

SERANGOON JUNIOR COLLEGE General Certificate of Education Advanced Level Higher 2

CHEMISTRY

9746/03

Preliminary Examination Paper 3 Free Response

19th August 2008 2 hours

Candidates answer on the separate paper.

Additional Materials: Answer Paper Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.Write in dark blue or black pen on both sides of the paper.You may use a soft pencil for any diagrams, graphs or rough work.Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any four questions.

A Data Booklet is provided.

You are reminded of the need for good English and clear presentation in your answers

The number of marks is given in the brackets [] at the end of each question or part question. At the end of the examination, fasten all your work securely together.

This document consists of 11 printed pages and 1 blank page

Answer any four questions.

1. The Haber Process is the nitrogen fixation reaction of nitrogen and hydrogen over magnetite, iron oxide, to produce ammonia. This process is important because ammonia is difficult to be produced on an industrial scale, and ammonia is the precursor for many nitrogen-containing products such as nitrate fertilizers and munitions.

$$N_2(g) + 3H_2(g) = 2 NH_3(g)$$
 $\Delta H^{e} = -92.4 \text{ kJ mol}^{-1}$

(a) Write an expression for K_p for the above reaction, stating its units.

[2]

$$K_{p} = \frac{\left(P_{NH_{3}}^{2}\right)}{\left(P_{N_{2}}\right)\left(P_{H_{2}}^{3}\right)} \underline{\text{atm}^{-2}} \text{ (or } \underline{\text{Pa}^{-2}} \text{ or } \underline{\text{torr}^{-2}} \text{ or } \underline{\text{kg m}^{-1} \text{ s}^{-2}} \text{ or } \underline{\text{N}^{-2}\text{m}^{4}})$$

(b) When a 1:3 mixture by volume of N₂ and H₂ at an initial pressure of 200 atm is allowed to reach equilibrium at 500 °C, it was found that the percentage yield of NH₃ is 30 %.

$$\left(\% \ yield = \frac{actual \ amount}{theoretical \ amount} \times 100\%\right)$$

- (i) Calculate the equilibrium partial pressures of N_2 and H_2 .
- (ii) Hence calculate a value of K_p at 500 °C.
- (iii) Suggest, with a reason, whether or not a higher temperature would favour the formation of ammonia.
- (iv) When some H_2 is added to the existing equilibrium mixture, the partial pressure of ammonia is increased to 50 atm. Calculate the new equilibrium partial pressure of H_2 .
- (v) The value of ΔG is 0 kJ mol⁻¹ at 196 °C. Use this information, and any other information to calculate the value of ΔS .
- (vi) Calculate ΔG for the forward reaction at 500 °C.
- (vii) Based on the answer in (vi), comment on the feasibility and relate it with the reaction conditions of 200 atm and 500 °C.

[8]

i. Using mole fraction,

$$P_{N_2} = \frac{1}{4} \times 200$$
$$= 50 atm$$
$$P_{H_2} = \frac{3}{4} \times 200$$

= 150 *atm*

 ii. $N_2(g) + 3H_2(g) = 2 NH_3(g)$

 Initial amount/atm
 50
 150
 0

 Change /atm
 -15
 -45
 +30

 Final amount/atm
 35
 105
 $\frac{30}{100} \times 100 = 30$

$$K_{p} = \frac{\left(P_{NH_{3}}^{2}\right)}{\left(P_{N_{2}}\right)\left(P_{H_{2}}^{3}\right)}$$
$$K_{p} = \frac{\left(30^{2}\right)}{\left(35\right)\left(105^{3}\right)}$$

= 2.22 x 10⁻⁵ atm⁻²

iii. Low temperature.

Forward reaction is **exothermic**.

iv.	N ₂ (g) +	3H ₂ (g)	2 NH ₃ (g)
Initial amount/atm	35	105 + x	30
Change /atm	-10	-30	+20
Final amount/atm	25	75 + x	50

$$K_{p} = \frac{(P_{NH_{3}}^{2})}{(P_{N_{2}})(P_{H_{2}}^{3})}$$

$$2.22 \times 10^{-5} = \frac{(50^2)}{(25)(75+x)^3}$$

x = <u>90.1 atm</u>

- **v.** $\Delta G = \Delta H T\Delta S$ $0 = (-92.4) - (196+273) \Delta S$ $\Delta S = -197 J \text{ mol}^{-1} \text{ K}^{-1}$
- vi. $\Delta G = \Delta H T\Delta S$ $\Delta G = (-92.4) - (500+273)(-0.197)$ $\Delta G = +59.9 \text{ kJ mol}^{-1}$
- vii. Positive ∆G value shows that the reaction is thermodynamically unfeasible / non-spontaneous. Thus, condition of <u>high pressure</u> and moderate temperature is needed to push the reaction forward.
- (c) Ammonia can be used as a reagent to make nitrogen-containing products.
 - (i) State the reagents and conditions that is needed for the conversion of ammonia

into

(i)

- Ι propanamine
- Π propanamide
- (ii) It is noted that in the formation of propanamine, a by-product is formed which has a melting point of 270 °C and gives an immediate precipitate with aqueous silver nitrate. Suggest a structure for this by-product.

[3]

- 1-chloropropane or CH₃CH₂CH₂CI I Heat Ш Propanoyl chloride, room temperature $\begin{bmatrix} CH_2CH_2CH_3 \\ H_3CH_2CH_2C - N - CH_2CH_2CH_3 \\ CH_2CH_2CH_3 \end{bmatrix} X^{-1}$ (ii)
 - (d) The compound propanamide, which is a product of ammonia, can be used to make other organic compounds.
 - Propanamide can undergo hydrolysis to form propanoic acid. (i)

How would you expect the rate of this reaction to compare to that of the hydrolysis of propanoyl chloride? Explain your answer using their respective reaction conditions.

(ii) State the intermediates and suggest the reagents and conditions needed for the conversion of propanoic acid into butanoic acid.

[5]

Rate of hydrolysis of propanamide is slower than that of (i) propanoyl chloride.

Propanamide only undergoes hydrolysis in the presence of aqueous acid or alkali with heating/reflux

Propanoyl chloride readily undergo hydrolysis with water at room temperature.

(ii) Propanoic acid → propan-1-ol

LiA/H₄ in dry ether, room temperature

Propan-1-ol → <u>1-chloropropane</u> PCI₅... rtp

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Chloropropane_→ <u>butanitrile</u>

Alcoholic KCN, reflux

Butanitrile \rightarrow butanoic acid

<u>Dilute H₂SO₄, heat</u>

- (e) When propanamide, propanoyl chloride and propanoic acid are added into separate portions of water, solutions of pH 1.0, 2.8 and 7.0 are formed.
 - (i) Suggest which pH value is associated with each compound.
 - (ii) Give a reason for your choice of pH of propanamide.

[2]

(i) For propanamide, <u>pH = 7.0</u>

For propanoic acid, **pH = 2.8**

For propanoyl chloride, $\mathbf{pH} = \mathbf{1.0}$

(ii) Amide is neutral. Lone pair of electron on the nitrogen in amide group is not available to accept a proton due to presence of electron withdrawing (oxygen on the) carbonyl group.

OR

Lone pair on nitrogen interacts with π electrons on the carbonyl group.

[Total: 20]

- 2 Trichloroethanoic acid (TCA), CC*l*₃COOH, widely used in biochemistry for the precipitation of macromolecules such as proteins. Solutions containing trichloroethanoic acid are also used in tattoo removal.
 - (a) Trichloroethanoic acid is prepared by the reaction of chlorine with ethanoic acid.

 $CH_3COOH + 3Cl_2 \rightarrow CCl_3COOH + 3HCl$

- (i) State the type of reaction for the preparation of trichloroethanoic acid.
- (ii) Suggest a suitable condition for this reaction.
- (iii) A by-product of this synthesis has a molecular formula of $C_4H_4O_4Cl_2$. Draw a suitable structure for this compound.

[3]

- i Free Radical Substitution
- ii Ultraviolet (uv) light / radiation

iii

$$\begin{array}{cccc} O & O & Cl & O \\ \parallel & \parallel \\ HO - CCHCHC - OH & HO - C - CHCH_2C - OH \\ Cl & Cl & OR & Cl \end{array}$$

(b) In a laboratory experiment, the decomposition of CC/₃COOH was conducted at 70 °C and the volume of carbon dioxide produced was monitored using 0.100 mol dm⁻³ and 0.200 mol dm⁻³ of trichloroethanoic acid separately.

$$CCl_3COOH \rightarrow CO_2 + CHCl_3$$

Graph of volume of CO_2 / dm³ against time / hour 4.5 4.0 [TCA] = 0.200 mol dm⁻³ 3.5 Volume of CO₂/ dm³ 3.0 2.5 2.0 [TCA] = 0.100 mol dm⁻³ 1.5 1.0 0.5 0.0 0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 Time / hour From the graph, determine the order of reaction and the rate constant, k. (i)

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- (ii) Determine the half life of reaction using rate constant that you have calculated in (i).
- (iii) Explain, using Maxwell Boltzmann distribution curve, the effect of lowering temperature to 60 °C.

[7]

i From graph **A**: initial rate = $1.5/1.2 = \frac{1.25 \text{ dm}^3 \text{ h}^{-1}}{1.25 \text{ dm}^3 \text{ m}^{-1}}$ From graph **B**: initial rate = $4.0/1.5 = \frac{2.66 \text{ dm}^3 \text{ h}^{-1}}{1.25 \text{ dm}^3 \text{ m}^{-1}}$

As [CC/₃COOH] increase <u>two times</u>, initial rate of reaction increases approximately <u>two times</u>. Hence order of reaction w.r.t. CC/₃COOH is <u>one</u>.

Using graph A, (or use graph B to calculate)

Rate = k[CCI₃COOH]

Convert volume of CO₂ to amount.

1.25 dm⁻³:
$$n_{CO_2} = \frac{101000 \times 1.25 \times 10^{-3}}{8.314 \times 343} = 0.04427 \, mol \, \underline{OR}$$

2.66 dm⁻³: $n_{CO_2} = \frac{101000 \times 2.66 \times 10^{-3}}{8.314 \times 343} = 0.09421 mol$
Since 1 mol TCA = 1 mol CO₂
Rate₁ = 0.04427 mol dm⁻³ h⁻¹
Rate₂ = 0.09421 mol dm⁻³ h⁻¹
0.04427 = k(0.100) [or 0.09446 = k(0.200)]
k = **0.4427 h⁻¹ or 0.471 h⁻¹**

8

ii

Using
$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$
 [½] and graph **A**
 $t_{1/2} = \frac{0.693}{0.4427} = 1.57 \text{ h}$ [½]

0

iii





From Maxwell-Boltzmann distribution curve

- \rightarrow When temperature of reaction **lowered**,
- \rightarrow The shaded area is <u>smaller</u>
- \rightarrow No. of rxt particles with energy \geq Ea <u>decreases</u>.
- → No. of effective collisions with energy \ge E_a <u>decreases</u>.
- \rightarrow Rate of reaction is proportional to frequency of effective collisions
- \rightarrow rate of reaction <u>decreases</u>.

(c) A student collected the CO₂ produced by delivering the gas into a measuring cylinder originally filled with water.

Some of the carbon dioxide dissolved in water to form carbonic acid, H_2CO_3 . The following equilibria were established.

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq)$$

 $H_2CO_3(aq) \longrightarrow H^+(aq) + HCO_3^-(aq) \qquad K_a = 4.27 \times 10^{-7} \text{ mol dm}^{-3}$

A 20.0 cm³ of 0.20 mol dm⁻³ H_2CO_3 was titrated with 0.20 mol dm⁻³ of aqueous sodium hydroxide, NaOH. 20.00 cm³ of NaOH was required for complete neutralisation of the following reaction.

 $H_2CO_3(aq) + NaOH(aq) \rightarrow NaHCO_3(aq) + H_2O(l)$

- (i) What do you understand by the term weak acid?
- (ii) Calculate the initial pH of the solution.
- (iii) Calculate the pH of the solution after adding 10.00 cm³ of NaOH.
- (iv) The pH at equivalence point is 8.35. Using an appropriate equation, account for this observation.
- (v) An acid-base indicator (HIn) has a K_a value of 3.00 x 10⁻⁵ mol dm⁻³.

$$HIn(aq) = H^{+}(aq) + In^{-}(aq)$$

The acidic form of the indicator (HIn) is red and the basic form (In⁻) is blue. Given that the indicator appears red when it contains at least 75% of HIn, and appears blue when it contains at least 75% of In⁻. What is the pH range for colour change of indicator? Based on your answer, suggest if this indicator is suitable for the H_2CO_3 titration.

(vi) Suggest a better method of collecting the CO₂ gas.

A **weak acid** is one which **dissociates <u>partially</u> in solution to give protons**, <u>H</u>⁺.

ii Let the equilibrium $[H^+]$ be x mol dm⁻³

$$H_{2}CO_{3}(aq) \xleftarrow{} H^{+}(aq) + HCO_{3}^{-}(aq)$$
Initial [] 0.200 0 0
Change [] - x x x
Eqm [] 0.200-x x x x

i

[10]

$$K_{a} = \frac{\left[H^{+}\right]\left[HCO_{3}^{-}\right]}{\left[H_{2}CO_{3}\right]}$$
$$= \frac{x^{2}}{0.200 - x}$$
$$4.27 \times 10^{-7} = \frac{x^{2}}{0.200}$$
$$x = 2.922 \times 10^{-4} \ mol \ dm^{-3}$$

iii When 10 cm³ of NaOH is added, the titration is at *half* equivalence point.

10

pH = pKa

iv

= <u>6.37</u>

 HCO_3^- (aq) + $H_2O(I) = H_2CO_3(aq) + OH^-(aq)$

- HCO_3^- undergoes <u>salt hydrolysis</u> and <u>releases</u> <u>OH⁻</u> into the solution.
- [OH⁻] > [H⁺]

pH at end-point is > 7 (basic)

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

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

For 75% red,

$$[H^{+}] = \frac{(3.00 \times 10^{-5})(75)}{25} = 0.00009 \, mol \, dm^{-3}$$

⇒ pH = 4.05
For 75% blue,

$$[H^{+}] = \frac{(3.00 \times 10^{-5})(25)}{75} = 0.00001 \, mol \, dm^{-3}$$

⇒ pH = 5

The indicator is not suitable as the <u>equivalence pH is not</u> within the range of rapid pH change.

vi Collect the gas using frictionless <u>svringe</u>. [1]

[Total: 20]

- 3 This question is about physical and chemical properties of Group II compounds.
 - (a) 400 cm³ of 0.015 mol dm⁻³ of magnesium nitrate was mixed with 600 cm³ of 0.2 mol dm⁻³ of aqueous ammonia [K_b of NH₃ = 1.74×10^{-5} mol dm⁻³].
 - (i) Write an expression for the solubility product, K_{sp} , of magnesium hydroxide.
 - (ii) Calculate the amount of Mg^{2^+} and NH_3 added.
 - (iii) Given that the K_{sp} of Mg(OH)₂ is 1.65 x 10⁻¹⁰ mol³dm⁻⁹, prove that there is precipitate of Mg(OH)₂ formed in the above resulting mixture.
 - (iv) The pH of this resulting solution is measured at 11.1. Calculate the concentration of Mg²⁺ ions in the solution.

[5]

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

ii Amount of Mg^{2+} added = 0.400 × 0.015 = 0.00600 mol Amount of NH_3 added = 0.600 × 0.2 = 0.120 mol

iii
$$[OH^-] = \sqrt{1.74 \times 10^{-5} \times 0.120} = 0.00144 \text{ mol dm}^{-3}$$

Ionic Product,

IP (Mg(OH)₂) =0.00600 × 0.00144² = $1.25 \times 10^{-8} \text{ mol}^3 \text{ dm}^{-9} > \text{K}_{sp}$ (Mg(OH)₂)

Therefore, precipitate formed.

iv Solution is saturated.

pH 11.1, $[OH^{-}] = 10^{-2.9} \text{ mol dm}^{-3}$ 1.65×10⁻¹⁰ = $[Mg^{2+}] (10^{-2.9})^2$ $[Mg^{2+}] = 1.04 \times 10^{-4} \text{ mol dm}^{-3}$

- (b) Magnesium nitrate decomposes at 330°C.
 - (i) Write a balanced chemical equation, with state symbols, for the decomposition of magnesium nitrate.
 - (ii) How would you expect the decomposition temperature of barium nitrate to differ from that of magnesium nitrate? Explain your answer.

[3]

i $Mg(NO_3)_2(s) \rightarrow MgO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

Decomposition temperature of barium nitrate would be <u>higher</u> than magnesium nitrate. Ba²⁺ ion, having larger ionic radius, has lower charge density than Mg²⁺ ion, thus it has <u>lower</u>

polarising power. Nitrate ion in barium nitrate is **less polarised** and thus barium nitrate is **more stable** (or decomposes at a higher temperature)

- (c) Solubility of Group II sulphates vary down the group.
 - (i) With an appropriate equation, define the *enthalpy change of solution of calcium sulphate.*
 - (ii) Given: $\Delta H^{e}_{lattice} (CaSO_4) = -2704 \text{ kJmol}^{-1}$ $\Delta H^{e}_{hydration} (Ca^{2+}) = -1562 \text{ kJmol}^{-1}$ $\Delta H^{e}_{hydration} (SO_4^{2-}) = -1160 \text{ kJmol}^{-1}$

Using *Hess' Law*, calculate the enthalpy change of solution of calcium sulphate. Based on the value that you have calculated, comment on the solubility of calcium sulphate.

(iii) Using relevant data from the *Data Booklet*, predict the relative solubility of calcium sulphate, barium sulphate and lead(II) sulphate.

[5]

i

 $CaSO_4(s) \rightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$

Energy change when <u>one mole</u> of CaSO₄ is <u>completely</u> <u>dissolved</u> in a solvent to form an <u>infinitely dilute</u> solution under standard conditions.

ii
$$\Delta H_{soln} = \Delta H_{hyd} - \Delta H_{latt}$$

=
$$[\Delta H_{hyd}(Ca^{2+}) + \Delta H_{hyd}(SO_4^{2-})] - \Delta H_{latt}$$

= <u>-18 kJ mol⁻¹</u>

 ΔH_{sol} of calcium sulphate is slightly exothermic (negative), thus it is most likely soluble in water.

- iii Ionic radius: $Ca^{2+} < Pb^{2+} < Ba^{2+}$ Solubility: $CaSO_4 > PbSO_4 > BaSO_4$
- (d) The table below shows the uses of some Group II compounds.

Compounds	Uses
MgO	As refractory lining in furnaces
CaCO ₃	Used in the furnace for removal of SO_2 in exhaust
MgSO ₄	As an anti-inflammatory agent

		(anhydrous)			
		(annyarous)			
(i) Explain, in refractory lir	Explain, in terms of bonding and structure, the use of magnesium oxide as a refractory lining in furnace.			
(i	i) Calcium ca reaction:	Calcium carbonate removes sulphur dioxide, forming calcium sulphite, via this reaction:			
		$CaCO_3(s) + SO_2(g) \rightarrow CaSO_3(s) + CO_2(g)$			
	A stream of 100 g of s experiment. and convert in the exhau	A stream of furnace exhaust containing sulphur dioxide gas was passed through 100 g of solid $CaCO_3$. The mass of solid was found to be 110 g after the experiment. Assuming all sulphur dioxide was removed from the stream of exhaust and converted to calcium sulphite, calculate the amount of sulphur dioxide present in the exhaust gas. [Taking A _r of Ca = 40.0, S = 32.0, C = 12.0 and O = 16.0]			
(ii	 Anhydrous boils (infect and the infe draw water 	Anhydrous magnesium sulphate paste is sold by pharmacists as a treatment for boils (infected areas of the skin). The paste is applied to a boil to draw out water and the infected matter. Suggest why anhydrous magnesium sulphate is able to draw water out of the treated boil.			
				[7]	
i M to ha ov <u>te</u>	gO has a <u>giant</u> gether by <u>stron</u> as a high melting vercome the stro mperature in fu	lattice structure o g ionic bond / elec g point: a large amo ng ionic bonds thu Irnaces .	f Mg ²⁺ and O ²⁺ ions held <u>strostatic attraction</u> . It punt of energy is needed to s it is <u>stable under high</u>		
ii Le	et x mol be the a	mount SO ₂ in the g	as stream		
In	itial amount of C	$aCO_3 = \frac{100}{(40+12+1)}$	$\overline{48)} = 1 mol$		
S	O₂ ≡ CaCO₃ ≡ C	aSO ₃			
Ar	mount of CaCO ₃	used = x mol			
Ar	mount of CaSO ₃	formed = x mol			
М	r of CaSO ₃ = 40-	f CaSO ₃ = 40+32+48 = 120.0			
1 1	10g = (1-x)100 +	120x			
	x = <u>0.5 mol</u>				
iii M Ar <u>bo</u> [M	g ²⁺ ion has smal nhydrous Mg ²⁺ io <u>oils</u> to form the I 1g(H ₂ O) ₆] ²⁺)	ll radius, thus <u>high</u> ons <u>able to attract</u> nydrated Mg ²⁺ (or o	<u>charge density</u> . <u>water molecules from</u> complex ions		
				[Total: 20]	

13



iv Water reacts with $AICI_3$ to from hydrated AI^{3+} and CI^{-} ions

 $AICI_3 + 6H_2O \longrightarrow [AI(H_2O)_6]^{3+} + 3CI^{-}$

 $AICI_3$ will not be able to act as a catalyst, thus the reaction stops.

(b) Name and outline the reaction mechanism in Step I.

[3]





During the research of the project, the student found that DDT was used to control insect-borne diseases in the military and in agricultural purposes. It was suggested that DDT is a carcinogen and a pollutant as well in 1962. DDT was eventually banned world-wide in 1972, except in some third-world countries to control the spread of malaria.

(c) DDT is a chlorine-based compound, thus it is inert to biological degradation over time. The student decides to remove all the chlorine by refluxing DDT with aqueous NaOH so that DDT becomes bio-degradable. Briefly discuss the feasibility of this experiment. [Equations are not necessary.]

[3]

Experiment is not feasible . This is because the halogenoalkanes will undergo (basic) hydrolysis / nucleophilic substitution. However,	
the halogenoarenes will <u>not be hydrolysed / not undergo</u>	
nucleophilic substitution. Hence hydrolyzed DD1 still contains	
Helegopearones are not easily substituted because the n orbitals of	
the balagen atom interact with the p orbitals of the six carbon atoms	
in the heatron ring to form a delegalized $-$ electron aloud OP	
In the benzene hing to form a delocalised π electron cloud OR	
Lone pair of electrons of chlorine is delocalised into the	
resistant to hydrolysis	

When the student went to take some aluminium chloride from the chemical store, he realized that **six** chemical bottles in another shelf were missing their labels. The labels are "Sodium"

Chloride", "Magnesium Chloride", "Magnesium Oxide", "Silicon Dioxide", "Phosphorus(V) Oxide" and "Phosphorus Pentachloride". He decided to perform some tests to deduce the identities of the chemicals in the unlabeled bottles, so that they can be re-labeled correctly.

The student named the six bottles **A to F**. The following solubility tests were conducted and the observations were as follow:

- Samples from bottles **A** and **B** are insoluble in water. However, sample **A** dissolves readily in hydrochloric acid, while sample **B** dissolves readily in aqueous sodium hydroxide.
- Samples from bottle **C** and **D** are soluble in water, but sample **C** gives a solution of pH 7, whereas sample **D** gives a solution of pH 5.
- Samples from bottles E and F melt at relatively low temperature as compared to A to D.
 Both of them reacted vigorously with water to form solutions containing strong acids.
 Furthermore, sample F gave off a thick white fume when reacted with water.
- (d) Suggest identities of A to F, writing the relevant balanced equations where necessary.

[6]

A = MgO

- $\mathbf{B} = SiO_2$
- **C** = NaCl
- $D = MgCl_2$
- $E = P_4O_{10}$
- $\mathbf{F} = PCI_5$
- MgO + 2HCI → MgCl₂ + H₂O
- SiO₂ + 2NaOH → Na₂SiO₃ + H₂O
- NaCl(s) \rightarrow Na⁺(aq) + Cl⁻(aq)
- MgCl₂ + 6H₂O \rightarrow [Mg(H₂O)₆]²⁺ + 2Cl⁻
- [Mg(H₂O)₆]²⁺ → [Mg(H₂O)₅OH]⁺ + H⁺
- $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$
- PCl₅ + 4H₂O → H₃PO₄ + 5HCl

[Total: 20]

- 17
- 5. Myoglobin, like haemoglobin, is the oxygen-carrying proteins in vertebrates. Myoglobin facilitates the transport of oxygen in muscle and serves as a reserve store of oxygen in that tissue. Haemoglobin, which is packaged in erythrocytes (red blood cells), is the oxygen carrier in blood.
 - (a) Myglobin is a compact protein with a single polypeptide chain of 153 amino acid residues, including the following residues: leucine, threonine, tyrosine and tryptophan.

The R groups of the amino acids are given below:



- (i) In an aqueous external environment, which of the above four amino acid residues are orientated inward and outward of the compact structure? State your reasoning.
- (ii) Draw the structures of the predominant species of tyrosine and tryptophan when they are placed in solutions of
 - I pH 2
 - II pH 12
- (iii) Draw the displayed formula of —leu—thr—, which is part of the polypeptide chain in myoglobin.
- (iv) Write a general equation to show how a peptide bond in the primary structure is hydrolysed by aqueous sodium hydroxide.
- (v) Tyrosine exists as a white crystalline solid while phenol exists as a liquid at room temperature. Account for this observation in terms of bonding and structure.

[13]

Leucine will orientate inwards while threonine, tyrosine and tyrptophan orient outwards
 Reasoning: leucine consists of non-polar R groups and hence forms van der Waals' forces with non-polar R groups of other amino acid residues; Threonine, tyrosine and tryptophan contain polar hydroxyl and amine group, hence form hydrogen bonding with polar water.

OR

Threonine will orientate outwards and leucine, tyrosine and tyrptophan orientate inwards.

Threonine contains a polar hydroxyl group and it has a relatively small non-polar alkyl group, therefore it can form hydrogen bonds with the water solvent. Tyrosine and tryptophan, although have polar hydroxyl and amine group, they have relatively large non-polar group, similar to leucine, that form van der Waal's attraction forces with non-polar R groups of other amino acid residue.

ii

Tyrosine





Tryptophan

pH =12





v Relative melting point: tyrosine has a <u>higher</u> melting point than phenol.

Explanation:

Tyrosine has <u>giant ionic structure</u> with strong <u>ionic bonds</u> between the <u>zwitterions</u>. Phenol is <u>simple molecular</u> <u>structure</u> with weaker <u>intermolecular hydrogen bonds</u> Hence, <u>more energy (or less energy)</u> is required to overcome the <u>stronger ionic bonds (weaker hydrogen bonds)</u>, hence higher melting point

- (b) Myoglobin consists of only 1 polypeptide chain arranged in a tertiary structure.
 - (i) Describe the tertiary structure of myoglobin.
 - (ii) Explain, in term of bonding and structure, why myoglobin tends to coagulate and precipitate when
 - I heated,
 - II subjected to changes in pH, and
 - **III** $Hg^{+}(aq)$ is added.

i Tertiary structure of myoglobin describes how the entire protein molecule coils into an overall 3-dimensional shape/conformation. Formed mainly due to the <u>folding or</u> <u>coiling of the secondary structures/polypeptide chains</u> and held together by <u>ionic bonding</u>, <u>hydrogen bonding</u>, <u>Van der</u> <u>Waals' interactions</u> and <u>disulphide bonds</u> between the side chains of the polypeptide.

ii I When heated

Disrupts weak Van der Waals' forces and hydrogen bonding (to a lesser extent) holding the quaternary, tertiary and secondary structures, resulting in a more disordered arrangement which is irreversible at high temperatures.

II When subject to pH changes

Disrupts the ionic bond holding the tertiary and quaternary structures in place as pH change protonates or deprotonates the charged R groups.

At **low pH**, **ionic R groups** will be **protonated** while at **high pH**, ionic R groups will be **deprotonated** which is irreversible at extreme pH changes.

III When Hg⁺ ion

Disrupt the original ionic bonds between the charged R groups of the amino acids by **forming new ionic bonds** with these charged R groups of amino acids.

Disrupt the formation of **<u>disulphide bonds</u>** by <u>forming</u> <u>bonds with –SH group</u> of cysteine residue. [7]

[Total: 20]

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