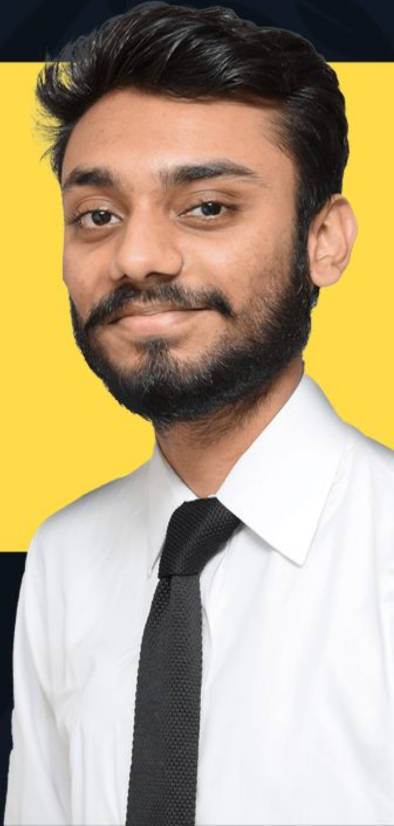
PROSPERITY ACADEMY

A2 CHEMISTRY 9701

Crash Course

RUHAB IQBAL



EQUILIBRIA

COMPLETE NOTES

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Bronsted Lowry theory of acids and bases:-

- An acid is a H^+ donor (H^+ is only a proton)
- A base is a H^+ acceptor

Conjugate acid - base pairs:-

$$\underset{\text{acid-I}}{HA} + \underset{\text{base-II}}{H_2O} \longrightarrow \underset{\text{acid-II}}{H_3O^+} + \underset{\text{base-I}}{A^-}$$

conjugate acid-base pairs

conjugate acid-base pairs

- Every base has a conjugate acid
- Every acid has a conjugat base

formed by transfer of only 1 H^+

- H_2O behaved as base, HA behaved as acid.
- A^- is the conjugate base of HA
- H_3O^+ is the conjugate acid of H_2O

a) $\underset{\text{acid-I}}{HCl} + \underset{\text{base-II}}{H_2O} \longrightarrow \underset{\text{acid-II}}{H_3O^+} + \underset{\text{base-I}}{Cl^-}$

b) $\underset{\text{acid-I}}{HNO_3} + \underset{\text{base-II}}{H_2O} \longrightarrow \underset{\text{acid-II}}{H_3O^+} + \underset{\text{base-I}}{NO_3^-}$

c) $\underset{\text{acid-I}}{CH_3COOH} + \underset{\text{base-II}}{OH^-} \longrightarrow \underset{\text{acid-II}}{H_2O} + \underset{\text{base-I}}{CH_3COO^-}$

d) $\underset{\text{acid-I}}{CH_3COOH} + \underset{\text{base-II}}{NH_3} \longrightarrow \underset{\text{acid-II}}{NH_4^+} + \underset{\text{base-I}}{CH_3COO^-}$

e) $\underset{\text{acid-I}}{HNO_3} + \underset{\text{base-II}}{OH^-} \longrightarrow \underset{\text{acid-II}}{H_2O} + \underset{\text{base-I}}{NO_3^-}$

f) $\underset{\text{acid-I}}{H_2SO_4} + \underset{\text{base-II}}{OH^-} \longrightarrow \underset{\text{base-I}}{HSO_4^-} + \underset{\text{acid-II}}{H_2O}$

pH:-

pH is defined as:- $\boxed{pH = -\log_{10}[H^+]}$ where $[H^+]$ is the concentration of H^+ ions in solution

- pH is lower for a stronger acid and higher for a weak acid.

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

Calculating the pH of strong acids

strong acids ↳ dissociate fully

a) 0.1 mol dm^{-3} of HCl (monoprotic)

disociates fully so

$[HCl] = [H^+]$

$pH = -\log_{10}[0.1]$

$= 1$

b) 0.5 mol dm^{-3} of HCl (monoprotic)

disociates fully so

$[HCl] = [H^+]$

$pH = -\log_{10}(0.5)$

$= 0.3$

c) 0.1 mol dm^{-3} of H_2SO_4 (diprotic)

disociates fully so

$2[H_2SO_4] = [H^+]$

$pH = -\log_{10}[0.2]$

$= 0.7$

- This method is suitable for strong acids as they disociate completely

Ionic Product of water :-

- Water ionises slightly :- $H_2O \rightleftharpoons [H^+][OH^-]$

- $K_c = \dfrac{[H^+]_{eqm}[OH^-]_{eqm}}{[H_2O]_{eqm}}$ $\Longrightarrow$ K_w (ionic product of water) $= [H^+][OH^-]$

$[H_2O]_{eqm}$ → too large in comparison to $[H^+]$ and $[OH^-]$ so we take this as constant and remove it

Calculating K_w at 25°C :-

pH of distilled water = 7

$[H^+] = 10^{-7}$ → as water is neutral $[H^+] = [OH^-]$ so $[OH^-] = 10^{-7}$

$K_w = [H^+][OH^-] = 10^{-7} \times 10^{-7} \Rightarrow \boxed{K_w = 10^{-14} \text{ at } 25°C}$ Remember this!

$\boxed{K_w \text{ is constant for a constant temp}}$

Calculating pH of strong alkalis :-

a) 0.025 mol dm^{-3} of NaOH

strong alkali so dissociates fully

$[NaOH] = [OH^-]$

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

$10^{-14} = [H^+][0.025]$

$[H^+] = 4 \times 10^{-13}$

$pH = -\log_{10}[H^+] = -\log_{10}[4 \times 10^{-13}] = 12.4$

b) 0.025 mol dm^{-3} of $Ba(OH)_2$

strong alkali so dissociates fully

$2[Ba(OH)_2] = [OH^-]$

$10^{-14} = [H^+][2 \times 0.025]$

$[H^+] = 2 \times 10^{-13}$

$pH = -\log_{10}[2 \times 10^{-13}]$

$pH = 12.7$

Neutrality:-

- Neutrality is achieved when $[H^+] = [OH^-]$
- $pH = 7$ is neutral only for $25°C$

At $100°C$, $K_w = 51 \times 10^{-14}$ of pure water. Calculate pH of water at $100°C$.

$K_w = [H^+][OH^-]$. As neutral so $[H^+] = [OH^-]$ so $K_w = [H^+]^2 \Rightarrow \sqrt{51 \times 10^{-14}} = [H^+]$

$pH = -\log_{10}[\sqrt{51 \times 10^{-14}}] = 6.15$ (At $100°C$, pH of neutrality is 6.15!)

Weak acids and Ka:-

- Weak acids only partially ionise :- $HA \rightleftharpoons H^+ + A^-$ where $[H^+] = [A^-]$ if only weak acid present in solution
- $\boxed{K_a = \frac{[H^+][A^-]}{[HA]}}$ - $\boxed{pK_a = -\log_{10} K_a}$

pKa is just like pH
- lower pKa means strong acid
- higher pKa means weak acid

- If we have only a weak acid in solution, then $[H^+] = [A^-]$ so,

$$K_a = \frac{[H^+][H^+]}{[HA]} \Rightarrow K_a = \frac{[H^+]^2}{[HA]} \Rightarrow [H^+] = \sqrt{[HA] \times K_a} \Rightarrow pH = -\log_{10}\left(\sqrt{[HA] \times K_a}\right)$$

Calculating pH of weak acids:-

a) 0.1 mol dm^{-3} of ethanoic acid, $K_a = 1.7 \times 10^{-5}$

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

$$[H^+]^2 = K_a \times [HA] \Rightarrow [H^+] = \sqrt{(1.7 \times 10^{-5}) \times (0.1)}$$

$$[H^+] = 1.3038 \times 10^{-3}$$

$$pH = -\log_{10}[1.3038 \times 10^{-3}] = 2.88 \simeq 2.9$$

b) Calculate K_a and pK_a of 0.15 mol dm^{-3} of propanoic acid (pH = 2.85)

$$[H^+] = 10^{-2.85} = 1.412 \times 10^{-3} \text{ mol dm}^{-3}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2}{[HA]} = \frac{(1.412 \times 10^{-3})^2}{0.15}$$

$$K_a = 1.33 \times 10^{-5}$$

$$pK_a = -\log_{10}(1.33 \times 10^{-5}) = 4.876$$

$K_a = 1.3 \times 10^{-5}$ $\qquad$ $pK_a = 4.9$

Strengths of Carboxylic acids:-

CH_3CO_2H $\qquad$ $CH_3CH_2CO_2H$

$pK_a = 4.8$ $\qquad$ $pK_a = 4.9$

$\xrightarrow{\text{gets weaker}}$

- Alkyl chain pushes electron density towards OH bond making it stronger and difficult to break

Acid 1	Acid 2	Acid 3
$CH_3CH_2CO_2H$	$CH_3CHClCO_2H$	$CH_2ClCH_2CO_2H$
$pK_a = 4.9$	$pK_a = 2.8$	$pK_a = 4.0$

- Acid 2 is stronger than Acid 1 as chlorine pulls electron density from O-H bond making it weaker and easier to break
- Acid 3 is weaker than Acid 2 as the Cl is farther away from O-H bond so it pulls electron density less strongly so the O-H bond does not break easily

5 Dicarboxylic acids dissociate in stages.

$$HO_2C(CH_2)_nCO_2H \overset{\text{stage 1}}{\rightleftharpoons} HO_2C(CH_2)_nCO_2^- + H^+ \overset{\text{stage 2}}{\rightleftharpoons} {}^-O_2C(CH_2)_nCO_2^- + 2H^+$$

(a) The pK_a values for stage 1 and stage 2 for some dicarboxylic acids are listed below.

n in $HO_2C(CH_2)_nCO_2H$	$pK_a(1)$ for stage 1	$pK_a(2)$ for stage 2
1	2.83	5.69
2	4.16	5.61
3	4.31	5.41

For comparison, the pK_a of ethanoic acid, CH_3CO_2H, is 4.76.

(i) State the mathematical relationship between pK_a and the acid dissociation constant K_a.

$pKa = -\log_{10}(Ka)$ [1]

(ii) With reference to the table above, suggest why the $pK_a(1)$ values

- are all smaller than the pK_a of ethanoic acid,

The CO_2H group pulls electron density towards it making the O-H bond weaker and easier to dissociate

- become larger as n increases.

The CO_2H group gets further away and so pulls e^- density less strongly [3]

(iii) Suggest why all the $pK_a(2)$ values in the table above are larger than the pK_a of ethanoic acid.

The removal of H^+ from an anion which attracts it due to its negative charge is more difficult [1]

(b) The monosodium salts of edible dicarboxylic acids are added to some foodstuffs as buffers.

(i) Explain what is meant by the term *buffer solution*.

A solution that maintains an almost constant pH on addition of small amounts of acid or alkali [2]

(ii) Write two equations to show how monosodium butanedioate, $HO_2CCH_2CH_2CO_2Na$, acts as a buffer.

$H^+ + HO_2CCH_2CH_2CO_2^- \longrightarrow HO_2CCH_2CH_2CO_2H$

$OH^- + HO_2CCH_2CH_2CO_2^- \longrightarrow H_2O + {}^-O_2CCH_2CH_2CO_2^-$ [2]

3 (a) Hydrogen cyanide, HCN, is a weak acid in aqueous solution.

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq) \qquad K_a = 6.2 \times 10^{-10}\,mol\,dm^{-3}$$

(i) Calculate the pH of 0.10 $mol\,dm^{-3}$ HCN(aq).

$pH = -\log_{10}[H^+] \longrightarrow pH = -\log_{10}[7.874\times10^{-6}]$

$= 5.1$

$Ka = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2}{[HA]}$

$\sqrt{(6.2\times10^{-10} \times 0.10)} = [H^+]$

$[H^+] = 7.874\times10^{-6}$

pH = 5.1 [2]

(c) When sodium oxide reacts with water an alkaline solution is obtained.

(i) Explain why the solution obtained is alkaline. You should use the Brønsted-Lowry theory of acids and bases in your answer.

$Na_2O + H_2O \longrightarrow 2Na^+ + 2OH^-$

The OH^- ions formed can accept H^+ and form H_2O and therefore function as Brønsted Lowry base [2]

(ii) Calculate the pH of the solution obtained when 3.10 g of sodium oxide are added to 400 cm^3 of water.

n of $Na_2O = \frac{3.1}{2(23)+16} = 0.05$ mol

n of $OH^- = 0.10$ mol

c of $OH^- = \frac{n}{V} = \frac{0.1}{400\times10^{-3}} = 0.25\ mol\,dm^{-3}$

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

$10^{-14} = [H^+][0.25]$

$[H^+] = 4\times10^{-14}$

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

$= -\log_{10}[4\times10^{-14}] = 13.4$

pH = 13.4 [3]

Buffer Solutions:- A solution which maintains an almost constant pH on the addition of small amounts of acid or alkali.

Buffer solutions can be made in 2 ways:-

1) A weak acid + its salt (this contains the acid's conjugate base)

for e.g. $CH_3COOH + CH_3COONa$ (Acid: CH_3COOH, conjugate base: CH_3COO^-)

- CH_3COOH partially dissociates - CH_3COONa completely dissociates
- An equilibrium is established $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

• if small amount of acid is added:-

$$H^+ + CH_3COO^- \longrightarrow CH_3COOH$$

• if small amount of alkali is added:-

$$OH^- + CH_3COOH \longrightarrow CH_3COO^- + H_2O$$

2) A weak base + its salt (this contains the base's conjugate acid)

for e.g. $NH_3 + NH_4Cl$ (Acid: NH_4^+, conjugate base: NH_3)

Equilibrium is established:- $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

• if small amounts of acid is added:-

$$H^+ + NH_3 \longrightarrow NH_4^+$$

• if small amounts of alkali is added:-

$$OH^- + NH_4^+ \longrightarrow NH_3 + H_2O$$

The Buffering of blood:-

This is done by Carbonic Acid i.e H_2CO_3, its conjugate base i.e HCO_3^- and CO_2 and a bit of help from the respiratory system.

Equilibrium : $H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$

or you can also write like this :- $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

On addition of small amounts of acid (lactic acid being produced during exercise)

$H^+ + HCO_3^- \longrightarrow H_2CO_3 \longrightarrow CO_2 + H_2O$

↳ not stable so dissociates to

equilibrium shifts to left hand side (acid is not removed!)

On addition of small amounts of alkali:

$OH^- + H_2CO_3 \rightleftharpoons HCO_3^- + H_2O$

if this is too much

H_2CO_3 is unstable and dissociates to $CO_2 + H_2O$ and forms equilibrium :- $H_2CO_3 \rightleftharpoons \underline{CO_2} + H_2O$

if CO_2 is not removed, then it will build up too much and equilibrium will shift to left hand side

CO_2 is removed by respiratory system

Calculating pH of buffer solution :-

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

for buffers $[H^+] \neq [A^-]$ as acid partially dissociates while salt completely dissociates

$$\Rightarrow [H^+] = \frac{K_a \times [HA]}{[A^-]} \Rightarrow pH = -\log_{10}[H^+]$$

* $[H^+] = \sqrt{K_a \times [HA]}$ only applies if weak acid is used! DONOT USE FOR BUFFERS!

* If equal concentrations of weak acid and its salt is mixed then:-

- $[HA] = A^-$ → produced by complete dissociation of salt

  $[HA]$ ↓ partially dissociates which is negligible

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

5 The phosphate buffer system operates in biological cells. The buffer contains dihydrogen phosphate, $H_2PO_4^-$, which acts as a weak acid.

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$$

(a) Write an expression for the K_a of $H_2PO_4^-$.

$$K_a = \frac{[HPO_4^{2-}][H^+]}{[H_2PO_4^-]}$$

[1]

(b) (i) Explain what is meant by the term *buffer solution*.

Done already

[2]

(ii) Write **two** equations to show how a solution containing a mixture of $H_2PO_4^-$ and HPO_4^{2-} acts as a buffer.

$H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O$

$H^+ + HPO_4^{2-} \longrightarrow H_2PO_4^-$

[2]

(c) The pH in many living cells is 7.40.

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \qquad K_a = 6.31 \times 10^{-8}\,mol\,dm^{-3}$$

Calculate the value of $[HPO_4^{2-}]/[H_2PO_4^-]$ needed to give a pH of 7.40 in the cells.

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

$[H^+] = 10^{-7.4} = 3.981 \times 10^{-8}$

$K_a = \frac{[H^+][A^-]}{[HA]} \Rightarrow \frac{6.31\times10^{-8}}{3.981\times10^{-8}} = \frac{[A^-]}{[HA]} = 1.585$

$[HPO_4^{2-}]/[H_2PO_4^-]$ = 1.59 [3]

(d) (i) The $H_2PO_4^-$ ion can also act as a base.

Write an equation to show $H_2PO_4^-$ acting as a base.

$H_2PO_4^- + H^+ \longrightarrow H_3PO_4$ [1]

(ii) The HPO_4^{2-} ion can also act as an acid.

Write an equation to show HPO_4^{2-} acting as an acid.

$HPO_4^{2-} + OH^- \rightarrow H_2O + PO_4^{3-}$ [1]

(b) (i) Isocyanic acid is a weak acid. $[H^+] = [A^-]$

$$HNCO \rightleftharpoons H^+ + NCO^- \qquad K_a = 1.2 \times 10^{-4}\,mol\,dm^{-3}$$

Calculate the pH of a $0.10\,mol\,dm^{-3}$ solution of isocyanic acid.

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

$K_a \times [HA] = [H^+]^2$

$\sqrt{1.2\times10^{-4} \times 0.10} = [H^+]$

$pH = -\log_{10}\left(\sqrt{1.2\times10^{-4} \times 0.10}\right)$

$pH = 2.46$

pH = 2.5 [2]

(ii) Sodium cyanate, NaNCO, is used in the production of isocyanic acid.
Sodium cyanate is prepared commercially by reacting urea, $(NH_2)_2CO$, with sodium carbonate. Other products in this reaction are carbon dioxide, ammonia and steam.

Write an equation for the production of NaNCO by this method.

$2(NH_2)_2CO_{(s)} + Na_2CO_{3(s)} \longrightarrow 2NaNCO_{(s)} + CO_{2(g)} + 2NH_{3(g)} + H_2O_{(g)}$ [1]

Formation of buffer solution

(c) Barium hydroxide, $Ba(OH)_2$, is completely ionised in aqueous solutions.
During the addition of $30.0\,cm^3$ of $0.100\,mol\,dm^{-3}$ $Ba(OH)_2$ to $20.0\,cm^3$ of $0.100\,mol\,dm^{-3}$ isocyanic acid, the pH was measured.

$Ba(OH)_2 : HNCO$
$1 : 2$

(i) Calculate the $[OH^-]$ at the end of the addition.

n of HCNO = $c \times V = 0.1 \times 20\times10^{-3} = 2\times10^{-3}$

n of $Ba(OH)_2$ neutralised = 1×10^{-3}

n of $Ba(OH)_2$ added originally = $c \times V = 0.1 \times 30\times10^{-3} = 3\times10^{-3}$

n of $Ba(OH)_2$ remaining = $(3-1)\times10^{-3} = 2\times10^{-3}$

n of OH^- remaining = 4×10^{-3}

$[OH^-] = \frac{4\times10^{-3}}{50\times10^{-3}} = 0.08$

$[OH^-]$ = 0.08 $mol\,dm^{-3}$ [2]

(ii) Use your value in **(i)** to calculate $[H^+]$ and the pH of the solution at the end of the addition.

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

$10^{-14} = [H^+][0.08]$

$[H^+] = 1.25\times10^{-13}$

$pH = -\log_{10}(1.25\times10^{-13}) = 12.9$

final $[H^+]$ = 1.25×10^{-13} $mol\,dm^{-3}$

final pH = 12.9

[2]

(b) (i) Write the expression for K_w, the ionic product of water.

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

[1]

(ii) The numerical value of K_w increases with increasing temperature. $H_2O \rightleftharpoons [H^+][OH^-]$

Place a tick (✓) in the appropriate column in each row to show the effect of increasing the temperature of water on the pH and on the ratio $[H^+]:[OH^-]$.

effect of increasing temperature of water	decrease	stay the same	increase
pH	✓		
ratio $[H^+]:[OH^-]$		✓	

[2]

(c) An aqueous solution of sodium hydroxide has a pH of 13.25 at 298 K.

Calculate the concentration of this sodium hydroxide solution.

$[H^+] = 10^{-13.25}$

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

$10^{-14} = [10^{-13.25}][OH^-]$

$[OH^-] = 0.1778$

concentration = 0.178 mol dm^{-3} [2]

(e) The K_a for ethanoic acid is 1.75×10^{-5} mol dm^{-3} at 298 K.

(i) When ethanoic acid is dissolved in water, an equilibrium mixture containing two acid-base pairs is formed.

Write an equation for this equilibrium. In the boxes label each species acidic or basic to show its behaviour in this equilibrium.

CH_3CO_2H	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$CH_3CO_2^-$
acid - I		base - II		acid - II		base - I

[2]

(ii) A buffer solution was prepared by adding 30.0 cm^3 of 0.25 mol dm^{-3} ethanoic acid, an excess, to 20.0 cm^3 of 0.15 mol dm^{-3} sodium hydroxide.

Calculate the pH of the buffer solution formed at 298 K. Give your answer to **one** decimal place.

n of NaOH = c×V = $0.15 \times 20\times10^{-3}$ = 3×10^{-3} mol = $[CH_3CO_2Na] = [CH_3CO_2^-] = [A^-]$

n of CH_3CO_2H = c×V = $0.25 \times 30\times10^{-3} = 7.5\times10^{-3}$

n of CH_3CO_2H remaining = $(7.5 - 3)\times10^{-3} = 4.5\times10^{-3} = [HA]$

$K_a = \frac{[H^+][A^-]}{[HA]} \Rightarrow 1.75\times10^{-5} = \frac{[H^+][3\times10^{-3}]}{[4.5\times10^{-3}]}$

$\Rightarrow [H^+] = 2.625\times10^{-5}$

$pH = -\log_{10}[2.625\times10^{-5}]$

$= 4.58$

pH = 4.6 [4]

3 (a) (i) Use mathematical expressions to define the following terms.

- pH = $-\log_{10}[H^+]$
- K_a for a weak acid, HA = $K_a = \frac{[H^+]^2}{[HA]}$

[2]

(ii) Write equations to show how a buffer solution consisting of a mixture of HA(aq) and NaA(aq) controls pH when an acid or an alkali is added.

$HA + OH^- \rightarrow A^- + H_2O$

$A^- + H^+ \rightarrow HA$

[2]

(b) When chlorine dissolves in water the following reaction occurs.

$$Cl_2(g) + H_2O(l) \rightarrow HClO(aq) + H^+(aq) + Cl^-(aq)$$

When solutions of chlorine are used for water purification, the pH of the solution of chlorine is kept near to pH 7 by the addition of a base.

Chlorine is dissolved in water to produce 1000 cm^3 (volume) of a solution containing 0.170 mol of HClO and 0.170 mol of HCl.

A buffer solution is then prepared by adding 0.200 mol of NaOH(s) to this solution. The NaOH reacts initially with the HCl.

Calculate the pH of the buffer solution.

[HClO is a weak acid with K_a = 2.9 × 10^{-8} mol dm^{-3}.]

n of HCl = 0.170

$NaOH + HClO \rightarrow Na^+ClO^- + H_2O$

n of NaOH = 0.200

n of NaOH remaing after reaction with HCl = 0.200 − 0.170 = 0.03 → $ClO^- = A^-$

n of HClO remaining after reaction with 0.03 mol of NaOH = 0.170 − 0.03 = 0.14

HA ← HClO

$K_a = \frac{[H^+][A^-]}{[HA]} \Rightarrow 2.9\times10^{-8} = \frac{[H^+][0.03]}{0.14}$

$[H^+] = 1.3533\times10^{-7}$

$pH = -\log_{10}(1.3533\times10^{-7})$
$= 6.87$

pH = 6.87 [3]

[Total: 7]

(b) Bromic(I) acid, HOBr(aq), is a weak acid. Its K_a is 2.0 × 10^{-9} mol dm^{-3}.

(i) Calculate the pH of 0.20 mol dm^{-3} HOBr(aq).

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

$[H^+] = \sqrt{2\times10^{-9}\times[0.20]}$
$= 2\times10^{-5}$

$pH = -\log_{10}(2\times10^{-5}) = 4.7$

pH = 4.7 [2]

(ii) 5.0 cm^3 of 0.20 mol dm^{-3} potassium hydroxide, KOH, are added to 20.0 cm^3 of 0.20 mol dm^{-3} HOBr(aq).

Calculate the pH of the buffer solution produced.

n of KOH = cxV = 0.20 × 5 × 10^{-3} = 1×10^{-3} mol

n of HOBr = cxV = 0.20 × 20 × 10^{-3} = 4×10^{-3} mol

n of HOBr remaining = $(4-1)\times10^{-3}$ = 3×10^{-3}

$[A^-] = 1\times10^{-3}/25\times10^{-3}$ $[HA] = 3\times10^{-3}/25$

$K_a = \frac{[H^+][A^-]}{[HA]} \Rightarrow \frac{2\times10^{-9}\times\frac{3\times10^{-3}}{25}}{1\times10^{-3}/25} = [H^+]$

$[H^+] = 6\times10^{-9}$

$pH = -\log_{10}(6\times10^{-9})$
$= 8.22$

pH = 8.2 [2]

[Total: 9]

Solubility Product:- A sparingly soluble salt will establish an equilibrium with its aqueous ions in water.

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

- $K_c = \dfrac{[Ag^+_{(aq)}][Cl^-_{(aq)}]}{[AgCl_{(s)}]}$ $\Longrightarrow$ $\boxed{K_{sp} = [Ag^+][Cl^-]}$

$[AgCl_{(s)}]$ → almost constant

solubility product

$[Ag^+]$: solubility of Ag^+

$[Cl^-]$: solubility of Cl^-

$[Ag^+] = [Cl^-]$

- solubility product remains constant for a constant temperature

Q. $AgCl_{(s)}$ is stirred into pure water at 25°C until equilibrium is reached, the concentration of silver chloride in the resulting solution is found to be 1.41×10^{-5} mol dm^{-3}. Find K_{sp}.

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

$K_{sp} = (1.41 \times 10^{-5})^2 = 1.99 \times 10^{-10}$ mol^2 dm^{-6}

Q. The K_{sp} value of Zinc sulphide at 25°C is 1.0×10^{-24} mol^2 dm^{-6}, find its solubility

$$ZnS \rightleftharpoons Zn^{2+} + S^{2-}$$

$K_{sp} = [Zn^{2+}][S^{2-}]$

$1 \times 10^{-24} = (x)(x) \Rightarrow x = \sqrt{1 \times 10^{-24}}$

$x = 1 \times 10^{-12}$ mol dm^{-3}

(b) The solubility of $Sr(OH)_2$ is 3.37×10^{-2} mol dm^{-3} at 0 °C.

(i) Write an expression for the solubility product of $Sr(OH)_2$.

$Sr(OH)_2 \rightleftharpoons Sr^{2+}_{(aq)} + 2OH^-$

$K_{sp} = [Sr^{2+}_{(aq)}][OH^-_{(aq)}]^2$

mol dm^{-3} (mol dm^{-3})^2

[1]

(ii) Calculate the value of K_{sp} at 0 °C. Include units in your answer.

$[Sr(OH)_2] = 3.37 \times 10^{-2} = [Sr^{2+}]$ $[OH^-] = 2 \times 3.37 \times 10^{-2}$

$K_{sp} = (3.37 \times 10^{-2})(2 \times 3.37 \times 10^{-2})^2$

$= 1.53 \times 10^{-4}$

K_{sp} = 1.53×10^{-4} units = mol^3 dm^{-9}

[2]

(d) The numerical value of the solubility product, K_{sp}, of CaF_2 is 3.45×10^{-11} at 298 K.

(i) Write an expression for the solubility product of CaF_2. Include its units.

$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$

$K_{sp} = [Ca^{2+}_{(aq)}][F^-_{(aq)}]^2$

units = mol^3 dm^{-9}

[2]

(ii) Calculate the solubility of CaF_2 at 298 K.

$[Ca^{2+}] = x$ $[F^-] = 2x$

$3.45 \times 10^{-11} = [x][2x]^2$

$3.45 \times 10^{-11} = 4x^3 \Rightarrow x = 2.05 \times 10^{-4}$

solubility = 2.05×10^{-4} mol dm^{-3} [1]

5 Silver sulfide, Ag_2S, is very insoluble in water.

(a) (i) Write an expression for the solubility product, K_{sp}, of $Ag_2S(s)$.

$Ag_2S \rightleftharpoons 2Ag^+ + S^{2-}$

$K_{sp} = [Ag^+_{(aq)}]^2 [S^{2-}_{(aq)}]$

[1]

(ii) The solubility of $Ag_2S(s)$ in water at 298 K is 1.16×10^{-17} mol dm^{-3}.

Calculate the numerical value of the solubility product, K_{sp}, of $Ag_2S(s)$ at 298 K.

$K_{sp} = [2 \times 1.16 \times 10^{-17}]^2 \times [1.16 \times 10^{-17}]$

$= 6.243 \times 10^{-51}$ mol^3 dm^{-9}

K_{sp} = 6.24×10^{-51} [2]

(iii) Calculate the minimum volume of water needed to dissolve 1.00 g of $Ag_2S(s)$ under standard conditions.

n of $Ag_2S = \frac{1}{2(107.9) + 32.1} = 4.03388 \times 10^{-3}$ mol

1.16×10^{-17} : 1 dm^3

4.03388×10^{-3} : x dm^3

$x = 3.477 \times 10^{14}$

volume = 3.48×10^{14} dm^3 [2]

Common ion effect:-

- A salt is less soluble in a solution which already contains the ions present in the salt.

- If a solution containing one of the ions of the salt is added to a saturated solution of the salt, some of the salt must precipitate out.

For e.g. A saturated solution of $MgCO_3$ is made

$$MgCO_3 \rightleftharpoons Mg^{2+} + CO_3^{2-}$$

if Na_2CO_3 solution is now added the $[CO_3^{2-}]$ increases so equilibrium shifts to left hand side so $MgCO_3$ is precipitated out

2 (a) The table lists values of solubility products, K_{sp}, of some Group 2 carbonates.

	solubility product in water at 298 K, K_{sp} / $mol^2 dm^{-6}$
$MgCO_3$	1.0×10^{-5}
$CaCO_3$	5.0×10^{-9}
$SrCO_3$	1.1×10^{-10}

Use the data in the table to describe the trend in the solubility of the Group 2 carbonates down the group.

solubility decreases .... [1]

(b) (i) Write an equation to show the equilibrium for the solubility product for $MgCO_3$. Include state symbols.

$MgCO_{3(s)} \rightleftharpoons Mg^{2+}_{(aq)} + CO_{3(aq)}^{2-}$ .... [1]

(ii) With reference to your equation in (i), suggest what is observed when a few cm^3 of concentrated Na_2CO_3(aq) are added to a saturated solution of $MgCO_3$. Explain your answer.

$MgCO_3$ precipitates out as addition of Na_2CO_3 increases concentration of CO_3^{2-} in solution. The equilibrium shifts to the left hand side and so $MgCO_3$ precipitates out. .... [2]

(c) Use the data in the table to calculate the solubility of $MgCO_3$ in water at 298 K, in $g\,dm^{-3}$.

$K_{sp} = [Mg^{2+}][CO_3^{2-}]$

$1 \times 10^{-5} = x^2$

$x = \sqrt{1 \times 10^{-5}}\ mol\,dm^{-3}$

$\text{solubility}(g/dm^3) = \dfrac{\sqrt{1 \times 10^{-5}} \times M_r}{dm^3}$

$= \sqrt{1 \times 10^{-5}} \times 84.3$

$= 0.2666$

solubility of $MgCO_3$ = 0.27 .... $g\,dm^{-3}$ [2]

Partition Coefficients:-

- If a particular solute is dissolved in an immiscible mixture of 2 liquids such as I_2 being dissolved in water and hexane

An equilibrium is established: $I_{2\,(aq)} \rightleftharpoons I_{2\,(hexane)}$

- $K_{partition} = \dfrac{[I_{2\,(hexane)}]_{eqm}}{[I_{2\,(aq)}]_{eqm}}$ (make sure you always show this expression as you could have defined it the other way round)

- K partition has no units.

If 0.35 g of iodine is shaken with 100 cm^3 of water and 100 cm^3 of hexane and the mixture allowed to establish equilibrium, the concentration of iodine in the aqueous layer is found to be 4.0×10^{-3} mol dm^{-3}.

Find the number of moles of iodine used initially.

$$n = \frac{0.35}{2(126.9)} = 1.379 \times 10^{-3}$$

Find the number of moles of iodine present in the aqueous layer.

$$n = c \times V = 4 \times 10^{-3} \times 100 \times 10^{-3} = 4 \times 10^{-4}$$

Find the concentration of iodine in the hexane layer.

$$n \text{ of } I_{2\,(hexane)} = 1.379 \times 10^{-3} - 4 \times 10^{-4} = 9.79 \times 10^{-4}$$

$$[I_{2\,(hexane)}] = \frac{9.79 \times 10^{-4}}{100 \times 10^{-3}} = 9.79 \times 10^{-3}$$

Hence find the partition coefficient.

For $I_{2\,(aq)} \rightleftharpoons I_{2\,(hexane)}$

$$K_{partition} = \frac{[I_{2\,(hexane)}]}{[I_{2\,(aq)}]} = \frac{9.79 \times 10^{-3}}{4 \times 10^{-3}} = 2.4475$$

$$= 2.4$$

(d) (i) Explain what is meant by the term *partition coefficient*, $K_{partition}$.

Ratio of concentration of solute in 2 immiscible solvents at equilibrium.

For: $X_{(y)} \rightleftharpoons Z_{(a)}$ $K_{partition} = \dfrac{[Z_{(a)}]}{[X_{(y)}]}$

[2]

(ii) The partition coefficient of organic compound **H** between dichloromethane and water is 4.75.

- 2.50 g of compound **H** was dissolved in water and made up to 100 cm³ in a volumetric flask.
- 50 cm³ of this aqueous solution were shaken with 10 cm³ of dichloromethane.

Calculate the mass of compound **H** that was extracted into the dichloromethane.

in 50 cm³, 1.25 g of H would be present

$H_{(aq)} \rightleftharpoons H_{(dichloromethane)} \Rightarrow K_{partition} = \dfrac{[H_{(dichloromethane)}]}{[H_{(aq)}]}$

let's say x g was extracted

$4.75 = \dfrac{x/10}{\frac{1.25-x}{50}} \Rightarrow 0.11875 - 0.095x = 0.1x$

$0.11875 = 0.195x$

$x = 0.60897\,g$

mass of compound **H** extracted = 0.61 g [2]

[Total: 14]

Successive extractions:- Using successive extractions with less amount of solvent portions will extract more mass.

(ii) When 100 cm³ of an aqueous solution containing 0.50 g of an organic compound **X** was shaken with 20 cm³ of hexane, it was found that 0.40 g of **X** was extracted into the hexane.

Calculate the partition coefficient of **X** between hexane and water.

$X_{(aq)} \rightleftharpoons X_{(hexane)}$

$K_{partition} = \dfrac{[X_{(hexane)}]}{[X_{(aq)}]} = \dfrac{0.40/20}{0.10/100} = 20$ (no units)

(iii) If **two** 10 cm³ portions of hexane were used instead of a single 20 cm³ portion, calculate the total amount of **X** extracted and compare this with the amount extracted using one 20 cm³ portion.

$K_{partition} = \dfrac{[X_{(hexane)}]}{[X_{(aq)}]}$, lets say x gets extracted in 1st time and y gets extracted 2nd time

$20 = \dfrac{x/10}{\frac{0.5-x}{100}}$

$0.1 - 0.2x = 0.1x$

$0.1 = 0.3x$

$x = 1/3\,g$

$20 = \dfrac{y/10}{\frac{0.5-\frac{1}{3}-y}{100}}$

$0.1 - \frac{1}{15} - 0.2y = 0.1y$

$\frac{1}{30} = 0.3y \Rightarrow y = 1/9$

extracted: $\frac{1}{3} + \frac{1}{9} = 0.44\,g$

$0.44 > 0.40$ so more extracted!

[5]

(b) When 20 cm^3 of ethoxyethane were shaken with 75 cm^3 of an aqueous solution containing 5.00 g of an organic compound, **J**, in 75 cm^3 of water, it was found that 2.14 g of **J** were extracted into the ethoxyethane.

Calculate the partition coefficient, $K_{partition}$, of **J** between ethoxyethane and water.

$J_{(aq)} \rightleftharpoons J_{(ethoxy\ ethane)}$

$$K_{partition} = \frac{[J_{(ethoxyethane)}]}{[J_{(aq)}]} = \frac{2.14/20}{\frac{5-2.14}{75}} = 2.8059$$

$K_{partition}$ = 2.8 no units [2]

(c) In a new experiment

- 10 cm^3 of ethoxyethane were shaken with 75 cm^3 of an aqueous solution containing 5.00 g of **J** and the layers were separated.
- The aqueous layer was shaken with a second 10 cm^3 portion of ethoxyethane and the layers were separated.
- The two organic layers were combined.

Use the value of $K_{partition}$ you calculated in **(b)** to calculate the total mass of **J** extracted by this procedure.

lets say x extracted 1st time

$$2.8 = \frac{x/10}{\frac{5-x}{75}} \Rightarrow \frac{14}{75} - \frac{14}{375}x = \frac{x}{10}$$

$x = 1.359$

y extracted 2nd time

$$2.8 = \frac{y/10}{\frac{3.64-y}{75}} = 0.136 - \frac{14}{375}y = \frac{y}{10}$$

$y = 0.990g$

total mass of **J** = 2.35 [2]