-8}$

$\Rightarrow$ x = 0.0383g

$\Rightarrow$ % dissolved $= \frac{0.0383 \times 100}{5} = 0.77\%$

(c) Let solubility be y gdm^{-3}

$[Pb^{2+}] = \frac{y}{303}$

$[SO_4^{2-}] \cong 0.05$ since $\frac{y}{303}$ is very small

$K_{sp} = \frac{y}{303} \times 0.05 = 1.6 \times 10^{-8}$

$\Rightarrow$ y = 9.7 $\times 10^{-6}$g

$\Rightarrow$ % dissolved $= \frac{9.7 \times 10^{-5} \times 100}{5}$

$= 1.94 \times 10^{-3}\%$

Trial 19

(a) AgBr(s) $\leftrightarrow$ Ag$^+$(aq) + Br$^-$(aq)

(b) (i) Let the solubility be x

$K_{sp} = [Ag^+][Br^-] = x^2 = 5.0 \times 10^{-13}$

x = 7.071 x 10-7moldm-3

Solubility = 7.071 $\times 10^{-7}$(108 +80)

$= 1.33 \times 10^{-4}$gdm^{-3}

(ii) Let the solubility be y

$[Ag^+] = y$

$[Br^-] = 0.1 + y \cong 0.1$ since y is very small

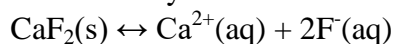$K_{sp} = 0.1y = 5.0 \times 10^{-13}$

y = 5.0 $\times 10^{-12}$ moldm^{-3}

Solubility = 5.0 $\times 10^{-12}$(108 +80)

$$= 9.4 \times 10^{-12} \text{gdm}^{-3}$$

(c) – Gravimetric titration
- conductimetric titration

Trial 20

(a) **(i)** - titration
- Precipitation
- Evaporation to dryness
(ii) Decrease
(b) (i) $CaF_2(s) \leftrightarrow Ca^{2+}(aq) + 2F^-(aq)$
(ii) $Ksp = [Ca^{2+}][F^-]^2 \text{ mol}^3\text{dm}^{-9}$
(c) Let solubility **be x**
$$CaF_2(s) \leftrightarrow Ca^{2+}(aq) + 2F^-(aq)$$
$$\quad x \qquad\qquad x \qquad 2x$$
$[Ca^{2+}] = x$
$[F^-] = 0.35 + 2x \approx 0.35 \text{moldm}^{-3}$

$Ks = 1.7 \times 10^{-10} = (0.35)^2 X$
The solubility of calcium fluoride $= x = 1.39 \times 10^{-9} \text{moldm}^{-3}$

(d) - selective precipitation
- Prediction of precipitation
- Indicator in gravimetric titration

Trial 21

(a) $PbCl_2(s) \leftrightarrow Pb^{2+}(aq) + 2Cl^-(aq)$
$Ksp = [Pb^{2+}][Cl^-]^2 \text{ mol}^3\text{dm}^{-9}$
(b) (i) Let solubility of $PbCl_2$ be x
$$PbCl_2(s) \leftrightarrow Pb^{2+}(aq) + 2Cl^-(aq)$$
$$\quad x \qquad\qquad x \qquad 2x$$
$Ksp = x(2x)^3 = 1.6 \times 10^{-5}$
$x = 0.016 \text{moldm-3}$
$[Pb^{2+}] = 0.016 \text{moldm}^{-3}$
$[Cl^-] = 0.032 \text{moldm}^{-3}$
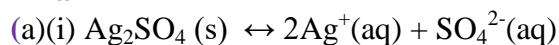(ii) RFm of $PbCl_2 = 207 + 35.5 \times 2 = 278$
Concentration of PbCl2 $= 0.016 \times 278 = 4.448 \text{gdm}^{-3}$
(c) (i) white precipitate
(ii) lead in lead ethanoate reduces the solubility of lead II chloride causing precipitation
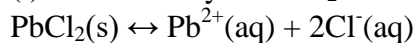
Trial 22
(a)(i) $Ag_2SO_4(s) \leftrightarrow 2Ag^+(aq) + SO_4^{2-}(aq)$
(ii) $Ksp = [Ag^+]^2[SO_4^{2-}] \text{ mol}^3\text{dm}^{-9}$
Let solubility be x

$Ksp = x(2x)^3 = 1.7 \times 10^{-5}$

$x = 0.016moldm-3$

$[SO_4^{2-}] = 0.016moldm^{-3}$

$[Ag^+] = 0.032moldm^{-3}$

(b)(i) decrease

(ii) increase

(c) (i) solubility decrease due to common ion effect

(ii) solubility

Trial 23

(a) - A given volume of saturated solution is titrated with standard hydrochloric acid solution using methyl orange indicator.

- The concentration of magnesium hydroxide is calculated

- $Ksp = [Mg^{2+}][OH^-]^2$

(b) (i) $[Mg^{2+}] = 1.44 \times 10^{-4}moldm^{-3}$

$[OH^-] = 2 \times 1.44 \times 10^{-4} = 2.88 \times 10^{-4}$ moldm-3

$Ksp = (1.44 \times 10^{-4})(2.88 \times 10^{-4})^2 = 1.19 \times 10^{-11}mol^3dm^{-9}$

(ii) Let the molar concentration of Mg(OH)2 be x

$[Mg^{2+}] = 0.1 + x \approx 0.1moldm^{-3}$ (since x is very small)

$[OH^-] = 2x$

$Ksp = 1.19 \times 10-11 = 0.1(2x)^2$

$x = 5.5 \times 10^{-6}$ moldm^{-3}

Formula mass of $Mg(OH)^2 = 24 + 2(16 +1) = 58$

Concentration $= 5.5 \times 10^{-6} \times 58 = 3.2 \times 10^{-4}gdm^{-3}$

Trial 24

(a)(i) $BaSO_4 (s) \leftrightarrow Ba^{2+}(aq) + SO_4^{2-}(aq)$

(ii) $Ksp = [Ba^{2+}][SO_4^{2-}]$

(b) $[Ba^{2+}] = 1.1 \times 10^{-5}$ moldm^{-3}

$[SO_4^{2-}] = 1.1 \times 10^{-5}$ moldm^{-3}

$Ksp = (= 1.1 \times 10^{-5})^2 = 1.121 \times 10^{-10}$ mol^{2}dm^{-3}

(c) Let solubility be x

$[Ba^{2+}] = 0.1 + x \approx 0.1moldm^{-3}$

$[SO_4^{2-}] = x$ moldm^{-3}

$0.1x = 1.121 \times 10^{-10}$

$x = 1.21 \times 10^{-9}moldm^{-3}$

Trial 25

(a) (i) AB; pH increases slowly due to excess H^+ still present after partial neutralization of H^+ by $^-$OH ions from the alkali

(ii) BC; at the end point pH increases rapidly due to excess $^-$OH ions on addition of slightly excess base

(iii) due to gradual increase in –OH ions on further addition of the base

(b) Theoretically y litmus is the best indicator, but practically methyl orange, and phenolphthalein can be used
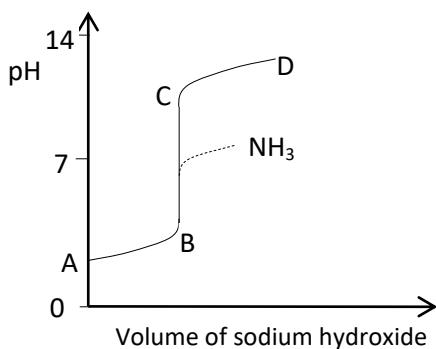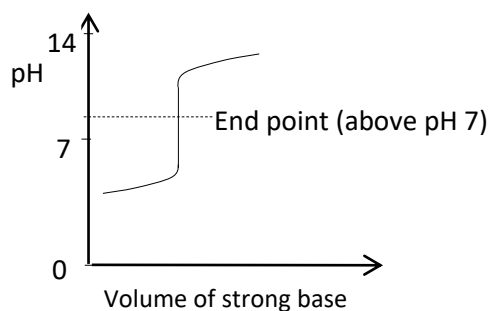

Trial 21

(i) Changes in pH during titration of a strong acid with strong base
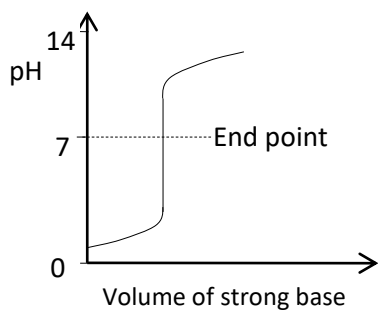
(i) Changes in pH during titration of a weak acid with strong base

(b) Titration of hydrochloric acid with sodium hydroxide

Initially before addition of the base, pH of the solution is very low due to high concentration of H+ ions from complete ionization of a strong acid. On addition of a base, the pH increases gradually due to excess acid still present after partial neutralization of H+ ion by the –OH ions from the base. At the end point pH increases very rapidly due to excess ‾OH ions. After the end point, pH increases gradually due increase in excess ‾OH ions

Titration of ethanoic with sodium hydroxide solution

Initially pH is lower (but higher than that of HCl) because ethanoic acid is a weaker acid thus only partially ionized into H^+ ions.

Addition of NaOH pH increase because of un neutralized acid forms a buffer with the sodium salt resisting increase in pH

At the end point of titration pH rises sharply even with a small base added because all the acid had reacted and extra base produces excess ‾OH ions.

The pH at the end point is above 7 because the salt formed undergoes hydrolysis to form ‾OH ions as follows

CH_3COO^- (aq) + H_2O (l) ↔ CH_3COOH (aq) + ‾OH (aq)
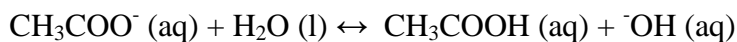
After the end point pH rises gradually due to excess sodium hydroxide or base added.

(c) CH_3COOH (aq) + NaOH (aq) → CH_3COONa (aq) + H_2O (l)
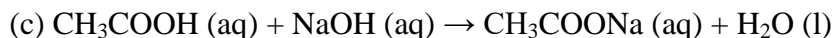
Addition of NaOH to CH_3COOH forms a salt of CH_3COONa which together with the excess un-neutralized acid still present constitute a buffer solution

Volume of excess un reacted acid =100-20 =80cm^3

Total volume of solution formed = 100+20

$$= 120cm^3$$

Moles of un reacted acid $= \dfrac{80 \; x \; 0.1}{1000} = 0.008$moles

Molarity of un neutralized acid in solution

120cm^3 contain   0.008moles

1000cm^3 contain $\dfrac{0.008 \; x \; 1000}{120} = 0.0667$moles

Moles of CH$_3$COONa formed $= \dfrac{20 \; x \; 0.1}{1000}$

$= 0.002$ moles

Molarity of CH$_3$COONa $= \dfrac{0.002 \; x \; 1000}{120}$

$= 0.00167$moles

But for buffer solutions, pH $= p^{Ka} + \log\dfrac{[salt]}{[acid)}$

pH $= -\log(1.75x \; 10\text{-}5) + \log\dfrac{0.0167]}{(0667)} = 4.168$

End