IONIC EQUILIBRIA

ACID-BASE EQUILIBRIA

Arrhenius theory of acid and base

Acid

Is a substance which on dissolving in water produces hydrogen ions.

Base

- Is a substance which on dissolving in water produces Hydroxyl ions
- Is a substance which combines with an acid to form a salt and water

Brønsted – Lowry theorem

Acid

Is a substance which donates a proton (***proton donor***)

Base

Is a substance which accepts a proton (***proton acceptor***)

Examples include;

a) $HCl_{(aq)}+ NH_{3(aq)} \rightarrow Cl^{-} + NH_4^{+}$

Acid; Base; conjugate Base of HCl; conjugate acid of NH_3

(b) $HCl + H_2O \rightarrow H_3O^{+} + Cl^{-}$

Conjugate Acid; (Hydronium/oxorium/hydroxonium); conjugate base;

(c.) $H_2O+NH_3 \rightarrow \bar{O}H + NH_4^{+}$

Conjugate Base; conjugate acid;

NB

i. Strong acids

Are acids which readily donate a proton to another molecule (base) eg H_2SO_4, etc ii.

Weak acids

Are acids which do not easily lose its proton with difficult eg

CH_3COOH ie $CH_3COOH(aq) \rightleftharpoons CH_3O\bar{O}(aq) + H^{+}$

$H_2SO_3(aq) \rightleftharpoons H^{+} + HSO_3^{-}$

iii. Strong base ;

A base which has a high affinity for protons eg NaOH

Lewis acid theory

Acid;

- Is a substance which can accept a pair of electrons.

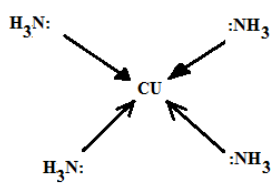
Base

Is a substance which donates a pair of electrons in a dative covalent bond

Eg (i) $F_3B + NH_3 \rightarrow F_3B \leftarrow :NH_3$

acid base

(ii) $Cu(aq) + 4NH_3(aq) \rightleftharpoons$



IONISATION CONSTANTS OF ACIDS AND BASES

a) Ionisation constants of weak acids (Ka)

Consider a weak monobasic acid(HA) of concentration C which ionizes in solution as follows;

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

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

Ka $= \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]}$, but $[HA]$= C

Ka $= \frac{[H^+(aq)][A^-(aq)]}{C}$ At equilibrium; $[H^+] = [A^-]$

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

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

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

Ka $= \frac{[H^+][CH_3OO^-]}{[CH_3COOH]}$ At equilibrium $[H^+] = [CH_3COO^-]$, If $[CH_3COOH]$ = C moldm^{-3}

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

Relationship between Ka and degree of Dissociation, α

Consider a weak monobasic acid(HA) of concentration C and degree of dissociation, α

	$HA(aq)$	$\rightleftharpoons H^+ (aq)$	$+ A^- (aq)$
Initial moles;	C	−	−
Moles reacted ;	Cα	Cα	Cα
Equilibrium moles	C − Cα	Cα	Cα

Ka $= \frac{[H^+][A^-]}{[HA]} = \frac{C\alpha\, C\alpha}{C - C\alpha} = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$,

For weak acids, α is small, $(1-\alpha) \cong 1$

Ka $= \frac{C\alpha^2}{(1)}$ = Cα^2

$\boldsymbol{\alpha} = \sqrt{\frac{K_a}{C}}$

Example

1. The acid dissociation constant of a dibasic acid is 4.39 × $10^{-5} mol^2dm^{-6}$ at 25^0C, Calculate the degree of ionization of a 0.01M solution of the acid. **UNEB 2010**

Solution

For weak acids, Ka $= \frac{C\alpha^2}{(1-\alpha)}$, But also for weak acids; α <<<< 1,

$(1-\alpha) \cong 1$

K_a = Cα^2

4.39 × 10^{-5} = 0.01 α^2

α = $\sqrt{\frac{4.39 \times 10^{-5}}{0.01}}$

α = 0.066

α = 6.6%

Activity

1. Calculate the degree of dissociation of a 0.01M ethanoic acid if K is $1.0 \times 10^{-5} mol^2 dm^{-6}$ at 298K

b) Ionisation constant for weak bases; K_b

Consider a weak base BOH of concentration C which ionizes in solution as follows.

$$BOH\ (aq) \rightleftharpoons B^+(aq) + \bar{O}H(aq)$$

$Kb = \frac{[B^+][\bar{O}H]}{[BOH]}$ but [BOH] = C $moldm^{-3}$

$Kb = \frac{[B^+][\bar{O}H]}{[C]}$ At equilibrium; $[B^+] = [\bar{O}H]$;

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

Assumptions

- ✓ At equilibrium; $[B^+] = [\bar{O}H]$;
- ✓ Concentration of unionized base is equal to the original concentration; because proportion of molecules ionized is small.

Relationship between Kb and α

Consider a weak base BOH of concentration C and degree of dissociation, α

	BOH (aq)	$\rightleftharpoons$	B^+(aq)	$\bar{O}H$(aq)
Initial concentration	C		–	–
Reacted moles	Cα		Cα	Cα
Equilibrium concn	C – Cα		Cα	Cα

$Kb = \frac{[B^+][\bar{O}H]}{[BOH]} = \frac{C\alpha\ C\alpha}{[C - C\alpha]} = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$

But for weak bases; α <<<< 1, $(1-\alpha) \cong 1$

$K_b = C\alpha^2$

$\alpha = \sqrt{\frac{K_b}{C}}$

Activity

1. Write;
   i. An equation for the ionization methylamine in water
   ii. The expression for the base dissociation constant, Kb for Methylamine
2. At 25^0C Ammonia has a base ionization constant, Kb of $1.8 \times 10^{-5} moldm^{-3}$
   a) Write an expression for Kb of Ammonia
   b) Calculate the concentration of $\bar{O}H$ in 0.1M Ammonia solution at 25^0C

State any assumptions made (**1997 No. 11 Paper 1, part of question)**

IONISATION OF WATER

Pure water undergoes self-ionization as follows

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

By law of mass action;

$K_{eq} = \frac{[H^+][\bar{O}H]}{[H_2O]}$

$K_{eq} [H_2O] = [H^+][\bar{O}H]$

Since the degree of ionization of water is small; $[H_2O_{(l)}]$ = constant

K_{eq} . constant = $[H^+][\bar{O}H]$, but K_{eq} . constant = K_w (ionization product of water/ionic product of water)

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

But pure water contains equal concentration of H^+ and $\bar{O}H$ ions ($1 \times 10^{-7}moldm^{-3}$)

$K_w = (1 \times 10^{-7}moldm^{-3})(1 \times 10^{-7}moldm^{-3})$

$\underline{K_w = (1 \times 10^{-14}moldm^{-6})}$

pH

Is the negative logarithm to the base 10 of the hydrogen ion concentration of a solution.

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

OR;

is the logarithm to base 10 of the reciprocal of the hydrogen ion concentration of a solution. i.e. pH = $\log_{10}\frac{1}{[H^+]}$

a) **pH of water:**

pure water contains equal concentration of hydroxyl and hydrogen ions ($1 \times 10^{-7}moldm^{-3}$); pH $= -\log_{10}[H^+] = -\log_{10}[1 \times 10^{-7}]$

pH = 7

b) **pH of acids:**

i. **strong acids:**

pH of strong acids depends **only on its concentration** because strong acid is fully ionized;

Examples

1. Calculate the pH of a 0.02M H_2SO_4

Solution

$[H_2SO_4]$ =0.02M

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

1 mole of H_2SO_4 form 2 moles of H^+

0.02moles of H_2SO_4 form (0.02) moles of H^+

= 0.04 moldm^{-3}

$\Rightarrow [H^+]$ =0.04 moldm^{-3}

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

= $-\log 0.04$

= 1.40

2. Calculate the pH value of $2\times 10^{-3}moldm^{-3}$ of HNO_3

Solution

$HNO_{3\,(aq)} \rightarrow H^+ + NO_3^-$

1 mole of $HNO_{3\,(aq)}$ produces 1 mole H^+

$[HNO_3] = [H^+] = 2 \times 10^{-3}moldm^{-3}$

ACTIVITY

1. Calculate the pH of the following concentration of the following acids

(a). 0.05moldm^{-3} HCl (b) 0.025moldm^{-3} Sulphuric acid

NB: ***A strong acid of concentration > 1.0moldm^{-3}; pH value < 0 eg for 2M HCl; pH = −0.3***;

ii) pH of weak acids

Consider ionization of weak acid HA whose concentration is C moldm^{-3}, and the degree of ionization **α**

$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + \bar{A}_{(aq)}$

By law of mass action;

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

But at equilibrium; $[H^+] = [\bar{A}]$

$K_a = \frac{[H^+]^2}{C}$

$[H^+]^2 = K_aC$

$[H^+] = \sqrt{KaC}$ ----------- (i)

Also; $\alpha = \sqrt{\frac{Ka}{C}}$ ------------ (ii)

Examples

1. Calculate the $[H^+]$ and the pH of a 0.01M solution of ethanoic acid. (K_a =1.8 × 10^{-5}moldm^{-3})

   Solution

   Concn of CH_3COOH = 0.01moldm^{-3}, K_a = 1.8 × 10^{-5}

   From $[H^+] = \sqrt{KaC}$

   $[H^+] = \sqrt{1.8 \times 10^{-5} \times 0.01}$

   $[H^+] = 4.24 \times 10^{-4}$moldm^{-3}

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

   $= -\log(4.24 \times 10^{-4})$

   = 3.37

2. The pH of a 0.001M solution of ethanoic acid is 3.59. Calculate the;
   i. dissociation constant of the acid.
   ii. Degree of dissociation at the concentration given.

   Solution

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

   $3.59 = -\log[H^+]$

   $\log[H^+] = -3.59$

   $[H^+] = log^{-1}(-3.59)$

   $= 2.57 \times 10^{-4}$moldm^{-3}

From $[H^+] = \sqrt{KaC}$

$[H^+]^2 = K_aC$

$K_a = \frac{[H^+]^2}{C} = \frac{(2.57 \times 10)^2}{0.001}$

= **6.61×10^{-5}moldm^{-3}**

ii. $\alpha = \sqrt{\frac{Ka}{C}} = \sqrt{\frac{6.61 \times 10^{-5}}{0.001}}$ = **0.26**

ACTIVITY

1. A solution of 0.05M propanoic acid had a pH of 4. Calculate its degree of dissociation and hence dissociation constant K_a

c) **pH of bases**

pH of bases can be obtained from the ionization pH of water. ie ;

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

Taking $-\log$ on both sides of the expression

– $\log K_w = -\log([H^+][\bar{O}H])$

– $\log K_w = -\log [H^+] + -\log [\bar{O}H]$

pK_w = pH + pOH

from $K_w = 1 \times 10^{-14}$

$pK_w = -\log [Kw]$

$pK_w = -\log [1 \times 10^{-14}]$

$pK_w = 14$

i. **pH of strong bases**

Examples

1. Calculate the pH of 0.001M Potassium hydroxide

$KOH_{(aq)} \rightarrow K^+_{(aq)} + \bar{O}H_{(aq)}$

1 moleof KOH produces 1 mole of $\bar{O}H$ ions

$[KOH] = [\bar{O}H] = 0.001 moldm^{-3}$

pOH = $-\log (0.001)$

pOH = 3

But from pK_w = pH + pOH

14 = pH + 3

pH = 14 – 3 = **11**

OR:

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

$1 \times 10^{-14} = [\bar{O}H][H^+]$

$[H^+] = \frac{1 \times 10^{-14}}{\bar{O}H} = \frac{1 \times 10^{-14}}{0.001} = 1 \times 10^{-11}$

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

$= -\log(1 \times 10^{-11})$

pH = 11

ii. **pH of weak bases**

Consider a weak base BOH of concentration $Cmoldm^{-3}$ and degree of dissociation, **α**

$BOH_{(aq)} \rightleftharpoons B^+_{(aq)} + \bar{O}H_{(aq)}$

By law of mass action,

$Kb = \frac{[B^+][\bar{O}H]}{[BOH]} = \frac{[B^+][\bar{O}H]}{[C]}$

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

$K_b = \frac{[\bar{O}H]^2}{C}$

$[\bar{O}H] = \sqrt{K_b C}$

$\alpha = \sqrt{\frac{K_b}{C}}$

Example

1. Calculate the pH of 0.1M aqueous ammonia whose K_b is 1.5×10^{-6}.

Solution

$NH_{3(aq)} + H_2O\ (l) \rightleftharpoons NH_4^+{}_{(aq)} + \bar{O}H_{(aq)}$

$K_b = \frac{[NH_4^+][\bar{O}H]}{[NH_3\,(aq)]}$, At equilibrium $[\bar{O}H] = [NH_4^+{}_{(aq)}]$

$K_b = \frac{[\bar{O}H]^2}{[NH_{3\,(aq)}]}$

$1.5 \times 10^{-6} = \frac{[\bar{O}H]^2}{0.1}$

$[\bar{O}H]^2 = 1.5 \times 10^{-6}$

$[\bar{O}H] = \sqrt{1.5 \times 10^{-6}} = 3.87 \times 10^{-4}$ moldm^{-3}

pOH = $-\log(3.87 \times 10^{-4})$

= 3.41

From pH = pKw – pOH

= 14 – 3.41 = **10.587**

ACTIVITY

1. 0.01M solution of phenylamine is 7.5% ionized
   (a) Write the expression for dissociation of phenylamine
   (b) Calculate;
      (i) K_b
      (ii) pH of the solution

BUFFER SOLUTION

Buffer solutions are ***solutions which resist changes in their pH when small amounts of acid or base is added to them.***

Types of buffer solutions

(i)acidic buffer

- consists of solution of a weak acid and its salt from a strong base. eg ***acetic acid and sodium acetate***, supplying a conjugate base of weak acid.
- Maintain nearly a constant pH value less than 7

(ii) Basic buffer

- Consists of a solution of a weak base and its salt from a strong acid. Eg ***ammonium hydroxide and ammonium chloride, supplying a conjugate acid of weak base.***
- Maintain nearly a constant pH value above 7

a) **Action of acidic buffer:**

Consider a solution of weak acid(acetic acid) and its highly ionisable salt (sodium acetate)

- ♣ Acetic acid is a weak acid, is not fully ionized while sodium acetate is a strong electrolyte, fully ionized.

  $CH_3COOH_{(aq)} \rightleftharpoons CH3CO\bar{O}_{(g)} + H^+{}_{(aq)}$

  $CH_3COONa_{(aq)} \rightarrow CH_3CO\bar{O}_{(g)} + Na^+{}_{(aq)}$

- ♣ Solution contains excess of acetate ions and a large amount of unionized acetic acid, and a small amount of hydrogen ions.
- ♣ Addition of H^+ to this solution (inform of acid eg HCl) will combine with the acetate ions forming unionized acetic acid.

$CH_3CO\bar{O}_{(aq)} + H^+_{(aq)} \rightleftharpoons CH3COOH_{(aq)}$

- ♣ H^+ are removed by excess ethanoate ions already present, solution retains its constant pH value.
- ♣ addition of $\bar{O}H$ ions to this solution from a base, it will be removed by reacting with the unionized acetic acid.

$CH_3COOH_{(aq)} + \bar{O}H_{(aq)} \rightleftharpoons CH3CO\bar{O}_{(aq)} + H_2O(l)$

- ♣ the solution also maintains its pH value.

pH calculations of acidic buffers

- Consider a buffer solution consisting of acetic acid and sodium acetate

$CH_3COOH_{(aq)} \rightleftharpoons CH3CO\bar{O}_{(g)} + H^+_{(aq)}$

$CH_3COONa_{(aq)} \rightarrow CH_3CO\bar{O}_{(g)} + Na^+_{(aq)}$

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

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

Assumptions:

- CH_3COONa is a strong electrolyte; fully ionizes; $[CH_3CO\bar{O}]$ = [salt]
- CH_3COOH is a weak acid, $[CH_3COOH]$ = [acid]

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

Taking –log on both sides of the expression;

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

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

$pH = pK_a - \log \frac{[acid]}{[salt]}$

$pH = pK_a + \log \frac{[salt]}{[acid]}$ "The Henderson – Hassel balch equation"

Examples

1. (a) Calculate the pH of a buffer solution which consists of 4.1g of Sodium ethanoate per litre of solution and 0.01M ethanoic acid whose $K_a = 1.7\times 10^{-5}moldm^{-3}$

solution

Relative molecular mass of $CH_3COONa = (2\times14)+(2\times O_{16})+(3\times1)+23 = 82$

1 mole of CH_3COONa weighs 82g

X moles of CH_3COONa weighs 4.1g

$X = (\frac{4.1}{82}) = 0.05moldm^{-3}$

[acid] = 0.01

$CH_3COOH_{(aq)} \rightleftharpoons CH_3CO\bar{O}_{(aq)} + H^+_{(aq)}$

$CH_3COONa_{(aq)} \rightarrow CH_3CO\bar{O}_{(aq)} + Na^+_{(aq)}$

From the ***Henderson – Hassel balch equation***;

$pH = pK_a + \log \frac{[salt]}{[acid]}$

pH = −logK$_a$+ $\log\frac{[salt]}{[acid]}$

pH = $-\log(1.7\times 10^{-5})+\log\frac{[0.05]}{[0.01]}$

pH = 5.47

(b). Calculate the pH change of the solution above if;

(i) 1cm^3 of 1M NaOH is added

(ii) 1cm^3 of 1M HCl is added

Solution

1000cm^3 of NaOH contain 1 mole

1cm^3 of solution contains $\left(\frac{1}{1000}\right)$ moles of NaOH

= 0.001 moles of NaOH

[NaOH] = [$\bar{O}H$] = 0.001 moles

$\bar{O}H$ ions reacts with unionized acetic acid, decreases the concentration of acid, increasing the concentration of salt ($CH_3CO\bar{O}$)

$CH_3COOH_{(aq)} + \bar{O}H_{(aq)} \rightleftharpoons CH_3CO\bar{O}_{(aq)} + H_2O$

New [salt] = 0.05+ 0.001= 0.051 mol l^{-1}

New [acid] = 0.01 – 0.001 = 0.009 mol l^{-1}

From pH = pK$_a$ + $\log\frac{[salt]}{[acid]}$

pH = $-\log(1.7\times 10^{-5})+\log\frac{[0.051]}{[0.009]}$

pH = 4.7696 + 0.753 = **5.523**

change in pH = 5.523 – 5.47

change in pH = 0.053 units

(b) 1000cm^3 of HCl contain 1 mole

1cm^3 of HCl contains $\left(\frac{1}{1000}\right)$ moles

[HCl] = [H^+] = 0.001moldm^{-3}

H^+ ions reacts with acetate ions , decreasing the concentration of salt , increasing the concentration of salt caid.

$CH_3CO\bar{O}_{(aq)} + H^+_{(aq)} \rightleftharpoons CH_3COOH_{(aq)}$

New [salt] = 0.05 – 0.001 = 0.049moldm^{-3}

New [acid]= 0.01 + 0.001 = 0.011 moldm^{-3}

From pH = pK$_a$ + $\log\frac{[salt]}{[acid]}$

pH = $-\log(1.7\times 10^{-5})+\log\frac{[0.049]}{[0.011]}$

pH = 5.418

change in pH = 5.418 – 5.47 = **– 0.052 units**

2. Calculate the mass of Sodium ethanoate that should be added to 0.1M ethanoic acid at 25^{O}C to give a solution of pH 5.5.

State any assumptions made (Ka of ethanoic acid = 1.8 × 10^{-5}moldm^{-3})

Solution

From pH = pK$_a$ + $\log\frac{[salt]}{[acid]}$

$$5.5 = -\log K_a + \log\frac{[salt]}{[acid]}$$

$$5.5 = -\log(1.8\times10^{-5}) + \log\frac{[salt]}{[0.1]}$$

$\log[salt] = -0.245$

$[salt] = 0.569 mol\ l^{-1}$

RMM of CH_3COONa = 82.

1 mole of CH_3COONa weighs 82g

0.569 moles of CH_3COONa weigh (82 × 0.569) = **46.62g**

Mass of CH_3COONa = 46.62g

Activity **UNEB 2001(paper 1 no.15, 1999(p1 No. 12), 2007 p1. 13a)**

(b) Action of basic buffers

Consider a solution of weak base(ammonium hydroxide) and its highly ionisable salt(Ammonium chloride)

-NH_4OH partially ionizes while NH_4Cl fully ionizes both producing NH_4^+

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + \bar{O}H_{(aq)}$$

$$NH_4Cl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

-Solution contains excess of NH_4^+, a large amount of unionized ammonium hydroxide, and a small amount of hydroxyl ions.

-Addition of a small amount of strong acid, HCl ,hydrogen ions added are removed by ammonium hydroxide;

$$NH_4OH_{(aq)} + H^+{}_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + H_2O$$

-Solution suffers no change in pH

-Addition of a small amount of a base, $\bar{O}H$ added are removed by reacting with NH_4^+ forming unionized ammonium hydroxide/ ammonia and water, thus

-pH remains constant;

$$NH_4^+{}_{(aq)} + \bar{O}H_{(aq)} \rightleftharpoons NH_4OH_{(aq)} \quad (NH_{3(aq)} + H_2O_{(l)})$$

pH calculation of Basic buffers:

- Consider a buffer solution consisting of ammonium hydroxide and ammonium chloride.

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + \bar{O}H_{(aq)}$$

$$NH_4Cl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

By law of mass action; $K_b = \frac{[NH_4^+][\bar{O}H]}{[NH_4OH]}$

$$K_b[NH_4OH] = [NH_4^+][\bar{O}H]$$

$$[\bar{O}H] = \frac{Kb[NH_4OH]}{NH_4^+}$$

Assumptions

i. Concentration unionized NH_4OH is equal to the concentration of base.

ii. NH_4Cl fully ionizes,$[NH_4^+]$ = [salt]

Therefore $[\bar{O}H] = K_b\frac{[base]}{[salt]}$

$$-\log[\bar{O}H] = -\log K_b + -\log\frac{[salt]}{[acid]}$$

$$pOH = pK_b - \log\frac{[salt]}{[acid]}$$

$$pOH = pK_b + \left(\log\frac{[salt]}{[acid]}\right)^{-1}$$

$$pOH = pKb + \log\frac{[salt]}{[base]}$$

But pKw = pH + pOH

$$pH = pKw - pKb + \log\frac{[salt]}{[base]}$$

Examples

1. A solution consists of 0.01M ammonia solution and 2.13g of ammonium chloride in a litre of solution (Kb for $NH_4OH = 1.8 \times 10^{-5} moldm^{-3}$)
   a) Calculate the pH of the solution
   b) pH change of solution on addition of $1cm^3$ of 1M HCl

   Solution

Relative molecular mass of NH_4Cl =53.5
1 mole of NH_4Cl weighs 53.5g
X mole of NH_4Cl will weigh 2.13g
$X = [NH_4Cl] = \frac{2.13}{53.5} = 0.0398 mol\ l^{-1}$

From $pOH = pKb + \log\frac{[salt]}{[base]} = -\log(1.8 \times 10^{-5}) + \log\frac{0.0398}{0.01} = 5.345$

pKw = pH + pOH , pH = pKw − pOH = 14-5.345= **8.655**

b) moles of HCl

$1000cm^3$ of solution contains 1 mole of HCl

$1cm^3$ of solution contains $\left(\frac{1}{1000}\right)$ moles

$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

1 mole of acid produces 1 mole of $H^+_{(aq)}$
Concentration of H^+ = 0.001moles

$H^+_{(aq)} + NH_4OH_{(aq)} \rightarrow NH_4^+{}_{(aq)} + H_2O\ (l)$

New [salt] = 0.0398 + 0.001 =0.0408 mol l^{-1}

New [Base] = 0.01 – 0.001 = 0.009mol l^{-1}

pOH = $-\log(1.8 \times 10^{-5}) + \log\frac{0.0408}{0.009}$

pOH = 5.401

pH = 14 – 5.401 = **8.59885**

pH change = 8.655 – 8.59855

pH change = 0.056units

2. calculate the pH of the solution which was made by adding 30cm^3 of 0.1M HCl to 80cm^3 of 0.1M ammonia solution ($K_b = 1.8 \times 10^{-5}$moll^{-1})

Solution

Moles of acid

1000cm^3 of solution contains 0.1moles of acid

30cm^3 of solution contains $\left(\frac{0.1}{1000} \times 30\right)$

= 0.003moles

Moles of NH_4OH

1000cm^3 of solution contains 0.1moles of base

80cm^3 of solution contains $\left(\frac{0.1}{1000} \times 80\right)$

= 0.008moles

$NH_4OH_{(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)} + H_2O$

Moles of acid that reacted = 0.003 = [salt]

Moles of base that reacted = 0.003

Moles of excess base = 0.008 – 0.003

= **0.005 moles**

Excess NH_4OH and salt formed (NH_4Cl) forms a basic buffer:

pOH = pKb + log $\frac{[salt]}{[base]}$

pOH = $-\log(1.8 \times 10^{-5}) + \log\left(\frac{0.003}{0.005}\right)$

pOH = **4.523**

pKw = pH + pOH

pH = 14 – 4.523

pH = 9.477

Activity

1. 0.01M ammonia solution was 4.5% ionized when dissolved in water
   a) Write the expression for the ionization of ammonia in water
   b) Calculate the base dissociation constant, K_b
   c) Calculate the concentration of ammonium chloride in grams per litre that must be added to the solution in (a) to give a pH of 8.83.

2. **UNEB 2012 (2) NO. 3C**

APPLICATIONS OF BUFFER SOLUTIONS:

- ✓ Controlling the pH of the reactions in industrial processes eg in fermentation process.
- ✓ electroplating metals
- ✓ Maintaining the pH of blood plasma constant i.e. 7.4 eg carbonic acid and its conjugate base ,HCO_3^-
- ✓ Used in preparations of standard solutions of definite pH
- ✓ Used in preservationof food.

- ✓ Control pH of shampoos.

SALT HYDROLYSIS

Is a process whereby a salt dissolved in water produces cations and anions which interact with water producing more H^+ and $\bar{O}H$ ions so that pH of the resultant solution is either greater than or less than 7.

(a) Hydrolysis of salt of strong base and weak acid.

These salts include;

- Sodium acetate (CH_3COONa) , Sodium carbonate (Na_2CO_3), Sodium cyanide (NaCN)

When Sodium acetate is dissolved in water;

- ✓ Salt being a strong electrolyte; is highly dissociated and water is slightly dissociated.

$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + \overline{OH}_{(aq)}$

Unionized
water

$CH_3COONa_{(aq)} \rightarrow CH_3CO\bar{O}_{(aq)} + Na^+_{(aq)}$

- ✓ Acetate ions react with hydrogen ions from water resulting in the excess of hydroxyl ions

$CH_3CO\bar{O}_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + \bar{O}H_{(aq)}$

- ✓ More water molecules ionize to restore water equilibrium producing more hydroxyl ions in excess; solution will have pH greater than 7;

a) **Hydrolysis constant K_h for a salt of a weak acid**

Consider salt BA formed from combination of a weak acid HA and a strong base, BOH

$\bar{A}_{(aq)} + H_2O_{(l)} \rightleftharpoons HA_{(aq)} + \bar{O}H_{(aq)}$

By law of mass action; $K_h = \frac{[HA][OH]}{[\bar{A}]}$--------- (i) ***(Assumption H_2O is large in excess)***

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

$$Kh = \frac{[OH]^2}{[A^-]}$$

Since $[A^-]$ = [salt]

$$Kh = \frac{[OH]^2}{[salt]}$$

Relationship between Kh, Ka, Kw

Multiplying the denominator and numerator of the expression (i) by the concentration of hydrogen ions;

$$K_h = \frac{[HA][OH]}{[\bar{A}]} \times \frac{[H^+]}{[H^+]}$$

$$K_h = \frac{[HA]}{[\bar{A}][H^+]} . [\bar{O}H][H^+]$$

But $[\bar{O}H][H^+] = Kw$ and $Ka = \frac{[HA]}{[\bar{A}][H^+]}$

$$K_h = \frac{1}{K_a} K_w$$

$$\boxed{K_h = \frac{K_w}{K_a}}$$

Degree of hydrolysis of a salt of weak acid and strong base:

-Is the fraction of the total salt that undergoes hydrolysis when equilibrium has been established;

Consider a salt of initial concentration, C moldm^{-3}, degree of hydrolysis, h

$A^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HA_{(aq)} + \bar{O}H_{(aq)}$

Initial conc	C	–	–
Moles Hydrolysed	ch	ch	ch
Eqm moles	(C − Ch)	ch	ch

By law of mass action: $K_h = \frac{[HA][\bar{O}H]}{[\bar{A}]}$

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

$K_h = \frac{[\bar{O}H]^2}{[\bar{A}]} = \frac{ch.ch}{c - ch} = \frac{c^2c^2}{c(1-h)}$

$K_h = \frac{ch^2}{(1-h)}$; For dilute solution, h is very small, 1 – h ≅ 1

$h = \sqrt{\frac{K_h}{c}}$ **Examples**

1. Calculate the degree of hydrolysis of 0.1M solution of potassium cyanide. (dissociation constant of hydrogen cyanide at 25^0C is 7.2×10^{-10} $moldm^{-3}$)

Solution

From $K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{7.2 \times 10^{-10}}$

$= 1.388889 \times 10^{-5}$ $moldm^{-3}$

But $h = \sqrt{\frac{K_h}{c}}$

$h = \sqrt{\frac{1.388889 \times 10^{-5}}{0.1}}$

h = 0.012 = 1.2%

2. Calculate the pH of solution of sodium ethanoate made by dissolving $8.4gdm^{-3}$ in water ($K_h = 5.5 \times 10^{-10)}$ $moldm^{-3}$)

Solution

$CH_3COONa_{(aq)} \rightarrow CH_3CO\bar{O}_{(aq)} + Na^+_{(aq)}$

$CH_3CO\bar{O}_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + \bar{O}H_{(aq)}$

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

But at equilibrium $[CH_3COOH] = [\bar{O}H]$

$Kh = \frac{[\bar{O}H]^2}{[CH_3CO\bar{O}]}$----------------------(i)

RFM of CH_3COONa = 82

1 mole of CH_3COONa weighs 82g

X mole of CH_3COONa weighs 8.4g

$X = \frac{8.4}{82} = 0.1024\ moldm^{-3}$

From (i) $[\bar{O}H]^2 = 0.1024 \times 5.5 \times 10^{-10}$

$[\bar{O}H] = 7.5 \times 10^{-6}$ moldm^{-3}

pOH = −log $[\bar{O}H]$

= $-\log(7.5 \times 10^{-6})$

pOH= **5.125**

pH = pKw – pOH

pH = 14 – 5.125

pH = 8.875

ACTIVITY

1. When a certain mass of sodium propanoate was dissolved in 1 litre of water, 10cm^{3}of this solution required 7.0cm^3 of 6.0 × 10^{-3} M for complete neutralization. Calculate the mass of sodium propanoate dissolved in 1 litre of water (K h = 6.0 × 10^{-10})
2. The pH of a solution formed by dissolving 7.2g of sodium benzoate in 1litre of water is 8.6. Calculate the hydrolysis constant of sodium benzoate

b) **Hydrolysis of a salt from strong acid and weak base eg NH_4Cl;**

When NH_4Cl is dissolved in water;

-Salt being a strong electrolyte; is highly dissociated; and water partially ionizes.

$NH_4Cl_{(s)} + {}_{(aq)} \rightarrow NH_4^+(aq) + Cl^-_{(aq)}$

$H_2O_{(l)} + \rightleftharpoons H^+_{(aq)} + \bar{O}H_{(aq)}$

- NH_4^+ reacts with $\bar{O}H$ ions from ionized water forming unionized NH_4OH

-concentration of hydroxyl ions is decreased.

-More water molecules ionize producing more hydrogen ions; molar concentration of hydrogen ions exceed the hydroxyl ions , pH becomes less than 7.

Hydrolysis constant of a salt from a weak base and strong acid

$NH_4Cl_{(s)} + {}_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-_{(aq)}$

$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H^+_{(aq)}$

OR $NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O_{(aq)}$

$K_h = \frac{[NH4OH][H^+]}{[NH_4^+]}$

At equilibrium $[NH4OH] = [H^+]$

$K_h = \frac{[H^+]^2}{[NH_4^+]}$

$K_h = \frac{[H^+]^2}{[salt]}$

$[H^+] = \sqrt{K_n[salt]}$

Degree of hydrolysis:

h = $\sqrt{\frac{K_h}{c}}$

$\mathbf{K_w} = \frac{K_h}{K_b}$

Activity.

1. Given that the dissociation constant of ammonium chloride at 25^0C is 1.8×10^{-5} .Calculate the hydrolysis constant and the degree of hydrolysis of ammonium chloride in 0.001M solution. What will be the hydrogen ion concentration of the solution?

2 (a). The pH of ammonium nitrate solution is 5.45. Explain this observation.

b) Calculate the hydrolysis constant of ammonium nitrate.

3. Methyl ammonium chloride undergoes hydrolysis according to the equation.

$$CH_3NH_3^+{}_{(aq)} + H_20_{(l)} \rightleftharpoons CH_2NH_{2(aq)} + H_3O^+{}_{(aq)}$$

a) Write the expression for its hydrolysis constant.

b) When 6.7g of methyl ammonium chloride was dissolved in $500cm^3$ of water, the pH was 2.33. Calculate the hydrolysis constant of the salt.

c) Calculate the volume of the above solution that would react completely with $10cm^3$ of 0.25M Sodium hydroxide solution..

4. Calculate the pH of 0.001M solution of phenyl ammonium chloride whose $K_h = 1.8 \times 10^{-3}$ $moldm^{-3}$.

ACID – BASE INDICATORS/ HYDROGEN ION INDICATORS

- Are substances that change colour according to the hydrogen concentration of the solution, in which they are added.
- Are weak acids or weak bases , therefore ;
  - are slightly dissociated when dissolved in water.
  - Its colour depends on the ***colour of the undissociated molecule*** and ***anion produced***(***negatively charged***.)

INDICATOR FUNCTIONING

(a). **Phenolphthalein (HPh)**

$$HPh_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + Ph^-{}_{(aq)}$$

Colourless — pink

Undissociated molecule — anion produced;

In acidic solution with high concentration of H^+,

- ✓ Hydrogen ions remove Ph^-, equilibrium shifts from right to left.
- ✓ Solution contains an excess of HPh molecules; showing colourless

In alkaline solution, with high concentration of $\bar{O}H$,

- ✓ Addition of $\bar{O}H$ removes the hydroxonium ions, producing water, decreasing the concentration of H_3O^+.
- ✓ Decrease in H_3O^+ concentration disturbs the equilibrium; more of the HPh ionizes producing Ph^- molecules; solution appears pink.

(b). **Methylorange**

$$HA_{(aq)} \rightleftharpoons H^+{}_{(aq)} + A^-{}_{(aq)}$$

Red — yellow

In acidic solution, with high concentration of Hydrogen ions,

- ✓ Hydrogen ions remove A^- ions, equilibrium shifts right to left.
- ✓ Solution contains an excess of HA molecules showing red colour;

In alkaline solution, with high concentration of hydroxyl ions;

- ✓ Addition of hydroxyl ions remove the hydrogen ions, producing water; decreasing concentration of hydrogen ions.
- ✓ More HA ionize producing A^- ions; colour of methyl orange appears yellow

QUESTION

a) Explain what is meant by the term **acid – base indicator.**

b) Explain how phenolphthalein acts as an indicator.

INDICATOR CONSTANT (K_{xn})

Consider unionized form of indicator, HIn which is a weak acid

$HIn_{(aq)} \rightleftharpoons H^+_{(aq)} + In^-_{(aq)}$

Colour **x** Colour **y**

By law of mass action;

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

WORKING RANGES OF INDICATORS

- ✓ Is the range of hydrogen ion concentration/pH ; over which different indicators change colour.

From $K_{In} = \frac{[H^+][In^-]}{[HIn]}$, $[H^+] = \frac{KIn\,[HIn^-]}{[In]}$

Taking negative logarithm on both sides

$$\log[H^+] = -\log K_{In}\frac{HIn}{[In^-]}$$

$$\log[H^+] = -\log K_{In} + -\log\frac{HIn}{In^-}$$

$$pH = p^{KIn} - \log\frac{HIn}{In^-}$$

$$pH = p^{KIn} + \log\frac{In^-}{HIn}$$ Henderson – Hasselbalch equation for Indicators

For colour Y; $[In^-] = 10[HIn]$

$\Rightarrow pH = p^{KIn} + \log\frac{In^-}{HIn}$,

$pH = p^{KIn} + 1$

For colour X; $[HIn] = 10[In^-]$

$\Rightarrow pH = p^{KIn} + \log\frac{In^-}{HIn}$

$pH = p^{KIn} - 1$

$$\mathbf{pH = p^{KIn} \pm 1}$$

Therefore range of pH over which indicator changes colour is **$pH = p^{KIn} \pm 1$,**

e.g for phenolphthalein, P^{Kin} (9.4), for pink (colour y), 9.4+1= 10.4; for colourless (colour x) 9.4-1=8.4, range of **8.3-10.4.**

Table showing some indicators, their colours and pH ranges

Indicator	P^{KIn}	pH range	Colour Acid	Base
Thymol blue	1.51	1.2-2.8	red	yellow
Methyl orange	3.70	3.0-4.5	red	yellow
Methyl red	5.10	4.2-6.3	red	yellow
Phenolphthalein	9.4	8.3-10.0	colourless	pink
Bromo thymol blue	7.0	6.0-7.3	yellow	blue

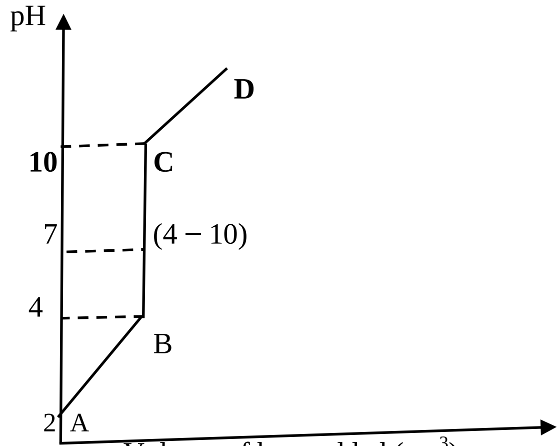
NB:

– Universal indicator is a ***mixture of indicators which give a gradual change in colour over a wide range of pH.***

pH CHANGES DURING ACID – BASE TITRATIONS

- ❖ Depends on the nature of acid and base used eg;

Strong base against strong acid (HCl Vs NaOH)



-. At A, pH is low, HCl is a strong acid which completely ionizes producing many hydrogen ions.

AB;
- Slow pH rise, hydrogen ion from acid is removed from hydroxyl ion added.

BC;
- Asharp rise in pH, (4−10), is due to a small amount of Sodium hydroxide added at the end point; when equivalent amounts of acid and base are added
- pH at end point 7; neutral salt formed is not hydrolysed.
- ***Methyl red, phenolphthalein, Bromothymol blue*** are the most suitable indicators used.

CD
- Rise in pH is due to excess NaOH added after the end point

Example

1. 20.0cm^{3}of a 0.02M sodium hydroxide was added to 30cm^{3}of 0.025M sulphuric acid.
   Calculate the;
   a) Molar concentration of the hydrogen ions in the initial sulphuric acid.
   b) Molar concentration of the hydrogen ions in the resultant solution
   c) pH of the resultant solution (**Uneb 1999 (No 5)**

Solution

a) $H_2SO_{4(aq)} \rightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$

1 mole ofH_2SO_4 produces 2 moles of H^+

0.025moles of H_2SO_4 produces (2×0.025)

= 0.05M

b) Moles of Sulphric acid

1000cm^3 of solution contains 0.025moles of H_2SO_4

30cm^3 of solution contains $\left(\frac{0.025 \times 30}{1000}\right)$ moles

$= 7.5 \times 10^{-4}$moles

Moles of sodium hydroxide

1000cm^3 of solution contains 0.02 moles of NaOH.

20.0cm^3 of solution contains $\left(\frac{0.02 \times 20}{1000}\right)$ moles

$= 4 \times 10^{-4}$ moles

$2NaOH_{(aq)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_20_{(l)}$

2 moles of NaOH reacts 1 mole of H_2SO_4

Moles of H_2SO_4 that reacted = $\frac{1}{2} \times 4.0 \times 10^{-4}$ moles = 2×10^{-4} moles

Moles of unreacted/ excess H_2SO_4 = $7.5 \times10^{-4} - 2\times10^{-4}$ = 5.5×10^{-4} moles

Total volume of solution = (20 + 30) cm^3

= $50.0cm^3$

$50cm^3$ of solution that contains 5.5×10^{-4} moles of H_2SO_4

$1000cm^3$ of solution contains $\left(\frac{5.5\times10^{-4}\times1000}{50}\right)$ moles

Molar concentration = 0.011M

Molar concentration of H^+ = (2 × 0.011)M

= 0.022M

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

$pH = -\log(0.022)$

pH = 1.66

2. Calculate the pH obtained by addition of $20cm^3$ of 0.1M NaOH to $40cm^3$ of 0.1M HCl

Solution

Moles of Hydrochloric acid;

$1000cm^3$ of solution contain 0.1 moles of HCl

$40cm^3$ of solution contains $\left(\frac{0.1\times40}{1000}\right)$ moles = 4×10^{-4} moles

Moles of sodium hydroxide;

$1000cm^3$ of solution contain 0.1moles of NaOH

$20cm^3$ of solution contains $\left(\frac{0.1\times20}{1000}\right)$ moles = 2×10^{-3}moles

$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_20_{(l)}$

From the reaction equation, 1 mole of NaOH reacts with 1 mole of HCl

Moles of HCl that reacted = moles of sodium hydroxide, 2×10^{-3} moles

Moles of unreacted/excess HCl = $(4 \times10^{-3} - 2\times10^{-3})$ = 2×10^{-3}moles

Total volume of solution = (20 + 40) cm^3 = $60.0cm^3$

$60cm^3$ of solution that contains 2×10^{-3} moles of HCl

$1000cm^3$ of solution contains $\left(\frac{2\times10^{-3}\times1000}{60}\right)$ moles = 0.033M

$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

1 mole of HCl ionizes to produce 1 mole of H^+

$[H^+]$ = 0.0333M

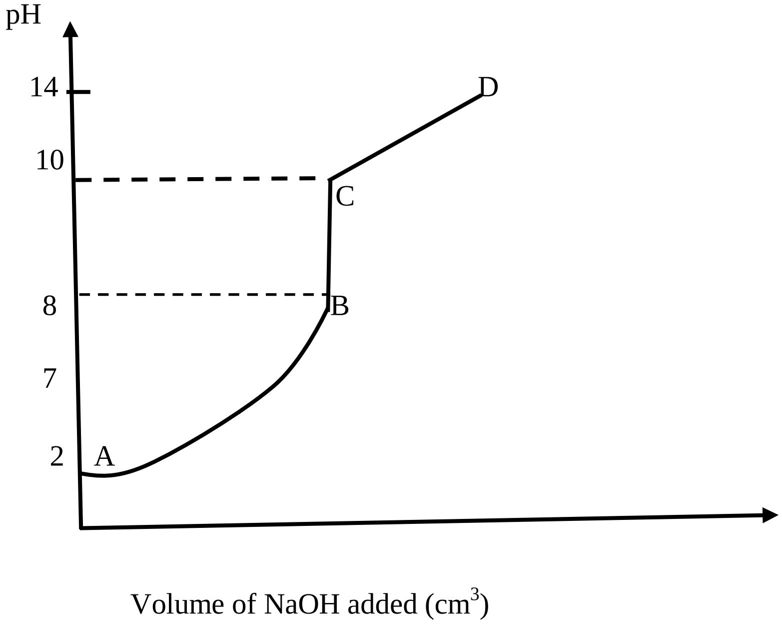
$pH = -\log[H^+]$

$pH = -\log(0.033)$

pH = 1.48

STRONG ALKALI VS WEAK ACID (CH_3COOH VS NaOH)

Titration curve of weak acid Vs strong base



- pH of the ethanoic acid is slightly higher compared to that of HCl. Ethanoic acid is a weak acid, only partly ionized in solution producing few hydrogen ions.
- Addition of NaOH, $\bar{O}$H from the NaOH reacts with H^+ of the solution, leading to an increase in pH along AB
- pH at endpoint, when equivalent amounts of NaOH and CH3COOH are present is greater than 7 ie 9
  reason
- NaOH reacts with ethanoic acid to produce sodium ethanoate
  $CH_3COOH_{(aq)} + NaOH_{(aq)} \rightarrow CH3COONa(s) + H_2O$
- Salt formed undergoes hydrolysis producing excess $\bar{O}$H ions;
  $CH_3COONa_{(aq)} \rightarrow CH_3CO\bar{O}_{(aq)} + Na^+_{(aq)}$
  $CH_3CO\bar{O}_{(aq)} + H_2O \rightleftharpoons CH_3COOH_{(aq)} + \bar{O}H_{(aq)}$
- Excess $\bar{O}$H produced rises the pH along BC from 8 – 10.
- Between CD rise in pH is due to the excess NaOH added
- **Phenolphthalein** is the most suitable indicator.

Example

1. Calculate the pH of the solution obtained when 20cm^3 of 0.1M NaOH is added to 10.0cm^3 of 0.1M CH_3COOH (Ka = 1.8×10^{-5}moldm^{-3})

   Solution

   Moles of ethanoic acid

   1000cm^3 of solution contains 0.1 mole of CH_3COOH

   100cm^3 of solution will contain $\left(\frac{0.1 \times 100}{1000}\right)$ moles = 0.01 moles

Moles of NaOH

1000cm^3 of solution contains 0.1 mole of NaOH

20cm^3 of solution will contain **0.002** moles

$CH_3COOH_{(aq)} + NaOH_{(aq)} \rightarrow CH_3COONa_{(aq)} + H_2O_{(l)}$

1 mole of acid reacts 1 mole of NaOH to produce 1 mole of salt

0.002 moles of acid reacts 0.002 moles of NaOH to produce 0.002 moles of salt

Moles of unreacted / excess acid = 0.01 – 0.002 = 0.008moles

Total volume of solution = 100 + 20 = 120cm^3

120cm^3 of solution contains 0.008 moles

1000cm^3 of solution contains $\left(\frac{0.008 \times 1000}{120}\right)$ moles

= 0.067 moles l^{-1}

Salt formed and unreacted acid form a buffer solution;

$pH = pKa + \log\frac{[salt]}{[acid]}$

[salt] = ?

120cm^3 of CH_3COONa contains 0.002moles

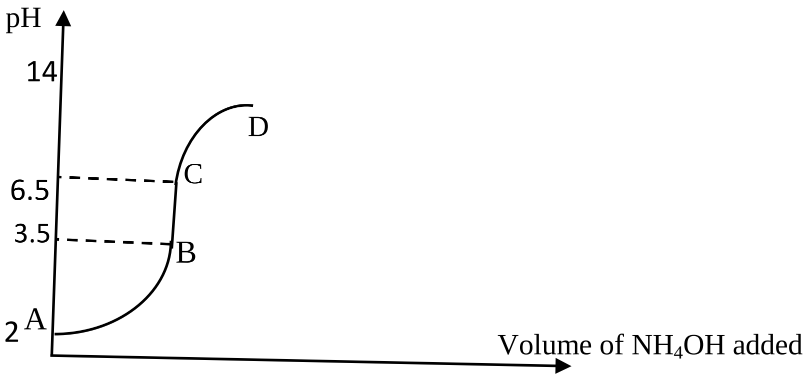
1000cm^3 of CH_3COONa contains $\left(\frac{0.002 \times 1000}{120}\right)$ moles = 0.01667M

$\Rightarrow pH = -\log(1.8 \times 10^{-5}) + \log\left[\frac{0.01667}{0.067}\right]$

= 4.14

activity UNEB: 2001 paper 2 (4b)

Titration of strong acids and weak base (HCl Vs NH_4OH)



A:

Low pH , HCl is a strong acid which fully ionizes in solution; giving a high concentration of hydrogen ions

AB;

As the NH_4OH is added;- $\bar{O}H$ ions from the base reacts with hydrogen ions in solution, pH rises

BC;

-pH rises from 3.5 to 6.5, ammonium solution reacts with HCl producing ammonium chloride.

-pH at end point is below 7;

Reason;-

$NH_4OH + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)} + H_2O_{(l)}$

-Salt formed undergoes hydrolysis in water

$NH_4Cl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$

$NH_4^+{}_{(aq)} + H_2O_{(aq)} \rightleftharpoons NH_4OH_{(aq)} + H^+{}_{(aq)}$

-Hydrolysis leaves excess of H^+ ions; hence pH less than 7
-Further rise in pH along CD is due to excess of NH_4OH is added.
-**Methyl orange** is a suitable indicator.

Example

Calculate the pH of a solution when 100cm^3 of 0.1M NH_4OH is added to 20 cm^3 of 0.1M HCl (Kb for NH_3 = 2.12×10^{-5})

Solution

Moles of NH_4OH

1000cm^3 of solution contains 0.1 moles of NaOH

100cm^3 of solution contains $\left(\frac{0.1 \times 100}{1000}\right)$ moles = 0.01 moles

Moles of HCl

1000cm^3 of solution contains 0.1 moles of HCl

20cm^3 of solution contains $\left(\frac{0.1 \times 20}{1000}\right)$ moles = 2×10^{-3}

$NH_4OH_{(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)} + H_2O_{(l)}$

From the equation of reaction above,
Excess moles of base = (0.01 – 0.002) = 0.008 moles
Total volume = (100 + 20) = 120cm^3
120 cm^3 of solution contains 0.008 moles of NH_4OH

1000 cm^3 of solution contains $\left(\frac{0.008 \times 1000}{120}\right)$ moles of NH_4OH

= 0.0167M

From $p^{OH} = p^{Kb} + \log\frac{[salt]}{[base]}$

$\Rightarrow p^{OH} = -\log(2.12 \times 10^{-5}) + \log\frac{(0.0167)}{(0.0667)}$

$p^{OH} = 4.07$

$\Rightarrow$from $p^{Kw} = p^{H} + p^{OH}$

$p^{H} = p^{Kw} - p^{OH}$

$= 14 - 4.07$

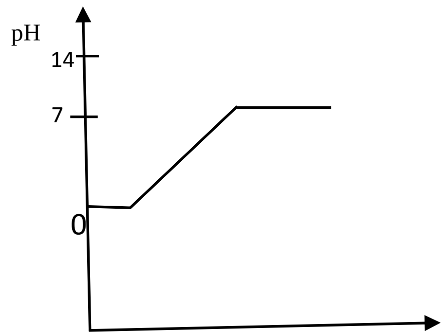
$p^{H} = 9.93$

Activity . Uneb 2012 (paper 2 , 3b)

Titrations of weak acids and weak bases eg CH_3COOH and NH_4OH

-p^H range between 6.5 – 7.5

-no suitable indicator can be used; there is no sharp change in pH art any point



Volumeof NH_4OHadded (cm^3)

SOLUBILITY PRODUCT

Consider a sparingly soluble salt silver bromate , $AgBrO_3$

-$AgBrO_3$ added to water, a saturated solution(containing both the ions & undissolved solute) is formed

-Equilibrium is established between ions and excess undissolved solute , $AgBrO_3$

$$AgBrO_{3(s)} \rightleftharpoons Ag^+_{(aq)} + BrO_3^-{}_{(aq)}$$

Excess
undissolved
Solute

By law of mass action, $Kc = \frac{[Ag^+(aq)][BrO_3^-(aq)]}{[AgBrO3(s)]}$

$$Kc\,[AgBrO3] = [Ag^+][BrO_3^-]$$

But; $[AgBrO3]$= constant

$Kc \times [AgBrO3]$= **Ksp** (**solubility product**)

Therefore, $Ksp = [Ag^+(aq)][BrO_3^-(aq)]$

Generally for a saturated solution of a sparingly soluble salt

$A_xBy_{(s)} \rightleftharpoons xA^{+y}{}_{(aq)} + yB\_x_{(aq)}$

$Ksp = [A^{+y}]^x[B^{-x}]^y$

Definition

-Solubility product (Ksp) is the ***product of the molar concentration of ions raised to their powers of stoichiometric coefficients in a saturated solution of a sparingly soluble salt of an ionic compound of a given temperature;***

ACTIVITY.

Write an expression for the solubility product of;

(i). Bi_2S_3 (ii). AgCl (iii). PbI_2 (iv). $Ca(OH)_2$

Limitations of solubility product/condtions of solubility product

-Valid for only saturated solutions

-Only valid at constant temperature

-Only applied for sparingly soluble salts

Example

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

Solution:

Relative formula mass of $Ca(OH)_2$ = 40 + (16 × 2) + (1×2) = 74

1 mole of $Ca(OH)_2$ weighs 74g

X mole of $Ca(OH)_2$ will weigh 2.78

$\therefore$ Molarity = $\frac{2.78}{74}$ = $0.038dm^{-3}$

$[Ca(OH)_2]$ = $0.038dm^{-3}$

$Ca(OH)_{2\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2\bar{O}H_{(aq)}$

$[Ca^{2+}] = 0.038dm^{-3}$

$[\bar{O}H] = 2 \times 0.038 = 0.076moldm^{-3}$

$Ksp = [Ca^{2+}][\bar{O}H]^2$

$= 0.038 \times (0.076)^2$

$Ksp = 2.19 \times 10^{-4}mol^3dm^{-9}$

2. The solubility product of silver Carbonate at $20^{0}C$ is 8×10^{-2} mol^3dm^{-9}. What is the solubility at this temperature?

Solution

From, $Ag_2CO_{3(s)} \rightleftharpoons Ag^{+}_{(aq)} + CO^{2-}_{3\,(aq)}$

If the solubility of $Ag_2CO_{3(s)}$ is S $moldm^{-3}$

$[Ag^+]$ = 2S $moldm^{-3}$

$[CO^{2-}_3]$ = S $moldm^{-3}$

$Ksp = [Ag^+][CO^{2-}_3]$

$8 \times 10^{-2} = (2S)^2S$

$8 \times 10^{-2} = 4S^3$

Solubility = $0.27moldm^{-3}$

Activity:

1. Calculate the solubility of silver ethanedioate ($Ag_2C_2O_4$) in water. (Ksp of $Ag_2C_2O_4 = 5\times 10^{-12}$ $mol^{-3}dm^{-9}$)

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

3. The solubility product of calcium Phosphate at $25^{0}C$ is $6 \times 10^{-29}mol^5dm^{-15}$. Calculate the solubility of Calcium phosphate in gdm^{-3} at $25^{0}C$.

FACTORS AFFECTING THE SOLUBILITY OF SPARINGLY SOLUBLE SALT.

(i) Common ion effect:

-Is the ***precipitation of a sparingly soluble ionic compound from a saturated solution by addition of another soluble compound containing a similar ion***

Consider a saturated solution of $PbSO_4$;

$PbSO_4 \rightleftharpoons Pb^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

Addition of $Pb(NO_3)_2$ solution;

-More Pb^{2+} ions, a common ion is produced; increasing the concentration of Pb^{2+} in the equilibrium.

-To restore the equilibrium, excess Pb^{2+} from Pb $(NO_3)_2$ reacts with SO_4^{2-} to precipitate $PbSO_4$

-This decreases solubility of $PbSO_4$

Example:

1. Calcium iodate, $Ca(IO_3)_2$ is sparingly soluble in water. Write an,

(a) (i) equation for the solubility of Ca $(IO_3)_2$

(ii) expression for the solubility product Ksp of $Ca(IO_3)_2$

(b) If the Ksp of $Ca(IO_3)_2$ at 25^0C is 1.95×10^{-4} $moldm^{-3}$. Calculate the solubility in $moldm^{-3}$. Calculate the solubility in $moldm^{-3}$ at 25^0C.

i. In water

ii. 0.1M solution of $NaIO_3$.

(c) Comment on your answer in (b) above **UNEB 2006(1) No. 17**

Solution

1 (a)(i) $Ca(IO_3)2_{(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2IO_3^-{}_{(aq)}$

(ii) $Ksp = [Ca^{2+}][IO_3^-]^2$

(b) (i). From , $Ca(IO_3)_{2(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2IO_3^-{}_{(aq)}$

Let the solubility of $Ca(IO_3)_2$ be m $moldm^{-3}$

$\Longrightarrow [Ca^{2+}] = m \quad [IO_3^-] = 2m$

From $Ksp = [Ca^{2+}][IO_3^-]^2$

$\Longrightarrow 1.9 \times 10^{-4} = (m)(2m)^2$

$4m^3 = 1.9 \times 10^{-4}$

$m = \sqrt[3]{\frac{.9 \times 10^{-4}}{4}}$

$= 0.036moldm^{-3}$

Solubility of Ca $(IO_3)_2$ is $0.036moldm^{-3}$ in water

(ii) 0.1M of $NaIO_3$

$NaIO_{3(aq)} \rightleftharpoons Na^+{}_{(aq)} + IO_3^-{}_{(aq)}$

Let the new solubility of $Ca(IO_3)_2$ in iodate solution be S' $moldm^{-3}$

$Ca(IO_3)_{2(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2IO_3^-$

Solubility of Ca^{2+} = S' $moldm^{-3}$

Solubility of IO_3^- = (2S' + 0.1)

But S' ⋘⋘ 0.1, (2S' + 0.1) ≅ 0.1

$Ksp = [Ca^{2+}]\ [IO_3^-]$

$1.95\times10^{-4} = S' (0.1)^2$

Solubility of $Ca(IO_3)_2$ in iodate solution $S' = 0.0195 moldm^{-3}$

(c.) Comment

− *Solubibilty of $Ca(IO_3)_2$ in $NaIO_3$ is lower than that in water; because in $NaIO_3$ concentration of IO_3^- is higher; therefore IO_3^- react with Ca^{2+} to precipitate out $Ca(IO_3)_2$.*

Activities:

UACE 2000(1) no 12, 2005(1) no 17, 2004(1) no 17, 2003(1) no 17, 2001(1) no 16(a, b(i).

ii) **Complex ion formation:**

-Increases solubility of a sparingly soluble salt i.e.

Consider solubility of AgCl in water,

$AgCl_{(s)} + \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

- Addition of ammonia solution, ammonia reacts with silver ions, forming diamine silver ion complex .

  $Ag^+_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [Ag(NH_3)_2]^+$
- Concentration of Ag^+ decreases;
- to restore equilibrium, AgCl solid ionizes to produce more Ag^+ ions, increasing the solubility.

Example.

a) State how the solubility of Ag_2SO_4 is affected if the following substances were added;

   i) Na_2SO_4

   ii) NH_4OH

b) Explain your answer in (a) **(UACE, 2001(1) no.16 (b)**

Solution

a) (i). solubility would decrease
   (ii) Solubility would increase

b) a(i)
   - Na_2SO_4 is a strong electrolyte; therefore strongly ionizes in aqueous solution to form a higher concentration of SO_4^{2-} ions
   - Ag^+ react with excess SO_4^{2-} ions ; forming solid silver sulphate, Ag_2SO_4; hence decreasing solubility.

   (ii) Ammonia react with Ag^+ to form a complex; decreasing the concentration of Ag^+ in solution; therefore more silver sulphate dissolves to restore the equilibrium, hence increasing solubility of the salt.

APPLICATION OF COMMON ION EFFECT

i. **Purification of common salt: (NaCl)**

-NaCl contains small quantities of $MgCl_2$ and $CaCl_2$ as impurities.

-This causes it to be deliquesecent (absorb water from the atmosphere and appear damp)

-Pure NaCl is obtained by ***passing HCl gas into a saturated solution of impure NaCl (Addition of HCl gas provides Cl^- which precipitate only pure NaCl)***

ii. **Salting out of soap:**

Saturated solution of soap, sodium stearate (Nast) contains the following ions;

$Nast_{(s)} \rightleftharpoons Na^+_{(aq)} + St^-_{(aq)}$

During saponification (soap making), concentrated solution of NaCl is added

More Na^+ are produced, excess Na^+ react with St^- to precipitate soap

$Na^+_{(aq)} + St^-_{(aq)} \rightarrow NaSt_{(s)}$

APPLICATIONS OF SOLUBILITY PRODUCT ON QUALITATIVE ANALYSIS

-Used in predicting precipitation of salts eg sulphides, hydroxides, chlorides, etc

NB: ***For saturated solution, ionic product is equal to solubility Product; therefore can be used to predict whether or not precipitation occurs.***

Therefore if,

i. Ionic product is greater than the solubility product, solution is **supersaturated,** precipitation will occur
ii. If ionic product is less than the solubility product , solution is **unsaturated**, precipitation will occur not occur.

Example:

1. Predict whether or not precipitation occurs when $0.001 moldm^{-3}$ solution of Ca^{2+} is mixed with an equal volume of a $0.001 moldm^{-3}$ solution of SO_4^{2-} at 25^OC. (Ksp of $CaSO_4 = 2\times10^{-5} mol^2dm^{-6}$ at 25^OC). Show your working.

Solution

-Mixing equal volumes of the two ions, molar concentration of the ions are halved, because each solution is diluted by mixing with the other.

$new[SO_4^{2-}] = \frac{0.001}{2} = 0.0005 moldm^{-3}$

$new\ [Ca^{2+}] = \frac{0.001}{2} = 0.0005 moldm^{-3}$

Ionic product immediately after mixing

Ionic product $= [Ca^{2+}][SO_4^{2-}]$

$= 0.0005 \times 0.0005$

$= 2.5 \times 10^{-7} mol^2dm^{-6}$

Ionic product, $2.5 \times 10^{-7}\ mol^2dm^{-6}$ is less than the solubility product; no precipitation occurs.

2. $20cm^3$ of 0.01M Barium chloride solution and $20cm^3$ of 0.005M solution of Sodium Sulphate are mixed at 25^OC. Determine whether or not precipitation occurs(Ksp of Barium sulphate is $1x10^{-20} mol^2dm^{-6}$).

Solution

$BaCl_{2(aq)} \rightleftharpoons Ba^{2+}_{(aq)} + 2Cl^-_{(aq)}$

0.01 0.01

$Na_2SO_{4)} \rightleftharpoons 2Na^+ + SO_4^{2-}$

0.005 0.005

Mixing 2 equal volumes, the concentration of the ions are halved,

$[Ba^{2+}] = \frac{0.01}{2} = 5\times10^{-3}moldm^{-3}$

$[SO_4^{2-}] = \frac{0.005}{2} = 2.5\times 10^{-3}moldm^{-3}$

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

$= (2.5\times 10^{-3})(5\times10^{-3}) = 1.25\times10^{-5}mol^2dm^{-6}$

Ionic product, $1.25\times10^{-5}mol^2dm^{-6}$ is greater than the solubility constant value, there precipitation will occur.

ACTIVITY

1. A solution containing Ag^+ was added to a solution containing 0.005M Chromate ions and 0.005M Cl^-. State which of the salts, AgCl or Ag_2CrO_4 was precipitated first. Give a reason for your answer.
2. A solution is 0.01M in cuprous ion, (Cu^+) and 0.001M in lead (II) ion. Cl^- is slowly added, will lead (II) Chloride (Ksp = $1.6\times10^{-5}mol^3/l^2$) or CuCl (Ksp = $3.2\times 10^{-7}mol^3/l^2$) precipitate first? Show your working.

Experimental determination of solubility product

Solubility product can be determined directly by;

- Direct titration or Titrimetric method
- Ion exchange
- Conductivity measurements

a) Direct titration

i. $Ca(OH)_2$

- A Known volume of water is placed in a bottle and a known mass of $Ca(OH)_2$ is added to it.
- The bottle is corked, shaken for about 35 minutes,at fixed temperature; allowed to settle for equilibrium to be attained.
- Know volumes of clear solution are then pippeted into a conical flask, titrated with a standard solution of HCl using methyl orange indicator.
- Knowing the number of molecules of HCl, number of moles and concentration of $\bar{O}H$ can be calculated.

  $Ca(OH)_2 + 2HCl_{(aq)} \rightarrow CaCl_{2(s)}) + 2H_2O_{(l)}$
- Concentration of Ca^{2+} can be determined from

  $[[Ca^{2+}] = ½[\bar{O}H]$ from mole ratio

  $\Rightarrow Ksp = [Ca^{2+}][\bar{O}H]^2$

ii. Potassium Iodate in water

- A known volume of distilled water is placed in a bottle and a known mass of Potassium iodate is added.
- The bottle is stoppered, shaken for a period of time, at fixed temperature, allowed to settle to reach equilibrium.
- After equilibrium has been attained, known volumes of the clear saturated solution are pipetted into a conical flask containing potassium iodide with dilute H_2SO_4

  $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_{2\ (aq)} + 3H_2O$
- Iodine liberated is then titrated with standard thiosulphate solution using starch as an indicator

$2S_2O_3^{2-}{}_{(aq)} + I_{2\,(g)} \rightarrow S_4O_6^{2-}{}_{(aq)} + 2I^-{}_{(aq)}$

- Titrate until when the solution turns blue, repeat and note the average volume of the thiosulphate solution used.
- Knowing the concentration of the thiosulphate, mole of Iodine liberated can be determined, from which concentration of iodate ions can be obtained.

$[IO_3^-] = [K^+]$

$Ksp = [IO_3^-]\,[K^+]$