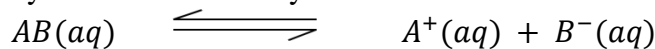**IONIC EQUILIBRIA**

This is an equilibrium established between the ions and the undissociated molecules of either a weak electrolyte or a solid of a sparingly soluble salt.

Consider a weak electrolyte AB which weakly ionizes in solution according to the equation.

$$AB(aq) \rightleftharpoons A^+(aq) + B^-(aq)$$

The extent to which AB has ionized is called the degree of ionization and is given the symbol (α)

$$AB(aq) \rightleftharpoons A^+(aq) + B^-(aq)$$

Initially	1	0	0
After ionization	1-α	α	α
Concn at eqm	c(1-α)	cα	cα

By law of Mass action

$$K\,eq = \frac{[A^+].[B^-]}{[AB]}$$

$$K\,eq = \frac{C\alpha.C\alpha}{C(1-\alpha)}$$

$$= \frac{c\alpha^2}{(1-\alpha)}$$

Maximum ionization for a weak electrolyte occurs at O concentration (zero) or infinite dilution. For a weak electrolyte even at infinite dilution the value of α is small such that $1 - \alpha \approx 1$.
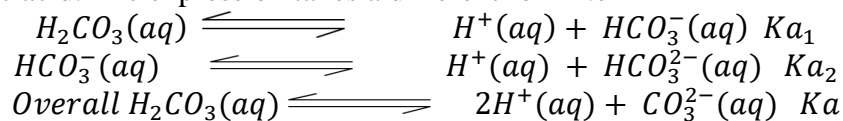This is called the Ostwald's dilition law which states that at infinite dilution weak electrolytes give the maximum ionization and the extent of ionization is still low even at infinite dilution.
From Ostwald's dilution law

$$K_{eq} = c\alpha^2$$

$$\alpha = \sqrt{\frac{K_{eq}}{C}}$$

The above expression is applicable to weak acids that ionize in a single step. For (Polyprotic acids) such as carbonic acid. The expression takes a different form i.e

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)\ Ka_1$$
$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + HCO_3^{2-}(aq)\ Ka_2$$
$$Overall\ H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)\ Ka$$

Initially	1	0	0
After ionization	1-α	2α	α
Concn at equbm	c(1-α)	2cα	cα

By law of mass action

$$K_a = \frac{[H^+]^2.[CO_3^{2-}]}{[H_2CO_3]}$$

$$\frac{(2C\alpha)^2.c\alpha}{c(1-\alpha)}$$

But 1-$\alpha \approx 1$

$$Ka = 4c^2\alpha^3$$

$$\alpha = \sqrt[3]{\frac{K_a}{4C^2}}$$

Note: The value of Ka_1 is greater than Ka_2 because it is easier to remove a proton from a molecular acid than removing it from the ionized acid HCO_3^- because after removal of the 1st proton the negative charge attained strongly attract the remaining proton. Therefore the increased electrostatic attraction between negative charge and the proton reduced the ionization of the acid lowering the value of Ka_2.

Consider a weak base that only slightly ionizes

$$BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$$

Initially	1	0	0
At eqbm	1-α	α	α
Concn at eqm	c(1-α)	cα	cα
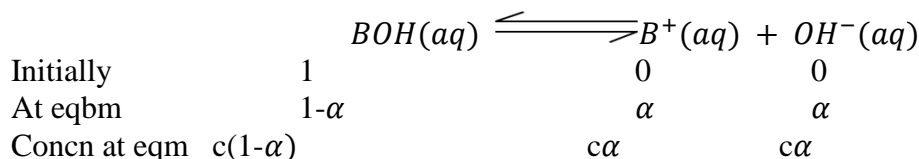
By law of mass action

$$Kc = \frac{[B^+].[OH]}{[BOH]}$$

$\frac{C\alpha.C\alpha}{C(1-\alpha)}$, $Kc = \frac{C\alpha^2}{(1-\alpha)}$, But 1-$\alpha \approx 1$, $Kc = C\alpha^2$, $\alpha = \sqrt{\frac{Kc}{C}}$

But for weak bases the constant is given as Kb.
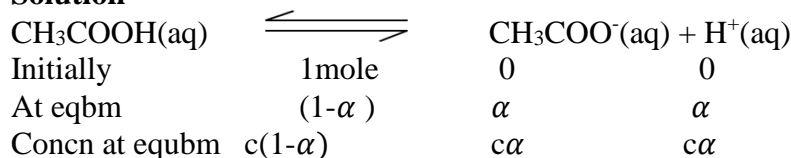
$$\propto = \sqrt{\frac{Kc}{C}}$$

Where Kb is the base ionization/ dissociation constant

Examples

1.Calculate the degree of ionization of a 0.1 m solution of ethanoic acid Ka = 1.8×10^{-3}

Solution

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

Initially	1mole	0	0
At eqbm	(1-α)	α	α
Concn at equbm	c(1-α)	cα	cα

$$Ka = \frac{[CH_3COO^-].[H^+]}{[CH_3COOH]}$$
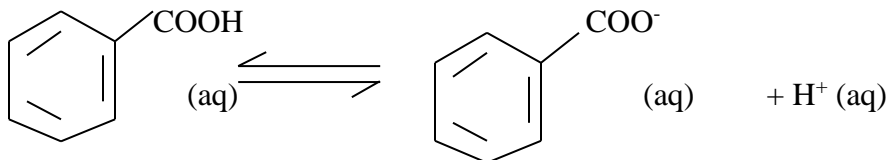$$= \frac{C\alpha.C\alpha}{C(1-\alpha)}$$
$$= \frac{C\alpha^2}{(1-\alpha)}$$

But 1-$\alpha \approx 1$
$$= C\alpha^2$$
$$\alpha = \sqrt{\frac{Ka}{C}}$$

2. Benzoic Acid is 0.2% ionized at 25^0C. calculate the acid ionization constant for a 0.1 M solution of Benzoic acid at this temperature.

	$COOH$ (aq)	$\rightleftharpoons$	COO^- (aq)	$+ H^+$ (aq)

Initially	1mole	0	0	
At eqm	$(1-\alpha)$	α	α	
Concn at eqm	$c(1-\alpha)$	$c\alpha$	$c\alpha$	

By law of mass action

$$Ka = \frac{C\alpha.C\alpha}{C(1-\alpha)}$$
$$= \frac{C\alpha^2}{1-\alpha}$$

But $\alpha = \frac{0.2}{100}$
$= 0.002$

$Ka = \frac{0.1(0.002)^2}{1-0.002}$
$= 4.008 \times 10^{-7}M$

3. (a) Calculate the degree of ionization of a 1M solution of ammonia at 25^0C
   (Kb for ammonia $= 1.75 \times 10^{-5} moldm^{-3}$)
(b) Determine the molar concentration of the hydrogen ions in the solution of ammonia in (a)
Solution

	$NH_4OH(aq) \rightleftharpoons$	$NH_4^+ (aq) +$	$OH^- (aq)$
Initially	1mole	0	0
At eq≡m	$(1-\alpha)$	α	α
Concn at eqm	$c(1-\alpha)$	$c\alpha$	$c\alpha$
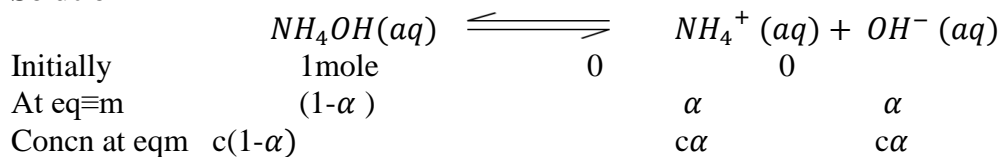
By law of mass action

$$Kb = \frac{[NH_4^+].[OH^-]}{[NH_4OH]}$$
$$Kb = \frac{C\alpha.C\alpha}{C(1-\alpha)}$$
$$\frac{C^2\alpha^2}{c(1-\alpha)}$$
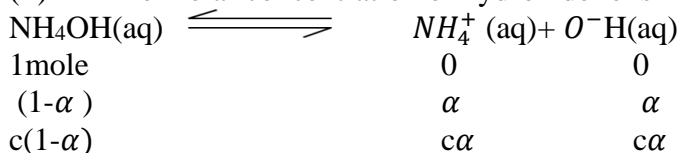$$Kb = C\alpha^2$$
When $1-\alpha \approx 1$
$$\alpha = \sqrt{\frac{Kb}{C}} = \sqrt{\frac{1.75 \times 10^{-5}}{1}}$$
$\propto = 4.18 \times 10^{-3}$

(b) $[O^-H] = C\alpha$
$= 1 \times 4.183 \times 10^{-3}$
$= 4.183 \times 10^{-3} moldm^{-3}$

Question: A 0.1M solution of ammonia is 4% ionized at 25^0C. calculate
   (i)   The base dissociation constant at this temperature
   (ii)   The molar concentration of hydroxide ions in solution
   $NH_4OH(aq) \rightleftharpoons NH_4^+ (aq) + O^-H(aq)$
   1mole   0   0
   (1-α) α α
   c(1-α)   cα cα

$$Kb = \frac{[NH_4^+].[O^-H]}{[NH_4OH]}$$
$$Kb = \frac{C\alpha.C\alpha}{C(1-\alpha)}$$
$$Kb = C\alpha^2$$

When 1-$\alpha \approx 1$

But $\alpha = \frac{4}{100} = 0.04$

$Kb = \frac{0.04^2 \; x \; 0.1}{1-0.04}$ because 0.04 is significant

$Kb = 1.67 \; x \; 10^{-4}$

$[OH] = C\alpha = 0.1 \; x \; 0.04$

$= 4 \; x \; 10^{-3}$ moldm-3
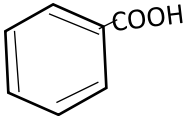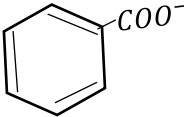
ACIDS AND BASES

An acid is a proton donor while a base is a proton acceptor.This is according to Bronsted and Lowry because the product formed after losing a proton can readily accept the proton to form back the acid.

Therefore, the species that donates a proton is called a conjugate acid and the product that can accept a proton is called a conjugate base.

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

Other examples

Conjugate acid	Proton +	conjugate Base
HCl		H^+ Cl^-
HNO_3	H^+	NO_3^-
CH_3COOH	CH_3COO^- H^+	
	H^+	

A base which it gains the proton from an acid and is therefore called conjugate base
 eg the base B

$B^-(aq)$ + $H^+(aq)$ BH
[conjugate base]   [Base]   [conjugate acid]

Other examples

Conjugate base	Proton+conjugate Acid	
NH_3	H^+	NH_4^+
CH_3NH_2	H^+	$CH_3^+NH_3$
H_2O	H^+	H_3O^+

Acids and Bases are therefore conjugate pairs and a conjugate pair defers by a proton
Lewis defines an acid as a lone pair of electrons acceptor while a base as a lone pair of electrons donor.

Consider the base ammonia
$$NH_3 \; + \; H^+ \; \rightleftharpoons \; NH_4^+$$
(Lone pair donor)(lone pair acceptor)
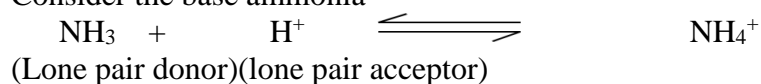
E.g. Ammonia is a Lewis base and Boron(III) Chloride is a Lewis acid
Water is a Lewis base for Hydrogen ions

<p style="text-align:center"><strong style="color:red">STRENGTH OF AN ACID</p>

A strong acid is one which completely ionizes or dissociates in aqueous solution e.g. all mineral acids.
A weak acid is one which only slightly ionizes in dilute aqueous solution releasing few hydrogen ions in solution e.g. all organic acids.
 According to Bronsted and Lowry, the strength of an acid is measured according to the ease with which it donates a proton. The strength of an acid or base depends on.
    i)   Nature of the solvent used. The more basic the solvent the stronger is the acid and the less basic the weaker is the acid eg Ethanoic acid is a weaker acid in water but a stronger acid in ammonia ie

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^- + H_3O^+(aq)$$
$$K_1 = \frac{[CH_3COO^-].[H_3O^+]}{[CH_3COOH]}$$

$$CH_3COOH(aq) + NH_3(aq) \rightleftharpoons CH_3COO^- + NH_4^+(aq)$$
$$K_2 = \frac{[CH_3COO^-].NH_4^+]}{[CH_3COOH]}$$
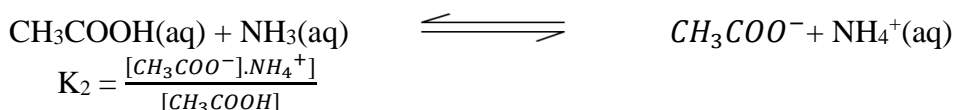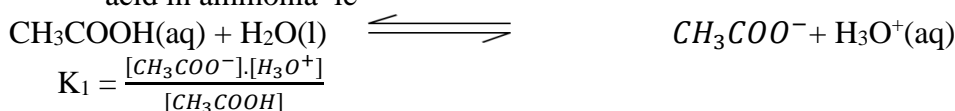
$K_2 > K_1$
    ii)   Bond strength between the hydrogen and the halogen atom (H-X bond), the stronger the bond the weaker the acid. This depends on the length of the bond which is determined by the atomic radius eg HCl is a weaker acid than HydroBromic acid(HBr) and hydro iodo acid(HI). Down the group, the atomic radius of the Halogens increases this makes the bond longer and weaker and the halogen can easily release a proton in

solution therefore HI Hydroiodic acid is the strongest acid followed by HBr followed by HCl and HF is the weakest.

iii)   Nature of the attached group to the acid e.g.

If the group is electron withdrawing, the strength of the acid is high but if the group is electron donating the strength of acid reduces. E.g. Chloroethanoic acid is a stronger acid than Ethanoic acid

Explanation

The methyl group in ethanoic acid is electron donating thus increases the electron density on the O-H bond which strengthens the bond and making it difficult to release a proton in water while the chlorine atom on chloroethanoic acid $ClCH_2COOH$ has a negative inductive effect(i.e. Electron withdrawing).Chlorine atom being more electronegative than carbon, withdraws electrons towards itself which reduces the electron density on the Oxygen –Hydrogen(O-H) Bond. This bond is therefore weaker and can easily release a proton.

STRENGTH OF THE BASE

Basic strength depends on the ease of donating electrons.

E.g. Phenyl amine is a weaker base than methyl amine (CH_3NH_2) because the methyl group has a positive inductive effect and tends to push the electrons towards the nitrogen atom and makes the lone pairs of electrons readily available for donation.

In phenyl amine the lone pair of electrons on the nitrogen atom interacts with the delocalized π (pie) bonding system of the benzene ring which makes them less available for donation.
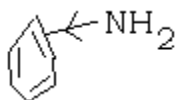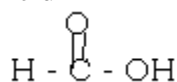

 Note: An increase in the number of electron donating groups increases the basic strength.Consider Amines A, B and C
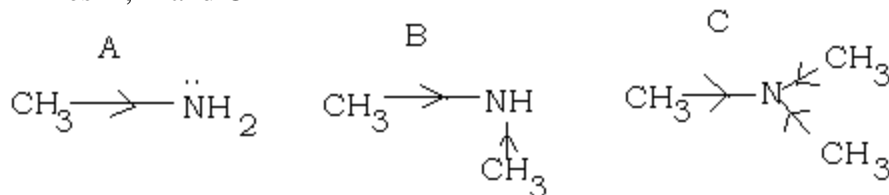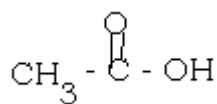

Molecule C is expected to be the strongest base but it is the weakest followed by A and B is the strongest base. In C the many methyl group increase the electron density around the Nitrogen atom but they mask the proton from accessing the lone pair of electrons. This is called steric hindrance. The strength of an acid or base is determined from the value of the dissociation or ionization constant, Kb or Ka. The greater the value the stronger the acid or base.
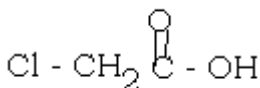
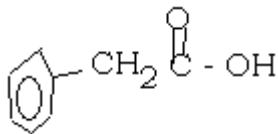Acid   Ka/moldm^{-3}

                                          2.0×10^{-4}

$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - OH$

                              1.8×10^{-5}

$Cl - CH_2 \overset{\overset{\displaystyle O}{\|}}{C} - OH$

                              1.6×10^{-3}

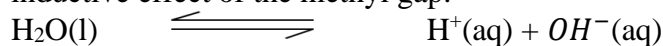(phenyl)$- CH_2 \overset{\overset{\displaystyle O}{\|}}{C} - OH$

                              1.8×10^{-3}

Chloro ethanoic acid and phenyl ethanol acid are the strongest acids because of the negative inductive effect of the attached gap. Ethanoic acid is the weakest acid because of the positive inductive effect of the methyl gap.

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

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

$K\ eq = \dfrac{[H^+].[\bar{o}H]}{[H_2O]}$ or $K\ eq = \dfrac{[H_3O]OH^-]}{[H_2O]^2}$

$Keq\ [H_2O] = [H^+].[OH] = Kw = [H^+].[OH^-]$

Note K eq. $[H_2O] = Kw$

In pure water at 25^0C $[H^+] = 1.0 \times 10^{-7}$

                        $[OH^-] = 1.0 \times 10^{-7}$

$Kw = 1.0 \times 10^{-7} \times 1.0 \times 10^{-7}$
$Kw = 1.0 \times 10^{-14}\ mol^2 dm^{-6}$

Water is a weak electrolyte and ionizes as above. The ionic product of water is defined as the product of the concentration of hydrogen ions or hydroxonium ions and hydroxide ions in pure water.

Note: Kw remains constant at constant temperature and is assigned a value of $1.0 \times 10^{-14}\ mol^2 dm^{-6}$ at 25 As the temperature increases, Kw increases and pH value is less than 7 ie the water becomes acidic .since ionization of water is endothermic, increasing the temperature increases the forward reaction increasing the concentration of hydrogen ions and this reduces pH.

Temp(^{0}C)	18	25	40	70
Kw/mol^{2}dm^{-6}	1.0×10^{-16}	1.0×10^{-14}	2.92×10^{-14}	1.69×10^{-13}

**The hydrogen Ion index (pH)**
This gives a measure of hydrogen ion concentration in solution. *It is the negative logarithm to base 10 of molar concentration hydrogen ions .*
                 $pH = -\log_{10}[H^+]$
For pure water, the hydrogen ions has a concentration of 1.0×10^{-7} and therefore the pH of pure water pH $= -\log (1.0 \times 10^{-7})$. For acidic solutions the pH is less than 7

eg 0.001M solution of HCl

HCl (aq) $\longrightarrow$ H^+(aq) + Cl^-(aq)

0.01   0.001

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

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

$= 3.0$
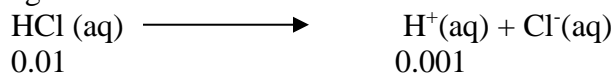
For alkaline solutions , the P.H is greater than seven for example for a solution containing 0.01M NaOH $[OH^-] = 0.01$

But from Kw = $[H^+].[OH^-]$

$$[H^+] = \frac{Kw}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.01}$$

$= 1.0 \times 10^{-12}$

$p.H = -\log[H^+]$

$= \log(1.0 \times 10^{-12}]$

$= 12$

RELATIONSHIP BETWEEN pH AND pOH

pOH is the negative logarithm to base ten of molar hydroxyl ion concentration

$pOH = -\log_{10}[OH^-]$

for pure water the hydroxide concentration is 1.0×10^{-7}

$pOH = -\log(1.0 \times 10^{-7}]$

$= 7.0$

pH and pOH are related by the ionic product of water ie

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

Introducing $-\log_{10}$

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

$\text{Log}_{10}(1.0 \times 10^{-14}) = -\log_{10}(1.0 \times 10^{-7}) + -\log(1.0 \times 10^{-7})$

$14 = 7+7$

$14 = 14$

And therefore

$PKw = pH + pOH$

$14 = pH + pOH$

For pure water, the sum of pH and pOH equals 14.

Calculating, pH of a strong electrolyte

    a) Strong acid

    b) Calculate the pH of a 0.01M solution of H_2SO_4
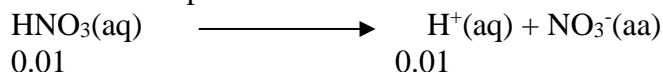
Solution

H_2SO_4(aq) $\longrightarrow$ $2H^+$(aq) + SO_4^{2-} (aq)

0.01   0.01 x 2
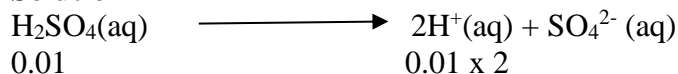
$[H^+] = 0.02M$

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

$= \log_{10}(0.02)$

$= 1.7$

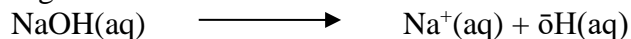Calculate the pH of a 0.01M solution of nitric acid solution

HNO_3(aq) $\longrightarrow$ H^+(aq) + NO_3^-(aa)

0.01   0.01

$[H^+] = 0.01m$

pH $= -\log [H^+]$

$\quad = -\log (0.01)$

$\quad = 2.00$

<div align="center">b) STRONG BASES</div>

E.g.Calculate the P.H of a 0.1M solution of NaOH

NaOH(aq) $\longrightarrow$ $Na^+(aq) + \bar{o}H(aq)$

But we know that Kw $= [H^+] . [\bar{o}H]$

$[H^+] = \dfrac{Kw}{[OH^-]} = \dfrac{1.0 \; x \; 10^{-14}}{0.1}$

$[H^+] = 1.0 \text{ x } 10^{-13}$

$pH = -\log_{10}(1.0 \text{ x } 10^{-13})$

$=13.00$

Alternatively

Since [OH] $= 0.1$

$pOH = -\log_{10}[\bar{o}H]$

$= -\log_{10}$

$= 1.00$

But $pH + pOH = 14$

$pH = 14 - pOH$

$= 14-1$

$= 13.00$

Calculate the pH of a solution made by mixing $20cm^3$ of a 0.1 M NaOH with $15cm^3$ of 0.1M HCl.
What is in excess will determine the pH of the solution.

Moles of HCl $= (\dfrac{0.1 \; x \; 5}{1000}) = 1.5 \text{ x } 10^{-3}$

Moles of NaOH $= \dfrac{0.1 \; x \; 20}{1000} = 2.0 \text{ x } 10^{-3}$

Moles of excess NaOH $= (2.0 \text{ x } 10^{-3} - 1.5 \text{ x } 10^{-3})$

$= 0.5 \text{ x } 10^{-3}$

Total volume $= 20 + 15 = 35cm^3$

$35cm^3$ contain $0.5 \text{ x } 10^{-3}$ moles of NaOH

$1000cm^3$ of solution contain $(\dfrac{0.5 \; x \; 10^{-3} \; x \; 1000}{3})$ moles of NaOH

$= 0.014M$

NaOH(aq) $\longrightarrow$ $Na^+(aq) + \bar{o}H(aq)$

0.014 $\qquad\qquad\qquad$ 0.014

$[H^+] = \dfrac{Kw}{OH^-} = \dfrac{1.0 \; x \; 10^{-14}}{0.014}$
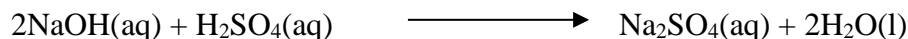
$= 7.143 \text{ x } 10^{-13}$
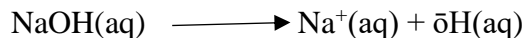
$pH = -\log_{10}[H^+]$

$= -\log [7.143 \text{ x } 10\text{-}13]$

$= 12.10$

Calculate the pH of a solution made by mixing $80cm^3$ of 0.1M H_2SO_4 with $20cm^3$ of 0.1M NaOH.

Solution

$2NaOH(aq) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$

Moles of sodium used $= (\dfrac{0.1}{1000} \text{ x } 20)$ moles

2 moles of NaOH react with 1 mole of H_2SO_4

Moles of NaOH reacted $= ½ (\frac{0.1 \times 20}{1000})$

1.0×10^{-3} moles

Initial moles of $H_2SO_4 = (\frac{0.1}{1000} \times 80)$

$= 8.0 \times 10^{-3}$ moles (moles supplied)

Excess moles of $H_2SO_4 = 8.0 \times 10^{-3}$

$= 7.0 \times 10^{-3}$ moles'

Initial vol $= 20 + 80 = 100cm^3$

Molar concentration of excess $H_2SO_4 = (7.0 \times 10 - 3 \times \frac{1000}{100})$

$= 0.07m$

$H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-} (aq)$

0.07   0.07 x 2

$[H^+] = 0.14M$

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

$= - log_{10} (0.14)$

$= 0.8539$

Calculate the pH of a solution obtained by mixing $25cm^3$ of 0.2M NaOH with $10cm^3$ of 0.1 M H_2SO_4

Solution

$2NaOH(aq) + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O(l)$
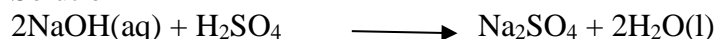
Moles of sulphuric acid

Used $= (\frac{0.1}{1000} \times 10)$

$= 1 \times 10^{-3}$ moles

But

1 mole of H_2SO_4 reacts with 2 moles of NaOH

(1×10^{-3}) moles of H_2SO_4 react with $1 \times 10^{-3} \times 2$

$= 2 \times 10^{-3}$ moles

Initial moles $= (\frac{0.2}{1000} \times 25)$ moles $= 5 \times 10^{-3}$ moles

Excess moles of base

$= (5 \times 10^{-3} – 2 \times 10^{-3})$ moles

$= 3 \times 10^{-3}$ moles

Concentration of the base

$(3 \times 10^{-3} \times {1000}/{35})m = 0.0857m$

NaOH $\longrightarrow$ $Na^+ + ōH$

0.0857   0.0857

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

$[H^+] = \frac{1.0 \times 10^{-4}}{0.0857}$

$= 1.6686 \times 10^{-13}$

$pH = -log [H^+]$

$= 11.2$

$= 12.93$

3. Calculate the concentration of $moldm^{-3}$ of Mg ions in a solution of magnesium hydroxide whose pH is 9.60 ($Kw = 1.0 \times 10^{-14}$)

Solution

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

9.6 = -log[H$^+$]

[H$^+$] = 2.5 x 10^{-10}

[H$^+$] = 10 x 10^{-14}

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

$[OH^-] = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-10}}$

ōH = 4 x10^{-5}moles

Mg(OH)$_2$ $\longrightarrow$ Mg^{2+} + 2OH^-

2moles of hydroxide ions are released for 1 mole of Mg^{2+}.

4 x 10^{-5} moles of (OH^-) ions react with $\frac{1 \times 4 \times 10^{-5}}{2}$

= 2.0 x 10^{-5}M

CALCULATING pH OF A WEAK ELECTROLYTE

Weak electrolytes partially ionizes in solution and their pH is derived from the dissociation constant/ionization constant at equilibrium.

Consider a weak acid CH$_3$COOH. This partially ionizes according to the equation

CH$_3$COOH(aq) $\rightleftharpoons$ CH$_3$COŌ(aa) + H$^+$(aa)

By law of mass action

$Ka = \frac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$

Assumptions

At eqm [CH$_3$COŌ] = [H$^+$]

$Ka = \frac{[H^+][H^+]}{[CH_3COOH]}$

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

[H$^+$] = $\sqrt{Ka[CH_3COOH]}$

pH = -log [H$^+$]

pH = -log$_{10}\sqrt{Ka[CH_3COOH]}$

Ex 1.

Calculate the pH of a 0.1M ethanoic acid at 25^{0}C (Ka for CH$_3$COOH at 25^{0}C is

(1.8 x 10^{-5} moldm^{-3})

Solution

$$CH_3COOH(aq) \rightleftharpoons CH_3CO\bar{O}(aq) + H^+(aq)$$
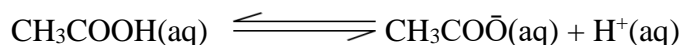
$$Ka = \frac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$$

Assumptions

At eqbm $[CH_3CO\bar{O}] = [H^+]$

$$Ka = \frac{[H^+]^2}{[CH_3COOH]}$$

$$[H^+] = \sqrt{Ka[CH_3COOH]}$$
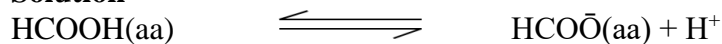
$$= \sqrt{1.8 \times 10^{-5} \times 0.1}$$

$$= 1.34 \times 10^{-3}$$

$pH = -\log [H^+]$
$= -\log_{10} (1.34 \times 10^{-3})$
$= 2.872$

Question. 0.1M solution of ethanoic acid has a pH of 2.4 at 25^0C. calculate the value of the ionization constant at this temperature.

Solution

$$HCOOH(aa) \rightleftharpoons HCO\bar{O}(aa) + H^+$$

$$Ka = \frac{[HCO\bar{O}].[H^+]}{[HCOOH]}$$

At equilibrium $[HCO\bar{O}] = [H^+]$

$$Ka = \frac{[H^+]^2}{[HCOOH]}$$

But from $-\log_{10} [H^+]^- = 2.4$

$\text{Log}_{10}[H^+]^{-1} = 2.4$

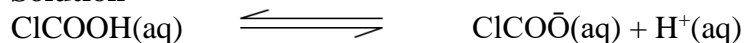$$10^{2.4} = \frac{1}{[H^+]}$$

$[H^+] = 3.0 \times 10^{-3}M$

$$Ka = \frac{[3.9 \times 10^{-3}]^2}{0.1}$$

$= 1.58 \times 10^{-4} \text{moldm}^{-3}$

A 0.01M solution of chloromethanoic Acid is 18% ionized. Calculate
   i)   The ionization constant of the acid at the same temperature
   ii)   The pH of the acid

Solution

$ClCOOH(aq)$	$\rightleftharpoons$	$ClCO\bar{O}(aq)$	$+ H^+(aq)$
Initially	1	0	0
At equilibrium	$(1-\alpha)$	α	α

$$Ka = \frac{[HCO\bar{O}].[H^+]}{[ClCOOH]} = \frac{C\alpha^2}{1-\alpha}$$

$$Ka = \frac{0.01 \times (0.18)^2}{1-0.18} = 3.95 \times 10^{-4}$$

pH from $Ka = \frac{[HCO\bar{O}].[H^+]}{[ClCOOH]}$

at equilibrium $(ClCO\bar{O}) = [H^+]$

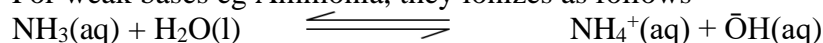$Ka = \frac{[H^+]^2}{[ClCOOH]}$

$[H^+] = \sqrt{Ka\,[ClCOOH]}$

$\quad = \sqrt{3.95 \times 10^{-5} x 0.07}$

$= 1.987 \times 10^{-3}$

But

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

$= -\log_{10}(1.987 \times 10^3]$

$= 2.7$

For weak bases eg Ammonia, they ionizes as follows

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$

By law of mass action

$Kb = \frac{[NH_4^+].[\bar{O}H]}{[NH_3]}$

Note: water is in large excess so its concentration remains constant

$Kb = \frac{[OH^-]^2}{[NH_3]}$

$[\bar{O}H] = \sqrt{Kb[NH_3]}$

$[H^+] = \frac{Kw}{[\bar{O}H]}$

$= \frac{Kw}{\sqrt{Kb[NH_3]}}$

Calculate the pH of a 0.1M solution of Ammonia at 25^0C ($Kb(NH_3) = 1.75 \times 10^{-5}$ moldm^{-3} at 23^0C.

Solution

$NH_3(aq) + H_2O(aq) \rightleftharpoons NH_4^+(aq) + \bar{O}H$
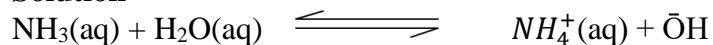
$Kb = \frac{[NH_4^+].[\bar{O}H]}{[NH_3]}$

At equilibrium $[NH_4^+] = [\bar{O}H]$

$Kb = \frac{[\bar{O}H]^2}{[NH_3]}$

$[\bar{O}H] = \sqrt{Kb[NH_3]}$

$= 1.75 \times 0.1 = 1.32 \times 10^{-3}M$

From $Kw = [H^+] . [\bar{O}H]$

$[H^+] = \frac{Kw}{[\bar{O}H]} = \frac{1.0 \times 10^{-14}}{1.32 \times 10^{-3}} = 7.58 \times 10^{-12}$

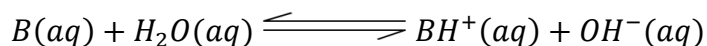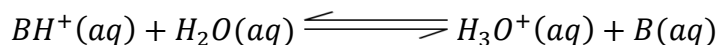$pH = -\log_{10}[H^+]$

$= -\log_{10}(7.5 \times 10^{-12})$

$= 11.12$

Relationship between Ka, Kb and Kw

Consider a base B and its ionization equilibrium

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

$$K_b = \frac{[BH^+][OH^-]}{[B]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(i)}$$

Now consider ionization equilibrium of the conjugate acid BH^+

$$BH^+(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + B(aq)$$

$$K_a = \frac{[H_3O^+][B]}{[BH^+]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(ii)}$$

Multiplying equation (i) by (ii), we get:

$$K_bK_a = \frac{[BH^+][OH^-]}{[B]} \cdot \frac{[H_3O^+][B]}{[BH^+]} = K_w$$

$$\therefore K_bK_a = K_w$$

And $p^{Ka} + p^{Kb} = p^{Kw}$

Recall $p^{Ka} = -\log_{10}[K_a]$

$$p^{Kb} = -\log_{10}[K_b] \text{ and } p^{Kw} = -\log_{10}[K_w]$$

Exercise(You will answer later)

Qn 1: The pH of a 0.1M propionic Acid is 3.8 at 25^0C
Calculate
    i.   The ionization constant for the Acid
    ii.   The PKa of the acid
    iii.   The degree of ionization of the acid at the same temperature
Qn2. A 0.01m solution of dimethylamine has a pH of 10.2 at 25^0C. calculation
    i.   The base dissociation constant (Kb)
    ii.   The degree of ionization of the base at the same temperature
          (Kw at 25^0C = 1.0 x 10^{-14})
Qn 3. Calculate the pH of a solution made by mixing 35cm^3 of 0.1M H_2SO_4 with 15cm^3 of 0.1M KOH
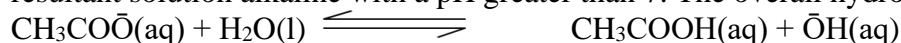
SALT HYDROLYSIS

Salts derived from strong acids and weak bases such as ammonium chloride, methyl ammonium Nitrate ($CH_3NH_3NO_3^-$) as well as those derived from weak acids and strong bases such as sodium ethanoate undergo hydrolysis in solution to give either an acidic or alkaline solution.

(1) Salts derived from strong bases and weak acids eg sodium ethanoate. This salt is derived from a weak acid ethanoic acid and a strong base sodium hydroxide.

The salt formed is a strong electrolyte which fully dissociates

The ethanoate ions liberated undergo hydrolysis by abstracting a proton from water. Because of the removal of H^+ from the water, the equilibrium becomes disturbed and to restore the equilibrium more water molecules ionize to liberate more hydroxide ions which remain in excess making the resultant solution alkaline with a pH greater than 7. The overall hydrolysis reaction is written as

$CH_3CO\bar{O}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \bar{O}H(aq)$

Since it is the anion that undergoes hydrolysis. This is called anionic hydrolysis.

From the above equation an expression from or the hydrolysis Kh can be written

$Kh = \dfrac{[CH_3COOH].[\bar{O}H]}{[CH_3CO\bar{O}]}$

The following assumptions are made when writing the above expression

i. Water is taken to be in large excess and its concn remains constant at equilibrium so it does n't appear in the expression for Kh.

ii. Sodium ethanoate is a strong salt and fully dissociates according to the equation.

$CH_3CO\bar{O}Na^+(aq) \longrightarrow CH_3CO\bar{O}(aq) + Na^+(aq)$
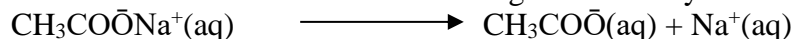
Since 1 mole of $CH_3CO\bar{O}Na^+$ releases 1 mole of ethanoate items, then $[CH_3CO\bar{O}Na^+] = [CH_3CO\bar{o}]$
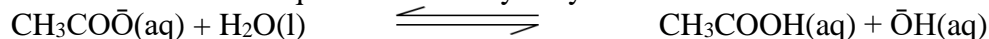
At equilibrium assumed that

$[CH_3COOH] = [\bar{O}H]$

So the expression for Kh can be written as

$Kh = \dfrac{[\bar{O}H]^2}{[CH_3CO\bar{O}]}$

Example

Sodium ethanoate undergoes hydrolysis when dissolved in water

i. Write an equation for the hydrolysis reaction

$CH_3CO\bar{O}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \bar{O}H(aq)$

ii. Write an expression for the hydrolysis constant

$Kh = \dfrac{[CH_3COOH].[\bar{O}H]}{[CH_3CO\bar{O}]}$

iii. Calculate the pH of the solution made by dissolving 8.4g of the salt in 1 L of water ($Kw = 1.0 \times 10^{-14}$, $Kh = 5.5 \times 10^{-10}$

Qn. Sodium propanoate ($CH_3CH_2CO\bar{O}Na^+$) undergoes hydrolysis.

i. Write equations for the hydrolysis reactions of sodium propanoate.

ii. Write the expression for the hydrolysis constant of sodium propanoate

iii. The pH of a 0.1M solution of sodium propanoate is 8.9. calculate the hydrolysis constant for the salt ($Kw = 1.0 \times 10^{-14} mol^2 dm^{-6}$)

Solution

(i) $CH_3CH_2CO\bar{O}(aq) + H_2O \rightleftharpoons CH_3CH_2COOH(aq) + \bar{O}H(aq)$
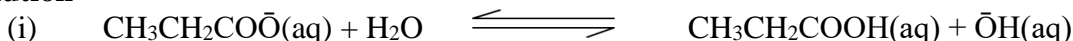
(ii) $Kh = \dfrac{[CH_3CH_2COOH].[\bar{o}H]}{[CH_3CH_2CO\bar{O}]}$

At equilibrium $[CH_3CH_2COOH] = [\bar{O}H]$

$Kh = \dfrac{[\bar{O}H]^2}{[CH_3CH_2CO\bar{O}]}$

From pH = -log $[H^+]$

$8.9 = -\log_{10}[H^-]$

$10^{8.9} = \dfrac{1}{[H^+]}$

$[\bar{O}H] = \dfrac{Kw}{[H^+]} = \dfrac{1.0 \; x \; 10^{-14}}{1.26 \; x \; 10^{-9}}$

$Kh = \dfrac{(7.9 \; x \; 10^{-6})^2}{0.1}$
= 6.241 x 10^{-10}M

DEGREE OF SALT HYDROLYSIS

Since water is a weak electrolyte is only slightly ionizes releasing very few H^+ then can be abstracted. Therefore much of the salt remains unhydrated. The extent of hydrolysis can be calculated. Consider the hydrolysis of sodium Benzoate

$C_6H_5CO\bar{O}(aq) + H_2O(l) \longrightarrow C_6H_5COOH(aq) + OH$

1   0   0

$C(1-\alpha)$ $C\alpha$ $C\alpha$
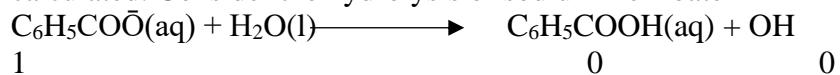
$Kh = \dfrac{[C_6H_5COOH].[\bar{O}H]}{[C_6H_5CO\bar{O}H]} = \dfrac{C\alpha^2}{1-\alpha}$

Since the extent of hydrolysis is very small
$1-\alpha \approx 1$
$Kh = c\alpha^2$
$\alpha = \sqrt{\dfrac{Kh}{C}}$

Example a 0.01M solution of sodium benzoate undergoes hydrolysis
    i.   Calculate the degree of hydrolysis
    ii.   Calculate the pH of the resultant solution (Kh = 5.0 x 10^{-10})

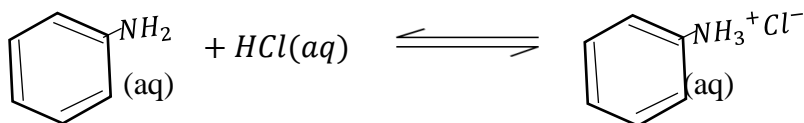**Solution**
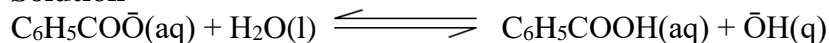
$C_6H_5CO\bar{O}(aq) + H_2O(l) \rightleftharpoons C_6H_5COOH(aq) + \bar{O}H(q)$
The degree of hydrolysis is α
$Kh = C\propto^2$
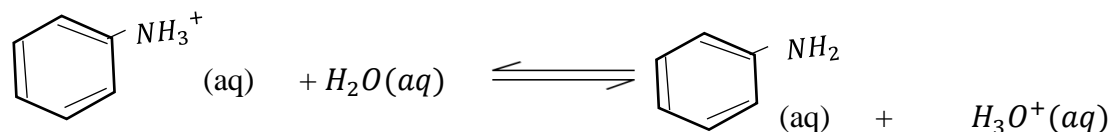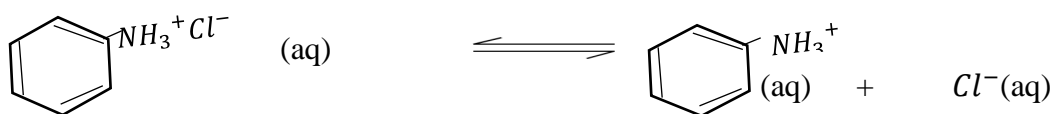$\alpha = \sqrt{\left(\dfrac{Kh}{C}\right)} = \sqrt{\dfrac{5.0 \; x \; 10^{-10}}{0.01}}$
$\alpha = 2.24$ x 10^{-4}

Phenyl amine

The salt formed is phenyl amine hydrochloride. The salt undergoes hydrolysis

$NH_3^+ Cl^-$ (aq) ⇌ NH_3^+ (aq) + Cl^-(aq)

NH_3^+ (aq) + $H_2O(aq)$ ⇌ NH_2 (aq) + $H_3O^+(aq)$
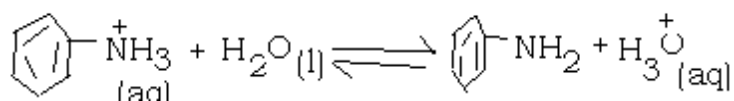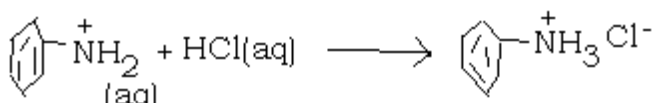
$H_2O(l)$ ⇌ $H^+(aq) + \bar{O}H(aq)$

Phenyl ammonium removes OH from the water equilibrium which becomes disturbed and to restore the ionic equilibrium of water, more water molecules ionise leaving an excess of hydrogen ions in solution making the resultant solution acidic.

Note: during catioc hydrolysis the cation donates a proton to water, so water behaves as a base by abstracting a proton and the hydrolysis reaction is written as

$NH_4^+ + H_2O(l)$ ⇌ $NH_3(aq) + H_3O^+(aq)$
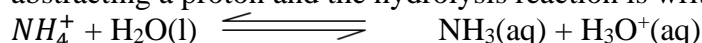
Calculate the mass of phenyl amine hydrochloride that should be added to 1 litre of H_2O to form a solution of pH 5.2 (Kh= 6.0 x 10^{-5}M.

The solution formed undergoes hydrolysis.

NH_2 (aq) + HCl(aq) ⟶ NH_3 Cl^-

NH_3 (aq) + $H_2O(l)$ ⇌ NH_2 + $H_3\overset{+}{O}$ (aq)

$$KL = \frac{\left[\underset{}{\bigcirc} NH_2 \right] \cdot \left[H_3 \overset{+}{O} \right]}{\left[\underset{}{\bigcirc} \overset{+}{N}H_3 \right]}$$

pH = -log$_{10}$ [H$_3$O$^+$]

5.2 = log$_{10}$ [H$_3$O$^+$]

$10^{5.2} = \dfrac{1}{[H_3O^+]}$

H$_3$O$^+$ = 6.3 x 10^{-6} M

Assumption at equilibrium

$$\left[\underset{}{\bigcirc}\text{—NH}_2\right] = \left[H_3\overset{+}{O}\right]$$

$$KL = \frac{\left[H_3\overset{+}{O}\right]^2}{\left[\underset{}{\bigcirc}\text{—}\overset{+}{N}H_3\right]}$$

$$6 \times 10^{-5} = \frac{(6.3 \times 10^{-6})^2}{\left[\underset{}{\bigcirc}\text{—}\overset{+}{N}H_3\right]}$$

$$\left[\underset{}{\bigcirc}\text{—}\overset{+}{N}H_3\right] = 6.6 \times 10^{7}$$

$$\left[\underset{}{\bigcirc}\text{—}\overset{+}{N}H_3\right] = \left[\underset{}{\bigcirc}\text{—}\overset{+}{N}H_3\,Cl^-\right]$$
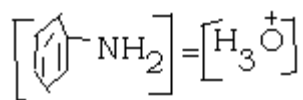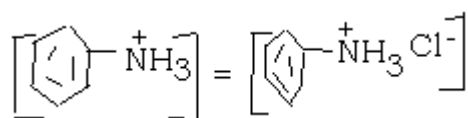
Molar mass of $C_6H_5NH_3Cl^-$

= (12 x 6) (1 x 8) + (1 x 14) + (1x35.5)

= 129.5 g/mol

Mass of salt

= 6.6 x 10⁻⁷ x 129.5

8.5 x 10⁻⁵gl⁻¹

Question: Phenyl ammonia nitrate undergoes hydrolysis

a(i) Write equation for the hydrolysis of the salt

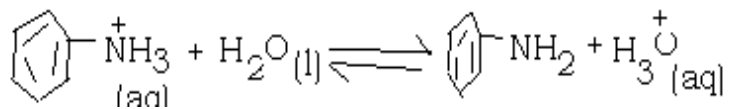(ii) Write the expression for the hydrolysis constant

(b) a 0.01M solution of phenyl ammonium nitrate has a pH of 3.2. calculate

(i) the hydrolysis constant

(ii) The degree of hydrolysis

(iii) The mass of the salt that should be added to the litre of water to increase the pH by 2 units.

Solution

$$Kh = \frac{[C_6H_5NH_2].[H_3O^+]}{[C_6H_5NH_3^+]}$$

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

3.2 = -log$_{10}$[H$^+$]

$$10^{3.2} = \frac{1}{[H^+]}$$

[H$^+$] = 6.3 x 10^{-4} M

Assumption

[C$_6$H$_5$NH$_2$] = [H$_3$O$^+$]

$$Kh = \frac{[H_3O^+)^2}{[C_6H_5NH_3]}$$

= 3.98 x 10^{-5}M

$$(ii) \ \alpha = \sqrt{\frac{Kl}{C}}$$

$$= \sqrt{\frac{3.98 \ x \ 10^{-5}}{0.01}} = 0.0631$$

(iii) New pH of solution

= 3.2+2 = 5.2

$$10^{5.2} = \frac{1}{[H_3O^+]}$$

[H$_3$O$^+$] = 6.31 x 10^{-6}M

$$Kh = \frac{[H_3O^+]^2}{[C_6H_5NH_3]}$$

[C$_6$H$_5$N$^+$H$_3$] = 1.0 x 10^{-6}M

[C$_6$H$_5$N$^+$H$_3$] = [[C$_6$H$_5$N$^+$H$_3$ NO$_3$]

Molar mass of C$_6$H$_5$N$^+$H$_3$NO$_3^-$

= (12 x 6) + (1x8) + (14x2) + (16 x 3)

= 156 ≈ x156

Mas of salt = 1.0 x 10⁻⁶ x 156

1.56 x 10⁻⁴g/l

Relationship between Ka, Kw and Kh

Consider the ionization of weak ethanoic acid

CH_3COOH ⇌ $CH_3CO\bar{O}(aq) + H^+(aq)$

$Ka = \frac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$……………………………………..(1)

Consider also the hydrolysis of sodium ethanoate ($CH_3CHO\bar{O}Na^+$)

$CH_3CO\bar{O}(aq) + H_2O(l)$ ⇌ $CH_3COOH + \bar{O}H(aq)$
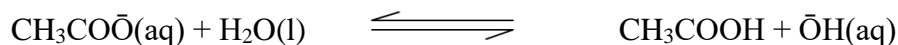
$Kh = \frac{[CH_3COOH].[\bar{O}H]}{[CH_3CO\bar{O}]}$……………………………………(2)

Consider also the ionization of water

$H_2O(l)$ ⇌ $H^+(aq) + \bar{O}H(aq)$……………….(3)
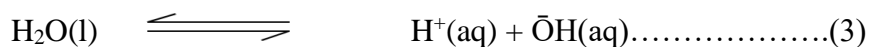
$Kw = [H^+][\bar{O}H]$

Dividing 3 by 1

$\frac{Kw}{Ka} = \frac{[H^+].[\bar{O}H]}{\frac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}} = \frac{[H^+].[\bar{O}H]x\,[CH_3COOH]}{[CH_3CO\bar{O}].[H^+]}$

$= \frac{[\bar{O}H].[CH_3COOH]}{[CH_3CO\bar{O}]}$

$\frac{Kw}{Ka} = Kh$

Relationship between Kh, Kw and Kb

Consider the ionization of a weak base e.g ammonia

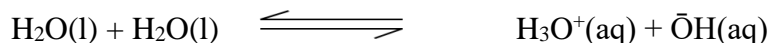$NH_3(aq) + H_2O(l)$ ⇌ $NH_4^+(aq) + \bar{O}H(aq)$
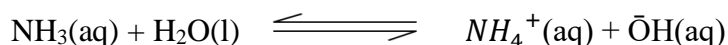
$$Kb = \frac{[NH_4^+].[\bar{O}H]}{[NH_3]}$$

Consider also the hydrolysis of ammonium chloride

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+$$
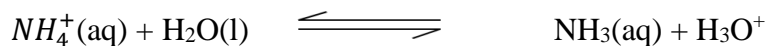
$$Kh = \frac{[NH_3].[H_3O^+]}{[NH_4^+]}$$

Consider the self ionization of water

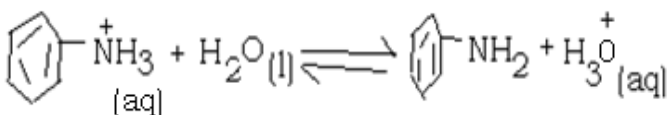$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + \bar{O}H(aq)$$

$$\frac{Kw}{kb} = \frac{[H_3O^+].[\bar{O}H]x\,[NH_3]}{[NH_4^+].[\bar{O}H]}$$

$$\frac{Kw}{Ka} = Kh$$

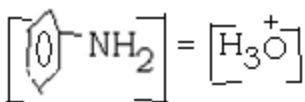Qn: Phenyl ammonium chloride undergoes hydrolysis. Calculate the pH of a 0.1 M solution of phenyl ammonium chlorine (Kb for phenyl amine is 1.7×10^{-5} mold m^{-3})

Solution

At equilibrium

But $Kh = \dfrac{Kw}{Kb} = \dfrac{1.0\ x\ 10^{-14}}{1.7\ x\ 10^{-5}} = 5.88 \times 10^{-10}$

$5.88 \times 10^{-10} = \frac{[H_3O^+]^2}{0.1}$
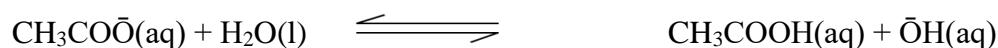
$[H_2O^+] = \sqrt{0.1 \times 5.88 \times 10^{-10}}$

$= 7.67 \times 10^{-6}$

$pH = -\log(7.67 \times 10^{-6})$

$= 5.12$

Qn: Calculate the mass of sodium ethanoate that should be added to 1 litre of water to make a solution of pH 8.9 (Ka for ethanoic acid is 1.8×10^{-5})

Solution

$CH_3CO\bar{O}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \bar{O}H(aq)$

$Kh = \frac{[CH_3COOH].[\bar{O}H]}{[CH_3CO\bar{O}]}$

At equilibrium. $(CH_3COOH) = [\bar{O}H]$

$Kh = \frac{[\bar{O}H]^2}{[CH_3CO\bar{O}]}$

But pH + pOH = 14

pOH = 14 – pH

(14-8.9) = 5.1

$pOH = \log_{10}[\bar{O}H]$

$5.1 = -\log_{10}[\bar{O}H]$

$[\bar{O}H] = \frac{1}{10^{5.1}} = 7.94 \times 10^{-6}M$

Substituting in the expression

$5.56 \times 10^{10} = \frac{(7.94 \times 10^{-6})^2}{(CH_3CO\bar{O})}$

$[CH_3CO\bar{O}] = 0.11M$

$[CH_3CO\bar{O}] = [CH_3CO\bar{O}Na^+]$

RFM of $CH_3CO\bar{O}Na^+$

$= (12 \times 2) + (3) + (16 \times 2) + (23) = 82$

Mass of $CH_3CO\bar{O}Na^+$

$= 82 \times 0.11$

= $9.02gl^{-1}$

BUFFER SOLUTIONS

A buffer solution is defined as a solution that consists of a weak acid with its salt from a strong base or a weak base with its salt from a strong acid which resists change in its pH when a small amount of an acid or a base is added to it . There are two types of buffer solutions ie basic buffers and Acidic Buffers an acidic buffer is obtained from a weak acid and its salt derived from a strong base. Eg
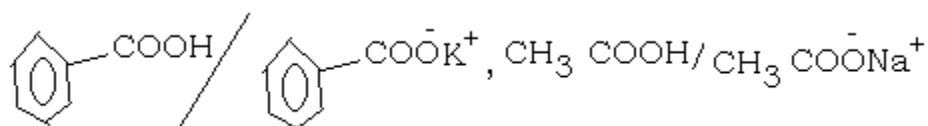
A basic buffer is made up of a weak base and its salt derived from a strong acid eg
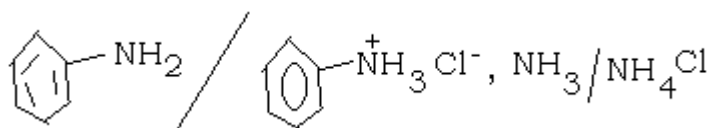
Action of a buffer solution
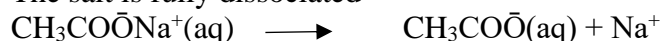
A buffer works by maintaining the pH constant when a small amount of acid or base is added to its solution
  a) Acidic buffer
Consider the $CH_3CO\bar{O}Na^+$ / CH_3COOH buffer solution. The acid is weakly ionized.
CH_3COOH $\rightleftharpoons$ $CH_3CO\bar{O}(aa) + H^+(aq)$
The salt is fully dissociated
$CH_3CO\bar{O}Na^+(aq)$ $\longrightarrow$ $CH_3CO\bar{O}(aq) + Na^+$
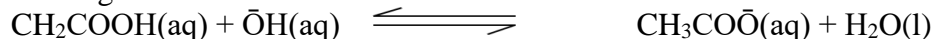(Excess)
The buffer contains a large excess of an ionized molecules of the acid (CH_3COOH) and a large excess of ethanoate ions. On addition of a small amount of the acid in form of hydrogen ions. The hydrogen ions are removed by ethanoate ions forming molecules of Ethanoic acid. Therefore the pH does not change.
$CH_3CO\bar{O}(aa) + H^+(aq)$ $\rightleftharpoons$ $CH_3COOH(aq)$
On addition of a small amount of the base in form of hydroxide ions, ($\bar{O}H$), they are removed by reacting with molecules of ethanoic acid
$CH_2CO\bar{O}H(aq) + \bar{O}H(aq)$ $\rightleftharpoons$ $CH_3CO\bar{O}(aq) + H_2O(l)$
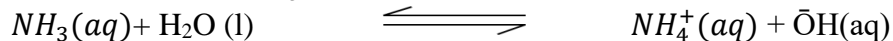Therefore the pH of the buffer solution remains constant.
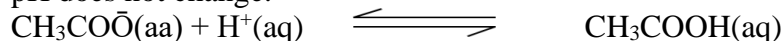
NB: The effectiveness of an acidic buffer depends on the presence of a large Supply of ethanoate ions to buffer the hydrogen ions and a large supply of ethanoic acid molecules to buffer the hydroxide ion introduced.
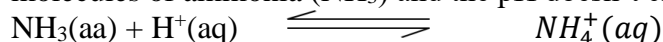
b) Basic buffer

Consider a buffer NH_3/NH_4Cl buffer. Ammonia is a weak base and only slightly ionized.
$NH_3(aq)$ + H$_2$O (l) $\rightleftharpoons$ $NH_4^+(aq)$ + $\bar{O}H(aq)$
Ammonia chloride is a strong salt and fully dissociated.
$NH_4^+Cl(aq)$ $\longrightarrow$ $NH_4^+(aq)$ + $Cl^-(aq)$
Therefore the solution contains a large excess of ammonium molecules and ammonium ions addition of a small amount of the acid in form of (H$^+$), they are removed by the undissociated molecules of ammonia (NH_3) and the pH doesn't change.
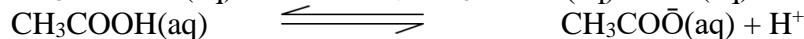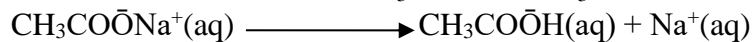NH$_3$(aa) + H$^+$(aq) $\rightleftharpoons$ $NH_4^+(aq)$
Addition of a small amount of the base in form of ($\bar{O}H$) they are removed by ammonium ions so the pH doesn't change.
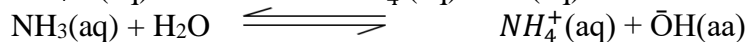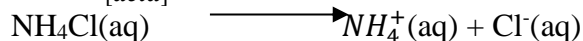$NH_4^+(aq)$ + OH(aq) $\longrightarrow$ NH$_4$OH(aq)
The effectiveness of a basic buffer therefore depends on the presence of a large number of ammonium ions to buffer the hydroxide ions.

Calculating the pH of buffer solution

Consider the acidic buffer CH$_3$COŌNa$^+$/CH$_3$COOH
CH$_3$COŌNa$^+$(aq) $\longrightarrow$ CH$_3$COŌH(aq) + Na$^+$(aq)
CH$_3$COOH(aq) $\rightleftharpoons$ CH$_3$COŌ(aq) + H$^+$
$Ka = \frac{[salt][H^+]}{[acid]}$
NH$_4$Cl(aq) $\longrightarrow$ NH_4^+(aq) + Cl$^-$(aq)
NH$_3$(aq) + H$_2$O $\rightleftharpoons$ NH_4^+(aq) + $\bar{O}H$(aa)
$Kb = \frac{[NH_4^+].[\bar{O}H]}{[NH_3]}$
$[\bar{O}H] = Kb\frac{[NH_3]}{[NH_4^+]}$
Introducing –log on both sides,
pOH=pKb+$log\left(\frac{[Salt]}{[Base]}\right)$This is Handerson Hasselbalsch equation.
Assumptions
$[NH_4^+]$ = [salt]
[NH$_3$] = [base]
Question. Calculate the pH of a solution made by mixing 0.5M of (CH$_3$COOH) with 0.5M of sodium Ethanoate.
Ka = (CH$_3$COOH) = 1.8 x 10^{-5})
Solution
CH$_3$COOH (aq) $\rightleftharpoons$ CH$_3$COŌ(aq) + H$^+$(aa)
CH$_3$COŌNa $^{(aq)}$ $\longrightarrow$ CH$_3$COŌ(aq) + Na$^+$(aq)
$Ka = \frac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$
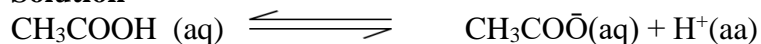
$[H^+] = Ka \dfrac{[CH_3COOH]}{[CH_3CO\bar{O}]}$
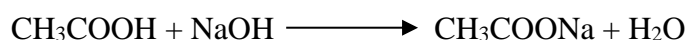
$= Ka \dfrac{[acid]}{[salt]}$

1.8×10^{-5}

pH = -log(1.8 x 10^{-5}0

pH = 4.74

2. Calculate the pH of a solution made by mixing 25cm^3 of 0.1M ethanoic acid with 10cm^3 of 0.1M sodium hydroxide

Ka = (CH$_3$COOH) = (1.8 x 10^{-5})

Question 2. Calculate the pH of a solution made by mixing 6gl^{-1} of CH$_3$COOH and 8.2gl^{-1} of CH$_3$CO$\bar{O}$Na$^+$ (Ka = 1.8 x 10^{-5} moldm^{-3})

CH$_3$COOH + NaOH $\longrightarrow$ CH$_3$COONa + H$_2$O

Note: The excess acid and the sodium ethanoate formed constitute a buffer.

Vol of excess acid = (25 – 10)

= 15cm^3

1000cm of excess acid contain 0.1 mole

15cm^3 of excess and contain $(\dfrac{0.1\ x\ 15}{100})$

35cm^3 of mixture contain $(\dfrac{0.1\ x\ 15}{100})$ moles

1000cm^3 of mixture contain $(\dfrac{0.1\ x\ 15\ x\ 1000}{1000\ x\ 35})$

= 0.0429M This is the concentration of the acid.

1 mole of NaOH = 1mole of CH$_3$COONa

Moles of NaOH = $(\dfrac{0.1\ x\ 10}{1000})$ moles

35cm^3 of mixture contain $(\dfrac{0.1\ x\ 10}{1000})$

1000cm^2 of mixture contain $(\dfrac{0.1\ x\ 10\ x\ 100}{1000\ x\ 35})$

= 0.0286M.This is the concentration of the salt.

pH = Pka + Log$_{10}\dfrac{[salt]}{[Acids]}$ (Handerson Hasselbalsch equation)

= 4.74 + log$_{10}$ $(\dfrac{0.0286}{0.0429})$ = 4.57

Calculate the pH of a solution made by mixing 50cm³ of 0.1M ethanoic acid with 0.1 mole of 50cm of sodium ethanoate. (Ka CH₃COOH = 1.8 x 10⁻⁵)

Question. Calculate the pH of a solution made by mixing $100cm^3$ of 0.1M ethanoic acid with $20cm^3$ of 0.1 M NaOH solution. (CH_3COOH) = 1.0×10^{-5})

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3CO\bar{O}Na^+(aa) + H_2O(a)$$
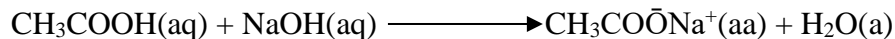
The salt formed and the excess acid constitute a buffer solution

Moles of NaOH used = ($\frac{0.1}{100}$ x 20) moles

Moles of CH_3COOH used = ($\frac{0.1}{100}$ x 20) moles

Moles of excess acid

$= (\frac{0.1 \, x \, 100}{1000}) - (\frac{0.1}{1000}$ x 20)

$= 0.01 - 0.002$

$= 0.008$ moles

1 mole of NaOH reacts with 1 mole of ethanoic acid to form 1 mole of $CH_3CO\bar{O}Na^+$

Moles of $CH_3CO\bar{O}Na^+$

Formed = ($\frac{0.1}{100}$ x 20)

$= 0.002$ moles

Total volumes of solution

$= 100 + 20 = 120$ cm^3

Molar concn of salt

$= 0.002 * \frac{1000}{120}$

$= 0.0167$M

Molar concn of excess acid

$= 0.008$ x $\frac{2000}{120}$

$= 0.067$M

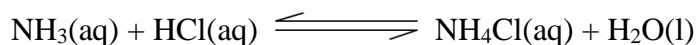Now substitute in the formula

pH = Pka + $Log_{10} \frac{[salt]}{[Acid]}$(Handerson Hasselbalsch equation)

Question: Calculate the pH of a solution by mixing 50cm^3 of 0.1M hydrochloric acid with 50cm^3 of 0.2M aqueous ammonia Kb (NH$_3$) = 1.75 x 10^{-5}moldm^{-3}

Solution

NH$_3$(aq) + HCl(aq) $\rightleftharpoons$ NH$_4$Cl(aq) + H$_2$O(l)

The salt formed and the excess ammonia constitute a buffer solution

Moles of HCl used   Moles of NH$_3$ used

$= \frac{0.1}{1000}$ x 50 $(\frac{0.2}{1000} x 50)$

Excess moles of NH$_3$

$= (\frac{0.2}{1000} x 50)-(\frac{0.1}{1000}$ x 50)

$= (\frac{0.1}{1000}$ x 50)

1mole of HCl reacts with the ammonia to give

1 mole of the salt

Moles of salt formed $= \frac{0.1}{1000}$ x 50

Total number = 50750 = 100cm^3

Molar concentration of excess

NH$_3 = \frac{0.1}{1000}$ x 50 x $\frac{1000}{100}$

Molar concentration of salt formed

$= \frac{0.1}{1000}$ x 50 x $\frac{1000}{100}$

NH$_4$Cl(aq) $\rightarrow$ NH_4^+(aq) + Cl$^-$

NH$_3$(aq) + H$_2$O(l) $\rightleftharpoons$ NH_4^+(aq) + ŌH(aq)
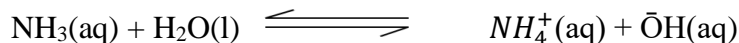
Kb $= \frac{[NH_4^+].[ŌH]}{[NH_3]}$

[ŌH] = Kb$\frac{[NH_3]}{[NH_4^+]}$

1.75 x 10^{-5} x $\frac{0.05}{0.05}$

[ŌH] = 1.75 x 10^{-5}

pOH = -log10 [ŌH]

= -log10[1.75 x 10^{-5})

pOH = 4.757

14 = pH + pOH

pH = 14 – 4.57

= 9.24

Question a 0.1m solution of ethanoic acid was titrated with a 0.1M NaOH solution. Calculate the pH of the solution when;

    i.   The titration has not been started.
    ii.   When the acid is half neutralized and when the acid is completely neutralized.
    iii.   Twice as much sodium has been added compared to that needed for neutralization
(Ka(CH$_3$COOH = 1.8 x 10^{-5})

Solution

Before the titration, pH is determined by 0.1M CH$_3$COOH

CH$_3$COOH(aq) $\rightleftharpoons$ CH$_3$COŌ(aq) + H$^+$
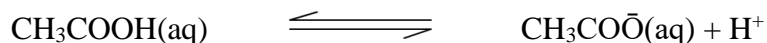
$Ka = \dfrac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$

At equilibrium = [CH$_3$COŌ] = [H$^+$]

$Ka = \dfrac{[H^+]^2}{[CH_3COOH]}$

$[H^+] = \sqrt{Ka[CH_3COOH]}$

$= \sqrt{1.8 \ x \ 10^{-5} x \ 0.1}$

[H$^+$] = 1.34 x 10^{-3}

pH = - log$_{10}$[H]

= -log$_{10}$[1.3 x 10^{-3}]

= 2.873

At half neutralization

CH$_3$COOH(aq) + NaOH(aq) $\longrightarrow$ CH$_3$COŌNa$^+$ + H$_2$O
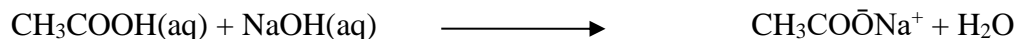
At half neutralization

½ [Acid] has reacted to form the salt

[Acid] = ½ (0.1) = 0.05

[Salt] = ½ (0.1) = 0.05

Therefore at half neutralization

[Acid] = [Base]

$CH_3COOH(aq) \longrightarrow CH_3CO\bar{O}(aq) + H^+$

$CH_3COOH(aq) \rightleftharpoons CH_3CO\bar{O}(aq) + H^+(aq)$
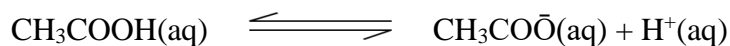
$Ka = \frac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$

$[H^+] = Ka \frac{[Acid]}{[salt]}$

$[H^+] = Ka$

$[H^+] = 1.8 \times 10^{-5}$

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

$= log_{10}(1.8 \times 10^{-5})$

$pH = 4.7$

At neutralization, the solution contains only the salt formed and the mixture water. All the acid has reacted to form 1 mole of the salt.

∴ [salt] = 0.1M

The salt formed hydrolyses

$CH_3CO\bar{O}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \bar{O}H(aq)$
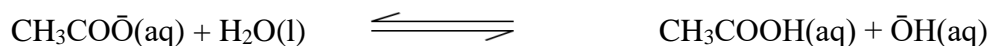
But $Kh = \frac{Kw}{Ka} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$

At eqbm (CH$_3$COOH] = [ŌH]

$Kh = \frac{[\bar{O}H]^2}{[CH_3CO\bar{O}]}$

$5.56 \times 10^{-10} = \frac{[\bar{O}H]^2}{[0.1]}$

$[OH]^= \sqrt{5.5 \times 10^{-1}}$

$pOH = -log_{10} 7.4565 \times 10^{-6}$

5.13

14 =pH + poH

pH = 8.87

excess NaOH = (0.2 – 0.1) = 0.1M

[NaOH) for neutralization 0.1M

Twice as much = 0.1 x 2 = 0.2 m

Excess (NaOH) in solution = (0.1 x 0.1)

= 0.1M

0.1M NaOH is responsible for the pH

$$NaOH(aq) \longrightarrow Na^+(aq) + \bar{O}H(aq)$$
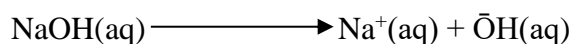
0.1   0.1

$[\bar{O}H]$ = 0.1M

pOH = -log(0.1)

= 1.0

pH = 14-1

= 13

$25cm^3$ of a 0.1M HCl were titrated with 0.1M ammonia calculate the pH of the solution when

  i.   The acid is half neutralized
  ii.   The acid is completely neutralized
  iii.   Twice as much ammonia has been added compared to that needed for neutralization.
($Kb(NH_3) = 1.75 \times 10^{-5}$).

Qn. Calculate the mass of sodium ethanoate that should be added to 1 litre of a 0.1 methanoic acid to give a solution of pH 5.56($Ka = (CH_3COOH) = 1.8 \times 10^{-5}$)

Solution

$$CH_3CO\bar{O}H(aq) \longrightarrow CH_3CO\bar{O}(aq) + Na^+(aq)$$

$$CH_3COOH(aq) \rightleftharpoons CHCO\bar{O}(aq) + H^+(aq)$$
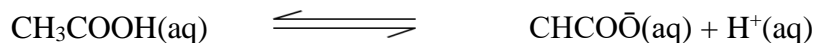
$Ka = \frac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$

$[H^+] = \frac{Ka[CH_3COOH]}{[CH_3CO\bar{O}]}$

$[H^+] = Ka \frac{[Acid]}{[salt]}$

But pH = $-\log_{10}[H^+]$ = 5.56

$[H^+]$ = 2.75 x 10^{-6}M

2.75 x 10^{-6} = $\frac{1.8\ x\ 10^{-5}x\ 0.1}{[salt]}$

[salt] = 0.65M

RFM of $CH_3CO\bar{O}Na^+$

=(12x2) + (3) + (16 x 2) + 23 = 82

Mass of salt = 0.65 x 82 = 53.3g/l

Effect of adding a small amount of acid or base on to the PH of a buffer.

Consider a buffer made up of CH_3COOH and $CH_3CO\bar{O}Na^+$.

CH_3COOH(aq) $\rightleftharpoons$ $\underline{CH_3CO\bar{O}}$(aq)+ H^+(aq)

$CH_3CO\bar{O}Na^+$(aq) $\longrightarrow$ $CH_3CO\bar{O}$(aq) + Na^+(aq)
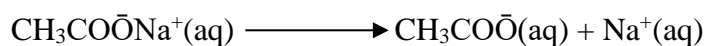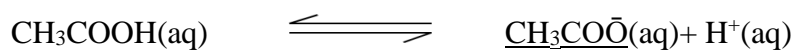
   (a) Addition of a small amount of acid (H^+ ion]. The H^+ ions react with the ethanoate ions forming ethanoic molecules.

$CHCO\bar{O}$(aq) + H^+(aq) $\rightleftharpoons$ CH_3COOH(aq)
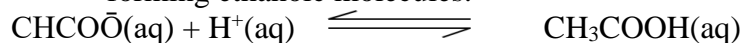
This decreases the [Salt] but increases [acid] by the same amount.

Question: A solution is made by mixing 0.5M ethanoic acid with 0.5 M sodium ethanoate.

Calculate

   (i)   The pH of the solution
   (ii)   The change in pH when a small amount of 0.01MHCl is added to a litre of the solution.

Solution

$CH_3CO\bar{O}Na^+$(aq) $\longrightarrow$ $CH_3CO\bar{O}$(aq) + Na^+(aq)

CH_3COOH(aa) $CH_3CO\bar{O}$(aa)+ H^+(aq)

Ka = $\frac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$

$[H^+]$ = Ka $\frac{[Acid]}{[salt]}$

$[H^+]$ = 1.8 x 10^{-5} x $\frac{0.5}{0.5}$

pH = 4.74

Addition of a small amount of 0.01MHCl. The H^+ ions are buffered by the $CH_3CO\bar{O}$ ions

$$CH_3CO\bar{O}(aa) + H^+(aq) \longrightarrow CH_3COOH(aq)$$

This increases the $[CH_3COOH]$ by 0.01M

A new $[CH_3COO-]$

$= 0.5 + 0.01$

$= 0.51M$

It decreases the $[CH_3CO\bar{o}]$ by 0.01M

A new $[salt] = 0.5 - 0.01$

$= 0.49$

$$[H^+] = Ka\frac{[Acid]}{[salt]}$$

$$[H^+] = 1.8 \times 10^{-5} \times \frac{0.51}{0.49}$$

$pH = 4.73$

change in $pH = 4.74 - 4.73$

$= 0.01$

So pH changes by 0.01 (very effective buffer)

Addition of a small amount of a base. The added $\bar{O}H$ ions react with the molecules of ethanoic acid.

$$CH_3COOH(aq) + \bar{O}H(aq) \longrightarrow CH_3CO\bar{O}(aq) + H_2O(l)$$

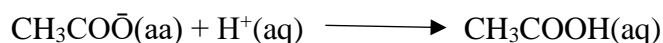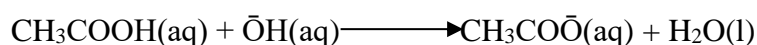This decrease the $[CH_3COOH]$ but increases the $[CH_3CO\bar{O}]$ by the same amount. Small amount of 0.001M NaOH is added to the buffer.

Application of Buffer solutions

    i)   Used in the field of medicine and Agriculture to prepare standard solutions since the pH of the living cells must be maintained. Eg Intravenous injections must be carefully buffered so that the pH of blood does not change from its normal value of about 7.4

    ii)   In fermentation, most fermentation processes must be buffered as any change in pH would cause death of the organisms.

    iii)   Applied in biochemistry e.g. in enzymatic studies where an enzyme would work effectively at a specific pH

    iv)   In Zone electrophoresis (separation technique used to analyze proteins, nucleic acids and bio polymers). During the process, different species in the sample are transported in a continuous electrolyte buffer system subject to a potential gradient and due to

different mobilities, the species in the sample will separate into separate well resolved peaks.

<div align="center">INDICATORS</div>

An acid – base indicator is a substance which is either a weak base or a weak acid that changes colour according to pH or the concentration of hydrogen ions of the solution in which it is placed. The ionized 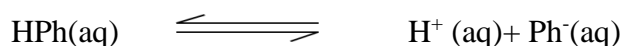molecules of the indicator have a different colour from the un ionized molecules. Common examples include phenolphthalein, methyl orange, methyl red, litmus, bromo phenol, thymol blue, Congo red, bromo cresol etc

Action of an indicator

Consider the ionization of phenolphthalein

$$HPh(aq) \rightleftharpoons H^+(aq) + Ph^-(aq)$$

The un ionised molecules of the indicator are colourless while the ionized are red (pink) In an acidic solution the concentration of hydrogen ions ($[H^+]$) is high and the equilibrium position shifts from right to left and the indicator appears colourless.

In Alkaline medium, the $[\bar{O}H]$ is high which react with the hydrogen ions forming water disturbing the equilibrium. To restore the equilibrium, more indicator molecules ionize causing an excess of indicator ions(In^-) and the indicator appears pink in alkaline solution.

Consider the ionization of methyl orange which is considered to be a weak base

$$HMe \rightleftharpoons H^+(aq) + Me^-(aq)$$
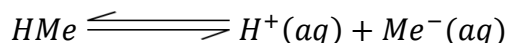
In acidic medium there is a high concn of hydrogen ions, $[H^+]$ which combine with methyl orange ions, forming the ionized indicator shifting the equilibrium from right to left and the indicator appears orange/red in acidic medium. This is due to undissociated HMe molecules formed.

In alkaline medium, there is a high concentration of hydroxide ions, $[\bar{O}H]$ which react with the H^+ shifting the equilibrium from right to the left and the indicator appears yellow in alkaline medium This is the colour of Me^- ions.

Indicator constant (KIn)

Consider the indicator which is a weak acid

$$HIn(aq) \rightleftharpoons H^+(aq) + In(aq)$$
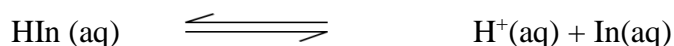
$$Kin = \frac{[H^+].[I_n^-]}{[HIn]}$$

Or $[H^+] = \frac{K_{In}.[HIn]}{[I_n^-]}$

The intermediate colour between the acidic and alkaline colour exists when

$$[HIn] = [In^-]$$

$[H^+] = KIn$

Each Indicator has its Kin value eg for phenolphthalein it is 7.0 x 10^{-10}

$[H^+]$ = Kin = 7.0 x 10^{-10}

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

= -log10(7.0 x 10^{-10})

= 9.15

For methyl orange has a pH of 3.7

working range of an indicator

The pH range within which an acid-base indicator changes from one colour to another is known as the pH working range of the indicator.

Titration	pH range	Suitable indicator
Strong acid-strong base	3.5-10	Phenolphthalein, methyl orange or litmus
Weak acid-strong base	7.5-10.3	Phenolphthalein
Strong acid-Weak base	3.5-6.5	Methyl orange

Acid-Base titration curves

These are curves obtained by plotting pH of the acid or base against the volume of the acid or base added. They are drawn using free hand.

Titration of a strong acid against a strong base
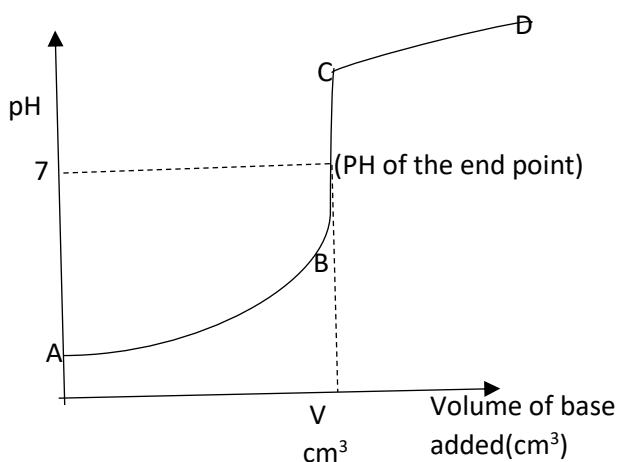
The initial pH at point A is low because Hydrochloric acid is a strong acid and is fully ionized in solution releasing many hydrogen ions which are responsible for the low pH. Along AB the pH increases gradually because the hydrogen ions are still in excess and any added $\bar{O}H$ are immediately neutralized forming water.

Point B is near the end point(equivalent point) and any additional drop added causes a sharp rise in pH along BC because NaOH is a strong alkali that completely dissociates. The resultant solution at the end point is neutral (pH =7) because the salt formed (NaCl) does not undergo hydrolysis, the gradual increase in pH along CD is because of excess base added.The end point can b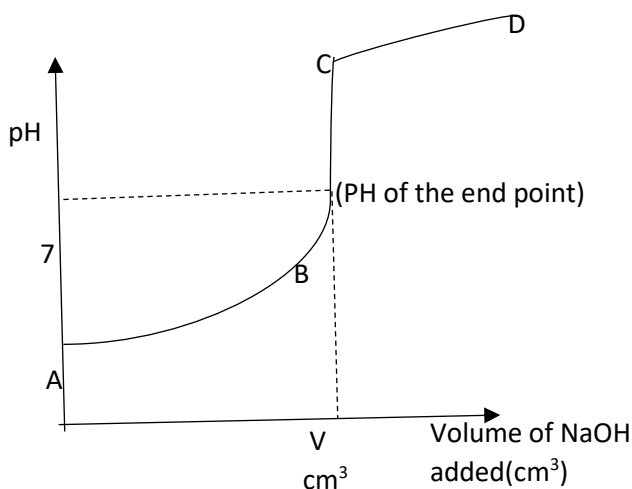e detected by any indicator which changes colour at the pH range between B & C but preferably the midpoint is taken as the pH of the resultant solution.

Weak acid against Strong base eg (CH₃COOH / NaOH)

Initially the pH is relatively high because ethanoic acid is a weak acid which partially ionizes to produce few hydrogen ions.Along AB the pH increases gradually because the acid and the salt formed constitute a buffer mixture that resists change in pH .Point B is near the end point and an additional drop of the base causes a sharp increase in pH along BC, the pH at the end point is greater than 7 because the salt formed undergoes hydrolysis to form hydroxide ions that make the solution alkaline.

$CH_3COOH(aq) + NaOH(aq) \rightleftharpoons CH_3CO\bar{O}Na^+(aq) + H_2(l)$

$CH_3CO\bar{O} (aq)+ H_2O(l) \longrightarrow CH_3COOH(aq) + \bar{O}H(aq)$

Strong acid against weak base eg (HCl / NH₄OH)
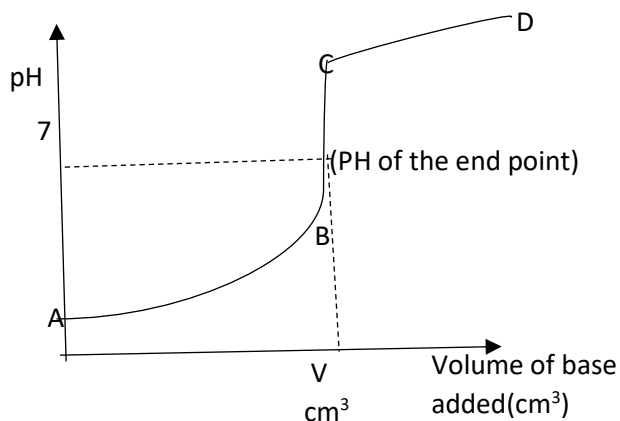
Initially the pH is low because the acid is fully ionized releasing many hydrogen ions in solution, the gradual increase in pH along AB is because the H^+ are still in excess and any added $(\bar{O}H)$ from ammonia are immediately neutralized.Also the weak base and the salt formed constitute a buffer solution that resists change in pH. point B is near the endpoint and any additional drop causes a sharp rise in Ph along BC because of a slight excess of hydroxide ions from the base. The pH at the end point is less than 7 because the salt formed ammonia chloride undergoes hydrolysis

$$NH_4^+ + H_2O \rightleftharpoons NH_3(aq) + H_3O^+$$
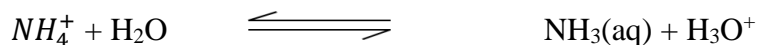
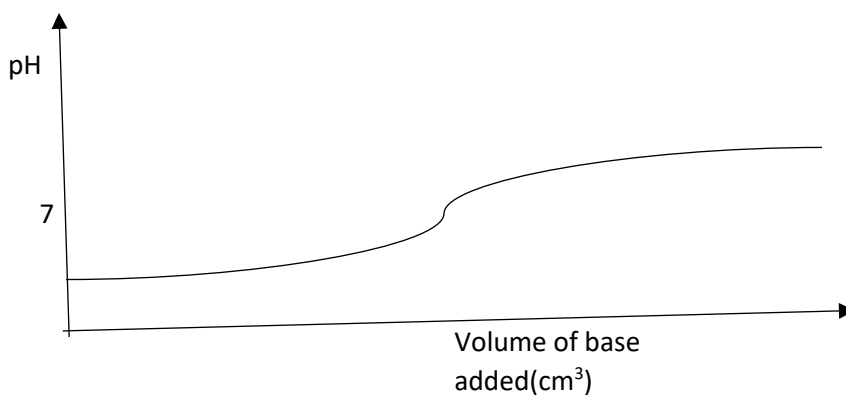The gradual increase in pH along CD is because of the excess base added and the buffering action of the (NH_4Cl/ Ammonium buffer).

Weak acid against weak base titration eg (Ammonia & Ethanoic acid)

In titration of a weak acid against a weak base there is no observed sharp rise in pH hence it can't be followed using an acid base indicator.

SOLUBILITY Equilibria.
Applicable to sparingly soluble salts i.e. a salt that slightly dissolves in water forming ions which remain in equilibrium with undissolved solid at a constant temperature.
Solubility is the molar concentration of a sparingly soluble ionic compound in its saturated solution at a given temperature.
Solubility product
Is the product of molar concentrations of the ions of a sparingly soluble ionic compound or salt that exist in its saturated solution raised to appropriate powers from the stoichiometric equation at a constant temperature.
Or the product of the concentration of the ions produced by a sparingly soluble salt raised to appropriate powers in a saturated solution at a given temperature.
Consider a sparingly soluble salt:
$$A_mB_n(s) + aq \rightleftharpoons mA^{n+}(aq) + nB^{m-}(aq)$$
$$K_{sp}=[A^{n+}]^m[B^{m-}]^n$$
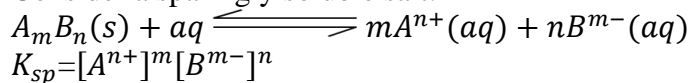
Also consider silver chloride dissolved in water.

$$AgCl(s) + aq \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
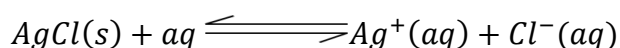
$K=\frac{[Ag^+][Cl^-]}{[AgCl]}$

$K \times [AgCl] = [Ag^+][Cl^-]$ but $K \times [AgCl] = K_{sp}$ Since $AgCl$ is in large excess,it is regarded as a constant which when multiplied by K gives rise to a new constant K_{sp}

$\therefore K_{sp}=[Ag^+][Cl^-]$

The solubility product of $AgCl$ is$1x10^{-10}mol^2dm^{-6}$ from experiments.

$\therefore if K_{sp} > [Ag^+][Cl^-]$ then the solution is unsaturated and more $AgCl$ can dissolve.

Also $if K_{sp} < [Ag^+][Cl^-]$ then then Ag^+ and Cl^- are withdrawn from the solution as a precipitate.

Examples of sparingly soluble salts

PbCl$_2$,PbSO$_4$,Ca(OH)$_2$,$Ca_3(PO_4)_2$,PbI$_2$,CaF$_2$,Ag$_2$CO$_3$,Al(OH)$_3$,Fe(OH)$_3$,CaIO$_3$ etc

AssignmentFor each of the salts,write stoichiometric equations for the dissociation in water and the K_{sp} expressions.

Factors affecting solubility of a sparingly soluble salt.
    a)   Common ion effect
    b)   Complex ion formation
    c)   Addition of a soluble salt which doesnot contain a common ion
   d)   Temperature.

Common ion effect

Is the precipitation of a sparingly soluble salt from its saturated solution by adding a solution of a more soluble compound containing one of its ions.

Or it is the decrease in solubility of a sparingly soluble electrolyte when a more soluble compound with a common ion is added to its saturated solution.

Eg if to a saturated solution of AgCl is added HCl or NaCl increases the concentration of chloride ions, Cl^- increases which react with Silver ions to precipitate Silver chloride.This reduces the solubility of Silver chloride.

If a solution of silver nitrate is added to a saturated solution of silver chloride,the solubility of AgCl reduces because silver ions react with chloride ions to precipitate Silver chloride.The solubility of AgCl decreases.

Addition of sulphuric acid to a saturated solution of barium sulphate

$BaSO_4(s) + aq \rightleftharpoons Ba^{2+}(aq) + SO_4{}^{2-}(aq)$
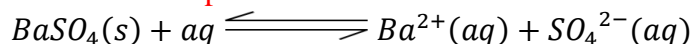
Sulphuric acid produces $SO_4{}^{2-}$ and hydrogen ions in solution.

The sulphate ions are the common ions to the $SO_4{}^{2-}$ from Barium sulphate.The concentration of $SO_4{}^{2-}$ ions increases and to keep the Ksp of Barium sulphate constant,the excess sulphate ions react with barium ions to precipitate Barium sulphate.Therefore adding a soluble salt containing a common ion decreases the solubility of a sparingly soluble salt.

Application of common ion effect.

    i)   Salting out of soap
A saturated solution of soap has an equilibrium

$NaSt(s) + aq \rightleftharpoons Na^+(aq) + St^-(aq)$
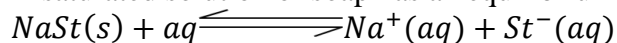
In the maufacture of soap, concentrated NaCl(Brine) is added to the above equilibrium.NaCl produces sodium ions that are common to the sodium ions in the saturated solution.This increases the concentration of sodium ions and to keep Ksp constant, Soap is precipitated.

   ii)   Purification of common salt.

Common salt contains $MgCl_2$ and $CaCl_2$ which make it deliquescent and make it to appear brown.It ispurified by bubbling HCl.This increases the concentration of Chloride ions and to keep Ksp constant,NaCl is precipitated and not $MgCl_2$ nor $CaCl_2$

Complex ion formation

A complex ion is an ion composed of a central metal atom datively bonded to neutral atoms or molecules with lone pairs of electrons or negatively charged ions.

Complex ion formation increases the solubility of a sparingly soluble salt.

Eg Silver chloride is almost insoluble in water but very soluble in ammonia solution.

Explanation.

$$AgCl(s) + aq \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
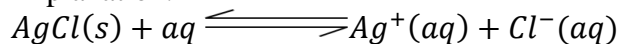
The solubilityproduct of $AgCl$ is $1x10^{-10}mol^2dm^{-6}$.This value is so small that almost all the silver chloride remains as a solid however if ammonia solution is added to it, the solid will immediately dissolve because of formation of a soluble complex diamine silver ion according to the equation

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq).$$ The silver ions are being removed from solution and therefore to restore equilibrium,more AgCl dissociates to form silver ions and chloride ions.

Also copper(II) hydroxide is almost insoluble in water but is readily soluble in excess aqueous ammonia.Explain

Also Lead(II)chloride is sparingly soluble in cold water but is considerably more soluble in concentrated hydrochloric acid

Explanation

The solubility of PbCl2 in water reaches its limit when $[Pb^{2+}][Cl^-]^2 = K_{sp}$which is very small in cold water.In concentrated hydrochloric acid,a complex ion is formed according to the equation

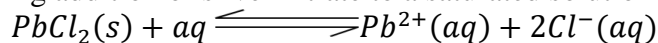$$Pb^{2+}(aq) + 2Cl^-\,(aq) + 2Cl^-\,(aq) \rightleftharpoons [PbCl_4]^{2-}(aq)$$
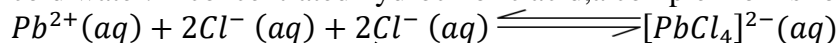
From conc HCl

Addition of a soluble salt which doesnot contain a common ion

This increases the solubility of a sparingly soluble salt.

Eg addition of silver nitrate to a saturated solution of lead(II) chloride

$$PbCl_2(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

The silver ions from silver nitrate react with chloride ions to precipitate AgCl.This reduces the concentration of chloride ions in a saturated solution of lead(II) chloride.Therefore to restore Ksp, more lead(II) chloride dissolves.This increases solubility.

Application of Solubility product.

   i)   Common ion effect
   ii)   Formation of Stalagmites and Stalactites found in Kasese Mabeere ganyinamwiru
   iii)   Predicting precipitation in qualitative analysis.

Precipitation reactions.

A salt with a lower solubility product precipitates out first.

Eg during titration of Chlorides with silver nitrate using Potassium chromate as the indicator,AgCl precipitates out before silver chromate because AgCl has a lower solubility product than Ag_2CrO_4.

Trial Question

a) What is meant by the term common ion effect
b) Silver chromate is sparingly soluble in water. Write:
   i)   The equation for the solubility of silver chromate in water
   ii)   The expression for the solubility product Ksp for silver chromate.
c) The solubility of silver chromate at 25°C is 3.21gdm^{-3}. Calculate the solubility product for silver chromate at 25°C.
d) Determine the molar concentration of silver ions required to precipitate silver chromate from an aqueous solution containing 0.002M chromate ions
e) A solution containing silver ions was added to a solution containing 0.002M chromate ions and 0.002M chloride ions. State which of the salts was precipitated first. Give a reason for your answer(Ksp for AgCl=$1.96x10^{-10}mol^2dm^{-6}$).

Precipitation of Metallic hydroxides

When ammonium hydroxide is added to an aqueous solution containing $Fe^{3+} and Zn^{2+}$ in presence of NH_4Cl only $Fe(OH)_3$precipitates.Explain
Ammonium hydroxide is a weak base and ionizes according to the equation

$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$
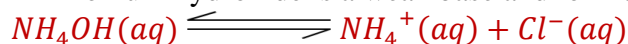
This ionization is surpressed by ionization of ammonium ions from NH_4Cl

$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$

This results in a decrease in concentration of hydroxide ions such that only hydroxides with low solubility product can be precipitated.Therefore $Fe(OH)_3$ is precipitated because it has a lower solubility product than $Zn(OH)_2$

Limitations of solubility products
   i)   The solution must be saturated
   ii)   The solution must be sparingly soluble
   iii)   Temperature should be constant

Example calculate the solubility of BaSO₄ in
   i.   Water
   ii.   0.1M sodium sulphate (Ksp BaSO₄ at 25⁰c = 1.0 x 10⁻¹⁰)
Calculate the amount of the BaSO₄ which was precitated as a result of dissolving barium sulphate in 0.1M sodium sulphate

BaSO₄(s) $\rightleftharpoons$ Ba^{2+}(aq) + SO_4^{2-}(aq)

Let solubility of BaSO₄ be S moldm⁻³
$[Ba^{2+}]$ = S
$[SO_4^{2-}]$ = S
Ksp = $[Ba^{2+}]$ $[SO_4^{2-}]$
1.0 x 10⁻¹⁰ = S.S
$S = \sqrt{1.0 \ x \ 10^{-10}}$
= 1 x 10⁻⁵M
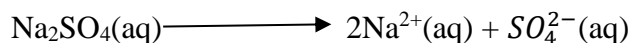
Na₂SO₄(aq) $\longrightarrow$ $2Na^{2+}$(aq) + SO_4^{2-}(aq)
Let the new solubility be s¹moldm⁻³

$[SO_4^{2-}] = [0.1 + S^1]$ moldm^{-3}
$[Ba^{2+}] = S^1$
But $0.1 >>> S^1$ such that $0.1 + S^1 = 0.1$
$0.1 \times S^1 = 1.0 \times 10^{-10}$
$S^1 = 1 \times 10^{-9}$ M
Moles precipitated $[1.0 \times 10^{-5} - 1.0 \times 10^{-9})$
Mass precipitated
Ba – RFM = 233
$(1.0 \times 10^{-5} - 1.0 \times 10^{-9}) \times 233$
$= 2.33 \times 10^{-3}$

Calculate the solubility of calcium chloride in
  i.   Water
  ii.   0.01 M solution of sodium fluoride
  iii.   1.0M solution of hydrogen fluoride (ksp for $CaF_2 = 4.0 \times 10^{-11}$, Ka for Hf = 5.6×10^{-4}M)

Solution
$CaF_2(l) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$
Let the solubility in water be s moldm^3
$[Ca^{2+}] = s$ $[F] = 2s$
$Ksp = [Ca^{2+}] [F^-]^2$
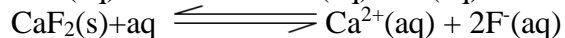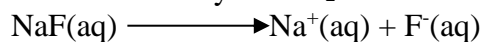$4.0 \times 10^{-11} = s(2s)^2$
$S^3 = \dfrac{4.0 \times 10^{-11}}{4}$
$S = \sqrt[3]{\dfrac{4.0 \times 10^{-11}}{4}}$
$= 2.15 \times 10^{-4}$M
Let the solubility of CaF_2 in 0.01M NaF be a moldm^{-3}
$NaF(aq) \longrightarrow Na^+(aq) + F^-(aq)$
$CaF_2(s) + aq \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$
$[Ca^{2+}] = a$ moldm^3
$[F^-] = 2a + 0.01$ moldm^{-3}
But $0.01 >>> a$
$[F^-] = 0.01$M
$4.0 \times 10^{-11} = 0.0001$ a
$= 4.0 \times 10^{-7}$ M
$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$
$Ka = \dfrac{[H^+][F^-]}{[HF]}$
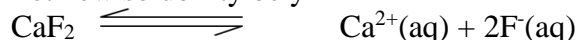$[H^+] = [F^-]$
Ka $5.6 \times 10^{-4} = \dfrac{[F^-]^2}{0.1}$
$[F^-] = \sqrt{0.1 \times 5.6 \times 10^{-4}}$
$= 7.4833 \times 10^{-3}$
Let new solubility be y
$CaF_2 \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$
$2y + 7.4833 \times 10^{-3} \approx 7.4833 \times 10^3$

$Ksp = [Ca^{2+}] [F^-]$
$4 \times 10^{-11} = a \times 7.4833 \times 10^{-3}$
$a = \dfrac{4 \times 10^{-11}}{(7.4833 \times 10^{-3})^2}$
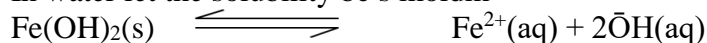$7.144 \times 10^{-7}M$

write the expression for the solubility product of iron (II) hydroxide and give the units.
$Ksp = [Fe^{2+}] [\bar{O}H]^2$

If the ksp of $Fe(OH)_2$ at 25^0c is 6.6×10^{-15}, calculate the solubility in moldm^{-3} of $Fe(OH)_2$ first in pure water then in 1.0M ammonia (Kb Ammonia $= 1.8 \times 10^{-5}M$)
In water let the solubility be s moldm^8
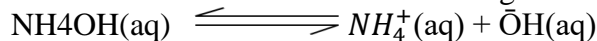$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2\bar{O}H(aq)$
$Ksp = [Fe^{2+}] . [OH]$
$6.6 \times 10^{-15} = s(2s)^2$
$S = \sqrt[3]{\dfrac{6.6 \times 10^{-15}}{4}}$
1.1817×10^{-5} moldm^{-3}
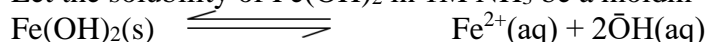
Ammonia ionizes in solution according to the equation
$NH4OH(aq) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$
$Kb = \dfrac{[NH_4^+][\bar{O}H]}{[NH_4OH]}$ at equilibrium
$1.8 \times 10^{-5} = \dfrac{[\bar{O}H]^2}{1.0}$
$[\bar{O}H] = \sqrt{1.8 \times 10^{-5} \times 1.0}$
$= 4.24 \times 10^{-3}$ M
Let the solubility of $Fe(OH)_2$ in 1M NH_3 be a moldm^3
$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2\bar{O}H(aq)$
a $(2a + 4.24 \times 10^{-3})$
but $2a <<<< 4.24 \times 10^{-3}$
such that $2a + 4.24 \times 10^{-3} \approx 4.24 \times 10^{-2}$ M
$ksp = [Fe^{2+}] [\bar{O}H]^2$
$6.6 \times 10^{-15} = a.(4.24 \times 10^{-3})^2$
$a = \dfrac{6.6 \times 10^{-15}}{1.798 \times 10^{-5}}$
$= 3.67 \times 10^{-10}M$
b) The Ksp of barium sulphate and strontrum sulphate are 1.1×10^{-10} and 2.8×10^{-7} mol^{2}dm^{-6} at 298K. sodium sulphate is gradually added to a solution containing 0.01M Barium chloride and 0.01M strontium chloride.
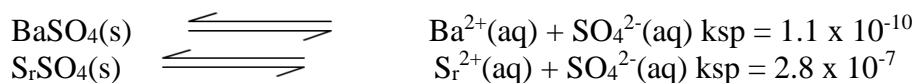(i) Which cation will precipitate first give a reason.
Solution
Barium ions precipitate out first leaving strontion ions in solution because barium sulphate has a lower solubility product hence a low solubility and its ksp is easily exceeded.
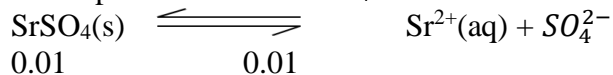Calculate the concentration of $BaSO_4$ in a solution which is saturated with both barium sulphate and strontion sulphate.
Solution

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \quad ksp = 1.1 \times 10^{-10}$$
$$SrSO_4(s) \rightleftharpoons Sr^{2+}(aq) + SO_4^{2-}(aq) \quad ksp = 2.8 \times 10^{-7}$$

Assumption

In a saturated solution of the two salts, the common ion comes from only the more soluble salt, so the sulphate are from $SrSO_4$

$$SrSO_4(s) \rightleftharpoons Sr^{2+}(aq) + SO_4^{2-}$$
$$0.01 \qquad\qquad 0.01$$

$Ksp = [Sr^{2+}][SO_4^{2-}]$

$[SO_4^{2-}] = \dfrac{ksp}{[Sr^{2+}]}$

$= \dfrac{2.8 \times 10^{-5}}{0.01}$

$= 2.8 \times 10^{-5}$

Barium sulphate

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

$1.10 \times 10^{-10} = [Ba^{2+}] \times 2.5 \times 10^{-5} M$

$[Ba^{2+}] = \dfrac{1.1 \times 10^{-10}}{2.5 \times 10^{5}}$

$[Ba^{2+}] = 3.93 \times 10^{-6} M$

Since 1 mole of $BaSO_4$ releases 1 mole of Ba^{2+}

Concentration of $BaSO_4 = [Ba^{2+}]$

$= 3.93 \times 10^{-6} M$

*Methods of determining solubility product constants*
   i)   Direct titration
   ii)   Measurement of electrolytic conductivity

Experiment to determine the solubility product of lead(II)bromide
   - Excess solid lead(II)bromide is added to a given volume of de ionised water
   - The mixture is shaken vigorously for some time in a clean beaker.
   - The mixture is allowed to settle at constant temperature for equilibrium to be established.
   - The mixture is filtered and the conductivity of the filtrate is measured using a conductivity metre
   - The molar conductivity of lead(II) ions and bromide ions are obtained from tables and are used to calculate the Molar conductivity of the Lead(II) bromide.
   - The concentration of Lead(II) bromide in the saturated solution is obtained from the formula $\dfrac{Conductivity}{Molar\ conductivity\ at\ infinite\ dilution} = x$

Treatment of results
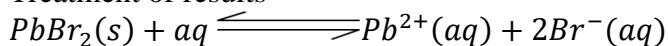
$$PbBr_2(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$$
$$K_{sp} = [Pb^{2+}][Br^-]^2$$

$[Pb^{2+}] = x$ and $[Br^-] = 2x$

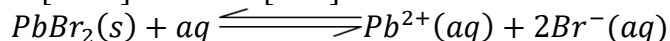$\therefore K_{sp} = x.(2x)^2$

$= 4x^3$

Experimental determination of the solubility product of Lead(II) bromide using titration

An excess of solid Lead(II) bromide is added to a known volume of water and the mixture shaken vigorously for about 5-10 minutes and allowed to settle at a given temperature until equilibrium is attained. The mixture is filtered and known volumes of the filtrate are titrated with standard silver nitrate solution using Potassium chromate as the indicator
The end point is reached when a red precipitate of silver chromate is formed.
The concentration of bromide ions is determined and hence that of chloride ions is calculated.
If $[Pb^{2+}] = x$ then $[Br^-] = 2x$
$$PbBr_2(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$$
$$K_{sp} = [Pb^{2+}][Br^-]^2, K_{sp} = x.(2x)^2$$
$$= 4x^3$$

Note if the salt is Calcium hydroxide, the indicator used is Phenolphthalein

    a) What is meant by the term common ion effect?
    b) Calcium iodate, $Ca(IO_3)_2$ is sparingly soluble in water
    c) Write
    i)   The equation for the solubility of calcium iodate in water.
    ii)   An expression for the solubility product, ksp of calcium iodate
    d) If the solubility product of calcium iodate at 25^0C is 1.95×10^{-3}. Calculate the solubility in moles per litre at 25^0C of calcium iodate in.
    i) Water
    iii)   0.01 M solution of sodium iodate
Comment on your answer