TEMASEK
JUNIOR COLLEGE

CHEMISTRY (H2) **9647/03**

Paper 3 Free Response

Tuesday **13th September 2011** **2 hours**

Candidates answer on separate paper.

Additional materials: Answer paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, Civics Group and Index number in the spaces provided on the cover page provided and 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 working.

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 brackets [ ] at the end of each question or part question.

At the end of the examination, fasten all your work securely together.

This question paper consists of 11 printed pages.

Answer any **four** questions.

1. **(a)** Nitrogen is chemically unreactive and will only react with oxygen under high temperatures to produce various atmospheric pollutants, such as nitrogen monoxide and nitrogen dioxide.

The table below shows the standard enthalpy change of formation of some nitrogen oxides.

Oxide	NO	NO_2	N_2O
ΔH^{θ}_{f} **/ kJ mol^{-1}**	+90.4	+33.9	+81.6

(i) Determine the density, in g cm^{-3}, of nitrogen dioxide gas at room temperature and pressure.

(ii) Nitrogen dioxide and dinitrogen oxide can react to give nitrogen monoxide:

$$NO_2(g) + N_2O(g) \rightarrow 3NO(g) \qquad \Delta S^{\theta}_{r} = +171.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

By using the data provided above, calculate the ΔG^{θ} for the above reaction at 800 K and hence predict if the reaction is spontaneous at 800 K. Assume that ΔH^{θ}_{f} and ΔS^{θ}_{r} do not change with temperature.

(iii) Dinitrogen oxide, N_2O, is a colourless gas and is also known as laughing gas.

Draw a 'dot-and-cross' diagram to illustrate the type of bonding present within the N_2O molecule, where nitrogen is the central atom. Name the shape of the molecule. [7]

(b) A solution contains 1.0×10^{-2} mol dm^{-3} of silver ions and 2.0×10^{-2} mol dm^{-3} of lead(II) ions. When an aqueous solution containing chloride ions is added to the solution, both silver chloride (K_{sp} value = 1.8×10^{-10}) and lead(II) chloride (K_{sp} value = 1.7×10^{-5}) precipitate from the solution.

Determine which salt precipitates first and the concentration of chloride which is necessary to begin the precipitation of each salt. [3]

(c) Explain the following observations with the aid of relevant equations.

(i) The second ionisation energies of the Group II elements decrease down the group.

(ii) Magnesium nitrate produces a brown gas on gentle heating whereas barium nitrate gives a brown gas on prolonged heating.

(iii) When 1.00 g of an unknown Group II carbonate, **M**CO_3 (where **M** is Mg, Ca or Ba), is heated, there is a loss in mass and a white residue, **X**, is formed.

When **X** is added to water, a weakly alkaline solution is obtained. No precipitate is observed when dilute sulfuric acid is added to the resulting solution formed.

Deduce the identity of the Group II element, **M**. [10]

[Total: 20]

2 **(a)** Sodium hydroxide is often used for acid-base titrations.

A student prepared a standard solution of sodium hydroxide by dissolving 10.0 g of sodium hydroxide in 250 cm^3 of water. In the process, he found the solution warm to the touch.

Given the information below, calculate the heat evolved when solid sodium hydroxide is dissolved in water.

Compound	ΔH_f / kJ mol^{-1}
NaOH(s)	–425
NaOH(aq)	–470

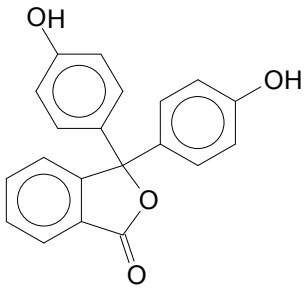
Hence, find the increase in temperature of the standard solution. [3]

(b) 3-nitrophenol and benzoic acid are weak Bronsted acids with pK_a values of 8.35 and 4.20 respectively.

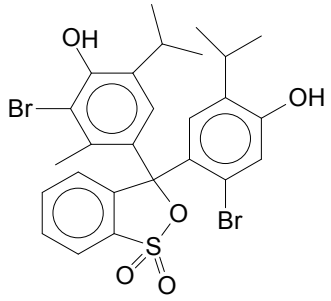
(i) Calculate the pH of 0.1 mol dm^{-3} of 3-nitrophenol.

(ii) Explain, in molecular terms, which is the stronger acid.

Phenolpthalein and bromothymol blue are common indicators for acid-base titrations.



Phenolphthalein
pK_a = 9.3



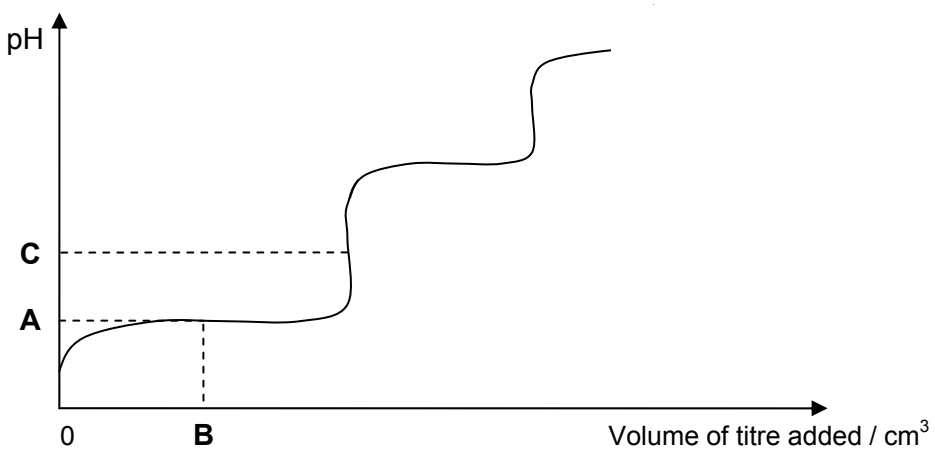
Bromothymol blue
pK_a = 7.1

A 25.0 cm^3 solution containing both 3-nitrophenol and benzoic acid was titrated against 1 mol dm^{-3} sodium hydroxide using 1 to 2 drops of phenolphthalein and bromothymol blue indicator.

(iii) Explain why both indicators are added in small amounts.

It was found that 14.40 cm^3 was needed to change the colour of the first indicator and a ***further*** 7.60 cm^3 was needed to change the colour of the second indicator.

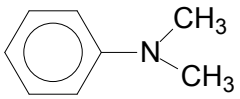
A sketch (**not to scale**) of the pH curve of the titration is shown below.



(iv) State the values for **A** and **B** on the graph.

(v) Calculate the concentration of benzoic acid and 3-nitrophenol in the solution. [8]

(c) Methyl orange is another acid-base indicator. It can be synthesised from N,N-dimethylphenylamine and diazonium salt.



N,N-dimethylphenylamine

Suggest a 3-step synthesis of N,N-dimethylphenylamine from benzene. [3]

(d) Amino acid glycine ($H_2N\text{-}CH_2\text{-}COOH$) is often used as a buffer to assay the enzyme pepsin. The isoelectric point of glycine is 6.07.

(i) What is meant by a *buffer*?

(ii) Draw the structure of glycine at pH 6.07.

(iii) Write equations to show how glycine acts as a buffer.

In the Miller-Urey experiment, amino acids can be formed from the irradiation of the gases ammonia, methane and water vapour with ultraviolet light. In the process, a by-product is formed.

(iv) Construct a balanced equation showing how glycine might have been produced in this experiment.

(v) Suggest a reason why ultraviolet light needs to be used in this experiment [6]

[Total: 20]

3. This question is about the chlorides of aluminium, silicon and phosphorus.

(a) State and explain the pH and the colour observed when some universal indicator is added to the solution formed from $AlCl_3$ dissolving in water. Write equations where appropriate. [3]

(b) In electrophilic substitution reactions, $AlCl_3$ can function as a Lewis acid catalyst to generate the electrophile from heterolytic fission.

(i) Deduce whether Al_2Cl_6 can also function as a catalyst in electrophilic substitution reactions.

(ii) Describe the mechanism of the reaction when benzene is reacted with ethanoyl chloride in the presence of $AlCl_3$. [4]

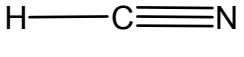
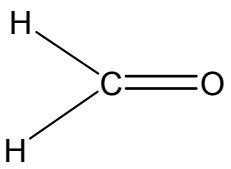
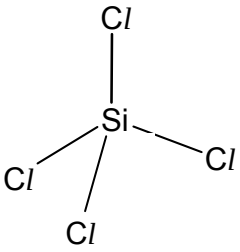
(c) When liquid $SiCl_4$ is added to water, a white solid of SiO_2 is immediately formed.

(i) Explain why $SiCl_4$ can be hydrolysed by water to form SiO_2.

(ii) The standard entropy change of the above reaction is positive. Write a balanced equation for the above reaction, with state symbols, and hence explain why the standard entropy change is positive.

(iii) Unlike the reaction with water, when liquid $SiCl_4$ is reacted with excess methanol, SiO_2 is not formed. Write a balanced equation for this reaction and describe what you may observe. [5]

(d) The following table shows three compounds and their respective types of hybridisation.

Compound			
Number of σ bonds around central atom	2	3	4
Type of hybridisation	sp	sp^2	sp^3

From the data above, deduce the type of hybridisation in PCl_5. [1]

(e) PCl_5 is often used as a chemical test as white fumes of HCl are liberated from organic compounds with specific functional groups.

(i) An organic compound **Y**, with molecular formula $C_4H_8O_2$, liberates white fumes when reacted with solid PCl_5 in the cold. It also forms an orange precipitate with 2,4-dinitrophenylhydrazine and does not react with Tollen's reagent. When heated with aqueous alkaline iodine, a bright yellow precipitate is obtained.

The organic compound formed by heating compound **Y** with acidified potassium manganate(VII) is able to liberate carbon dioxide when added to sodium carbonate solution.

Deduce the structure of **Y**, explaining your reasoning.

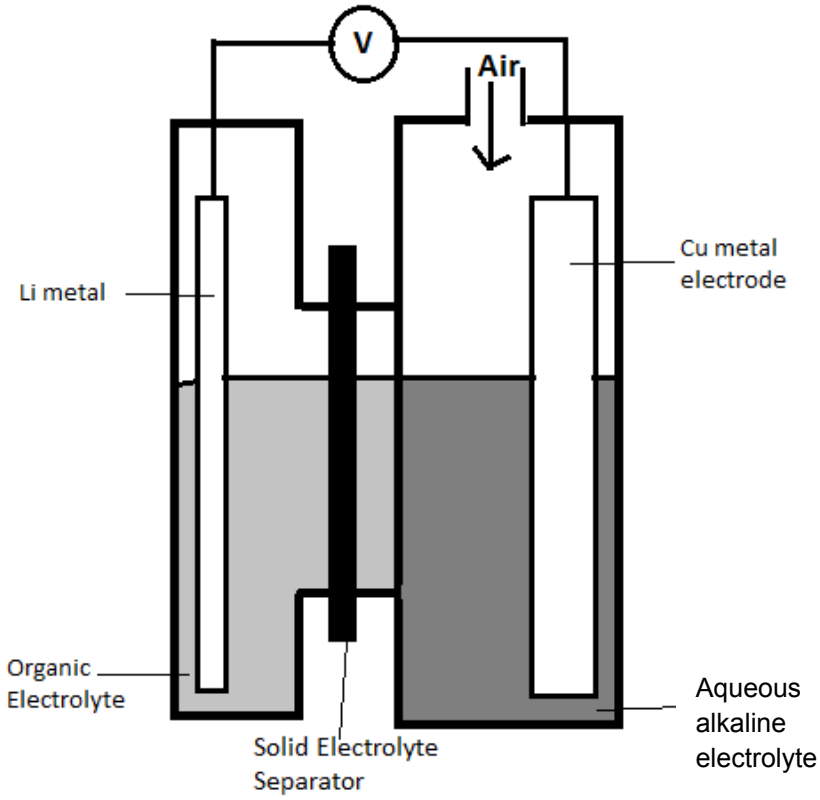
(ii) A student has a bottle of red wine that is supposed to contain 20% alcohol by volume. He decided to verify the presence of the alcohol by adding solid PCl_5 at room temperature to 25.0 cm^3 of the liquor.

Explain, with the aid of an equation, whether his choice of chemical test was appropriate. [7]

[Total: 20]

4. Copper and its compounds can be found everywhere in our daily life. Copper is abundant on Earth. Known worldwide resources of copper are estimated at nearly 5.8 trillion pounds of which only about 0.7 trillion have been mined throughout history.

(a) Researchers in Japan have recently developed a low-cost lithium-copper air fuel cell consisting of a copper cathode immersed in an aqueous alkaline electrolyte and a lithium anode immersed in an organic electrolyte. Mixing of the two electrolyte solutions is prevented by using a solid electrolyte separator where only lithium ions can pass through the separator.



The copper electrode is oxidised by oxygen in the air to generate copper(I) oxide. During discharge, copper(I) oxide will be reduced to copper solid at the cathode. Similarly, during discharge, lithium will be oxidised to give lithium ions at the anode and pass through the separator into the aqueous alkaline electrolyte.

(i) Write half-equations, occurring at each electrode, when the battery discharges.

(ii) The voltage of this cell is found to be +2.30 V. With reference to the *Data Booklet*, estimate the E^{θ} of the reduction of copper(I) oxide to copper half cell and state any assumptions you make.

(iii) Suggest a reason why an aqueous alkaline electrolyte cannot be used solely in this lithium-copper air fuel cell. [5]

(b) Copper is also widely used in other voltaic cells. An example of another voltaic cell is when a copper metal plate was dipped into an aqueous solution of 2.0 mol dm^{-3} copper(II) sulphate solution and this half-cell was connected via a salt bridge, to the following half-cell in standard conditions,

$$2CO_2 + 2H^+ + 2e \rightleftharpoons H_2C_2O_4 \qquad E^{\theta} = -0.49\ V$$

A student calculated the overall cell e.m.f to be +0.83V but the overall cell e.m.f was measured to be +0.86 V.

(i) State the cell-diagram for the above voltaic cell.

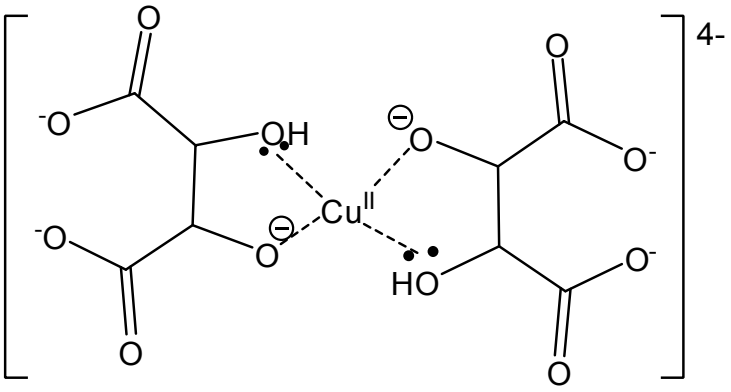
(ii) Describe as far as possible what you would expect to see when the two half-cells are connected together via a salt-bridge.

(iii) Account for the difference in the calculated and measured overall cell e.m.f in the above voltaic cell. [5]

(c) Keratin belongs to a family of fibrous structural protein. It consists of disulfide bonds and is the key structural material making up the outer layer of human skin.

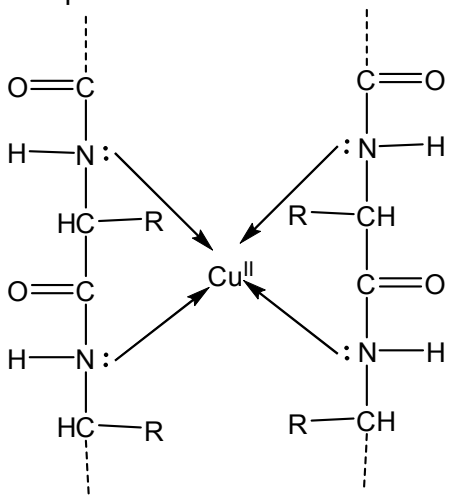
Copper(II) ion is found to be able to disrupt the structure of Keratin. However, together with an aqueous solution of potassium hydroxide and potassium sodium tartarate, copper(II) ion is able to determine the presence of peptide bonds. This test is commonly known as the Biuret Test.

The initial Biuret reagent is blue in colour as aqueous tartrate ions binds to Cu^{2+} as ligands giving the bistartratocuprate(II) complex as shown below.



(i) Explain why the initial Biuret reagent is coloured while an aqueous solution of potassium sodium tartarate is colourless.

(ii) In the presence of proteins, the Biuret reagent reacts with peptide bonds in the proteins to form a complex as shown below:



The solution turns from blue to violet. Suggest what has happened to cause the colour change in the Biuret reagent.

(iii) Explain in chemical terms how the R-group interactions in Keratin are broken in the presence of Cu^{2+} ion.

(iv) Suggest another factor that would affect the R-group interactions in Keratin. Explain your answer briefly in chemical terms. [8]

(d) Aqueous copper(II) sulfate undergoes the following reactions.

$$CuSO_4(aq) \xrightarrow{\text{excess } NH_3(aq)} \mathbf{P} \xrightarrow{\text{excess } KCN(aq)} \underset{\substack{[Cu(CN)_4]^{2-} \\ \text{violet complex}}}{\mathbf{Q}}$$

(i) Construct a balanced equation for the formation of the complex ion **P** and suggest the formula of the complex ion present in **P**.

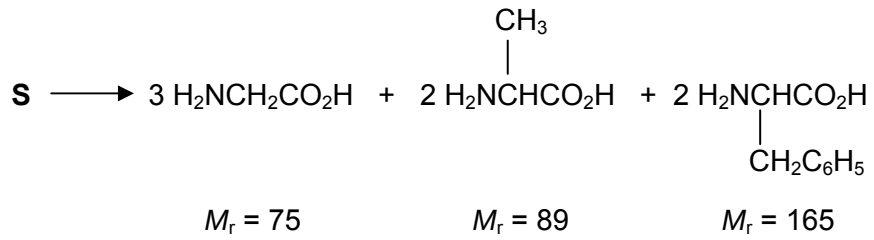
(ii) State the type of ligands bound to Cu^{2+} cation in the violet complex **Q** and hence state the coordination number of the Cu^{2+} cation in **Q**. [2]

[Total:20]

5. **(a)** **(i)** Explain briefly what is meant by the term *tertiary structure of a protein*.

(ii) Describe how proteins can be broken down into amino acids in the laboratory **without** the aid of enzymes. [2]

(b) When a small polypeptide **S** was broken down in this way, three different amino acids were produced according to the following reaction.



(i) How many peptide bonds were broken during this reaction?

(ii) Calculate the M_r of the polypeptide **S**. [2]

(c) Much research has been carried out in recent years investigating the exact structure of silk. Spider silk is a natural structural protein, which belongs to the same group as collagen and keratin. In a postulated model of this structure, the high electron density regions comprise crystalline sub-structures with high β-sheet content.

Spider silk contains a high proportion of the amino acids glycine and alanine.

(i) Draw the structure of the tripeptide Gly-Ala-Gly, showing the displayed structure of the peptide linkages.

(ii) What type of reaction takes place during the formation of a peptide?

(iii) Explain why silk is water repellent.

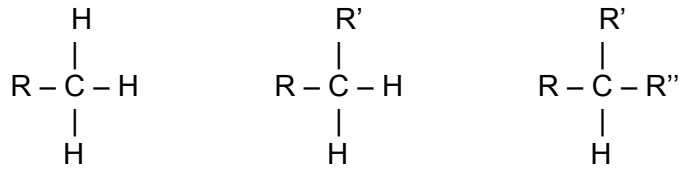
(iv) Describe how a polypeptide chain is held in the shape of a β-pleated sheet. [6]

(d) 'When a mixture of 2,4-dimethylpentane and chlorine is irradiated, reaction starts immediately. However, the reaction does not stop immediately when irradiation stops'.

(i) Account for the above observation.

(ii) State the possible monochlorinated products and predict their mole ratio.

(iii) The hydrogen in an organic molecule can be classified as primary, secondary or tertiary hydrogen as illustrated below.



Primary H Secondary H Tertiary H

You are provided with the following bond dissociation enthalpy data:

Bond	**Bond dissociation enthalpy / kJ mol^{-1}**
H–C*l*	+432
C*l*–C*l*	+243
H–CH_2CH_3	+420
H–$CH(CH_3)_2$	+401
H–$C(CH_3)_3$	+390
C*l*–CH_2CH_3	+338
C*l*–$CH(CH_3)_2$	+339
C*l*–$C(CH_3)_3$	+330

Using the equation for the monochlorination of an alkane below, estimate the respective enthalpy changes of the monochlorination of primary, secondary and tertiary hydrogen atoms in 2,4-dimethylpentane.

$$RH + Cl–Cl \longrightarrow RCl + H–Cl$$

(iv) From your answer in (iii), suggest a factor that could have affected the yield of the monochlorinated products from 2,4-dimethylpentane. Explain your answer.

(v) The mole ratio of 1°, 2° and 3° monochlorinated products was found to be 1.71 : 1: 1.43 experimentally.

Suggest a reason why there is a higher fraction of the 3° monochlorinated product compared to that of the secondary monochlorinated product. [10]

[Total:20]

END OF PAPER

Answers:

1 (a) (i) $PV = nRT$

$m / V = \rho = \dfrac{P \times M_r}{RT}$

$\therefore$ density of $NO_2 = \dfrac{1.01 \times 10^5 \times 46.0}{8.31 \times 298}$

- $= 1880 \text{ g m}^{-3}$ (to 3 s.f)
- $= 1.88 \times 10^{-3} \text{ g cm}^{-3}$

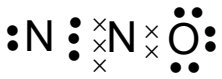
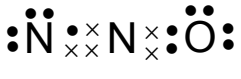
(ii) $NO_2(g) + N_2O(g) \rightarrow 3NO(g)$

- $\Delta H^\theta_r = \sum \Delta H^\theta_f(\text{products}) - \sum \Delta H^\theta_f(\text{reactants})$
  $= 3(+90.4) - (+33.9 + 81.6)$
  $= +155.7 \text{ kJmol}^{-1}$

- At 800 K, $\Delta G_r = \Delta H^\theta_r - T\Delta S^\theta_r$
  $= +155.7 - 800(+171.4 \times 10^{-3})$
  $= +18.6 \text{ kJ mol}^{-1}$

- Since $\Delta G_r > 0$ at 800 K, the reaction is not spontaneous.

(iii)

-  OR 

[Correct number of dots and crosses for N and 2 O atoms.]

- Linear molecule

(b)

- For AgCl to precipitate , $[Ag^+][Cl^-] > 1.8 \times 10^{-10}$
  $(1.8 \times 10^{-2}) \times [Cl^-] > 1.8 \times 10^{-10}$
  $[Cl^-] > 1.8 \times 10^{-8} \text{ mol dm}^{-3}$

- For $PbCl_2$ to precipitate, $[Pb^{2+}][Cl^-]^2 > 1.7 \times 10^{-5}$
  $(2.0 \times 10^{-2}) \times [Cl^-]^2 > 1.7 \times 10^{-5}$
  $[Cl^-] > 2.9 \times 10^{-2} \text{ mol dm}^{-3}$

- AgCl will precipitate out from the solution first as it requires a much smaller concentration of Cl^-.

(c) (i)

- $X^+(g) \rightarrow X^{2+}(g) + e$
- Going down the X^+ ions of Group II, both the nuclear charge and screening effect increase. As the <u>increase in screening effect outweighs the increase in nuclear charge</u>, the effective nuclear charge of the X^+ cations decreases down the group.
- Hence moving down the group, the valence electron in the X^+ cation becomes <u>further away from the nucleus</u> and is <u>less strongly attracted</u>, thus needing less energy for its removal.

(ii)
- Mg^{2+} ion has a <u>higher charge density</u> than Ba^{2+} ion and hence is more polarising. Mg^{2+} ions <u>polarise the large NO_3^- ions to a greater extent</u> and hence causes the N – O bonds to be weakened. Thus $Mg(NO_3)_2$ is less thermally stable and decomposes at a lower temperature than $Ba(NO_3)_2$.
- Equations:
  $Mg(NO_3)_2 \rightarrow MgO + ½\ O_2 + 2NO_2$
  $Ba(NO_3)_2 \rightarrow BaO + ½\ O_2 + 2NO_2$

(iii)
- **M** is magnesium.
- $MgCO_3$ undergoes <u>decomposition</u> when heated. Since it forms $CO_2(g)$ which escapes when it is formed, there is a loss in mass during heating.
  $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$
- When **X** which is MgO is added to water, it reacts to form <u>insoluble $Mg(OH)_2$</u>. As the concentration of aqueous OH^- is low, the resulting solution is only weakly alkaline.
  $MgO + H_2O \rightarrow Mg(OH)_2$
- Adding $H_2SO_4(aq)$ to the above mixture produces <u>$MgSO_4$ which is soluble in water</u>. Hence no precipitate is observed.
- 1 mark for the two equations for decomposition of $MgCO_3$ and reaction of MgO with water.

2 **(a)** $NaOH(s) + aq \rightarrow NaOH(aq)$

$\Delta H_{sol} = \Delta H_{f\ of\ NaOH\ (aq)} - \Delta H_{f\ of\ NaOH\ (s)} = -470 - (-425)$

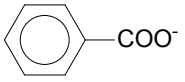
● $= -45.0\ kJ\ mol^{-1}$

Number of moles of NaOH = $\frac{10.0}{40}$ = 0.250 mol

- Heat evolved = 45 x 0.25 = 11.3 kJ
- Temperature increase = $\frac{Q}{mc} = \frac{11.3 \times 1000}{(250)(4.18)}$ = 10.8 °C

(b) **(i)** $[H^+] = \sqrt{K_a.c} = \sqrt{10^{-8.35} \times 0.1} = 2.11 \times 10^{-6}\ mol\ dm^{-3}$

- $pH = -lg[H^+] = 4.68$

(ii)
- Benzoic acid is a <u>stronger acid</u> as it has a lower pK_a value.
- For phenoxide ion formed from the dissociation of 3-nitrophenol, the lone pair of electrons on oxygen is delocalised into the benzene ring and the nitro group being electron withdrawing further disperses the negative charge on the phenoxide ion resulting in a stable anion formed. However benzoic acid is a stronger acid as  is <u>more stable</u> than phenoxide ion due to the <u>delocalisation of negative charge over two electronegative oxygen atoms</u>, resulting in a much more stabilised ion as the <u>negative charge is better dispersed and is more likely to release H^+.</u>

(iii) ● Phenolpthalein and bromothymol blue are both weak acids. Small amounts are used so that it will not affect accuracy of the end-point titre value. (If larger amounts are used, a larger titre value will be obtained)

(iv) ● **A**: pH = 4.20 ● **B**: Volume of titre = 7.20 cm^3

(v) (first endpoint with bromothymol blue)

● concentration of benzoic acid = (14.40/1000 x 1) / (25.0/1000)

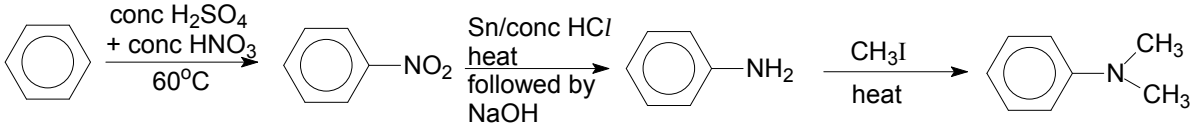
= 0.576 mol dm^{-3}

(second endpoint with phenolphthalein)

● concentration of 3-nitrophenol = (7.60/1000 x 1) / (25.0/1000)

= 0.304 mol dm^{-3}

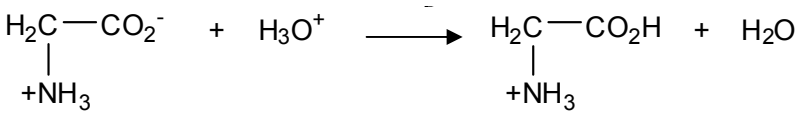
(c) ●●●



(d) **(i)** ● Buffers are solutions that resist changes in pH upon additions of <u>small</u> amounts of acid or alkali.

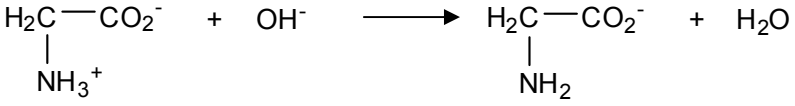
(ii) ● $H_3\overset{+}{N}–CH_2–COO^-$

(iii) ● When small amounts of acid is present,



H^+ is removed thus there is negligible change in pH.

● When small amounts of base is present,



OH^- is removed thus there is negligible change in pH.

(iv) ● $2CH_4 + 2H_2O + NH_3 \rightarrow H_2NCH_2COOH + 5H_2$

(v) ● Large amounts of energy is required to break the strong covalent bonds.

OR Energy is required to overcome activation energy for the reaction

OR Energy is required to break the covalent bonds to form free radicals

(also can be accepted)

3. **(a)**

- Solution formed is <u>orange (pH~3-4).</u>
- $AlCl_3$ undergoes <u>both hydration and hydrolysis</u> as <u>Al^{3+} has a high charge density</u>, hence a <u>high polarizing power</u>. It draws electrons away from its surrounding water molecules and weakens the O-H bond.

$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

$[Al(H_2O)_6]^{3+}(aq) \rightarrow [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq)$

- 1 mark for both equations

(b) **(i)**

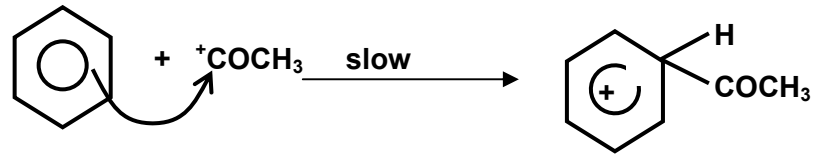
- No, because Al_2Cl_6 is not <u>electron-deficient</u> and is unable to <u>accept a lone pair to form a dative bond</u>.

(ii)

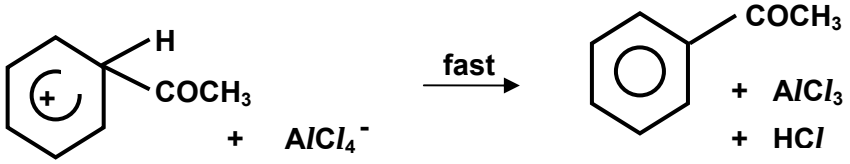
- Step 1: Generation of electrophile

$AlCl_3 + CH_3COCl \rightleftharpoons {}^+COCH_3 + AlCl_4^-$

- Step 2:



- Step 3:



(c) **(i)**

- $SiCl_4$ is a <u>(simple) covalent chloride</u> that <u>undergoes hydrolysis</u> in water. Hydrolysis occurs due <u>to energetically accessible vacant 3d-orbitals</u> available for dative bonding with water.

(ii)

- $SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$
- The standard entropy change is positive because <u>4 moles of gas is being produced</u> in the reaction, <u>increasing the degree of randomness / disorderliness</u> of the system.

(iii)

- $SiCl_4 + 4CH_3OH \rightarrow Si(OCH_3)_4 + 4HCl$
- <u>Steamy white fumes</u> will be observed.

(d)

- Since there are <u>5 σ bonds</u> (5 electron pairs) around P, there should be 5 hybrid orbitals. Since there is only 1 3s orbital and 3 3p orbitals, the fifth orbital has to be a 3d orbital. Hence type of hybridization is <u>sp^3d.</u>

(e) **(i)**

- **Y** liberates white fumes with PCl_5, therefore it contains <u>–OH group</u>.
- **Y** forms orange ppt with Brady's reagent, therefore it contains a carbonyl group. **Y** does not react with Tollen's reagent, therefore it can only be a <u>ketone</u>.
- **Y** forms a yellow ppt in the tri-iodomethane test, hence it contains either <u>CH_3CO-R or $CH_3CH(OH)$-R</u> where R is H or an alkyl chain.
- **Y** is oxidised to form a carboxylic acid, hence it must contain a <u>primary alcohol</u>.

Therefore, **Y** must be

- $CH_3COCH_2CH_2OH$

(ii)
- His choice of chemical test was <u>inappropriate</u> because the PCl_5 would have <u>undergone hydrolysis</u> to form phosphoric and hydrochloric acid.
- $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

4. (a) (i)
- Anode : $Li \rightarrow Li^+ + e^-$
- Cathode : $Cu_2O + H_2O + 2e^- \rightarrow 2Cu + 2OH^-$

(ii)
- $\mathbf{E_{Li^+/Li}} = -3.04V$
  $E_{cell} = E_{red} - E_{oxid}$
  $+2.30 = \mathbf{E_{Cu_2O/Cu}} - (-3.04)$
  $\mathbf{E_{Cu_2O/Cu}} = 2.30 - 3.04 = -0.74V$

Assumptions made:
- 298K (25^{o}C) &
  Concentration of aqueous alkaline electrolyte = 1.0 moldm^{-3}

(iii)
- <u>Li</u>, being a Group I metal is reactive and would <u>react with water in the aqueous electrolyte</u>. Hence the Li anode has to be immersed in an organic electrolyte.

(b) (i)
- $Pt(s) \mid CO_2(g) \mid H_2C_2O_4(aq) \parallel Cu_2^+(aq) \mid Cu(s)$

(ii)
1) <u>Effervescence/ Bubbles of CO_2 gas</u> will be seen around the <u>anode</u> (Pt electrode)
2) Reddish-brown <u>Cu electrode</u> will <u>increase in size</u> (grow thicker)
3) <u>Blue colour</u> in the aqueous <u>solution</u> will <u>fade</u> as $[Cu^{2+}]$ decreases.

3 points – 2 marks; 2 points – 1mark; 0 -1 points – 0 mark.

(iii) $Cu^{2+} + 2e^- \rightleftharpoons Cu$
$E^{\ominus}_{Cu^{2+}/Cu} = +0.34$ V (when $[Cu^{2+}] = 1$ mol dm^{-3})

- As the concentration of Cu^{2+} is at 2.0 mol dm^{-3}, <u>by Le Chatelier's Principle</u>, the system will try <u>to decrease the concentration of Cu^{2+}</u> by <u>shifting the position of the above equilibrium to the right</u>. The tendency of Cu^{2+} to be reduced is increased and the actual <u>$E_{Cu^{2+}/Cu}$ is more positive</u> than +0.34 V.

- Since measured $E_{cell} = E_{Cu^{2+}/Cu} - E_{CO_2/H_2C_2O_4}$, the value of E_{cell} would be more positive than +0.83 V.

(c) (i)

- Biuret reagent is a complex ion where aqueous tartrate ions bind to Cu^{2+} ion. Cu^{2+} ion contains partially filled 3d-orbitals where in the presence of ligands, it causes a splitting of the energy of 3d-orbitals into 2 groups with an energy gap between them, ΔE. (crystal field splitting).

- When a d-electron from lower energy group is promoted to the higher energy group (*d-d electron transition*), radiation in the *visible* region of the electromagnetic spectrum corresponding to ΔE is absorbed.
  Hence, the light energy not absorbed will be seen as the colour of the complex. (Complementary colour observed).

- For potassium sodium tartarate, it does not have electrons in the 3d-orbitals and hence these d-d electron transitions would not occur, thus no radiation in the visible region of the electromagnetic spectrum would be absorbed. Hence, these compounds are colourless.

(ii)

- Ligand exchange has occurred.
- Different ligands cause splitting of the d-orbitals resulting in different energy gaps, which correspond to different wavelengths of visible light being absorbed. Hence different colours are observed.

(iii)

- Heavy metal ions such as Cu^{2+} can combine reversibly with the –SH groups in cysteine residues, hence disrupting disulfide bonds.

OR

- Heavy metal ions such as Cu^{2+} can form ionic bonds with the carboxylic acid anions on the side chain of the protein molecule. This will disrupt ionic bonds formed between the side chains of the protein molecule.

(iv)

- By heat
- An increase in temperature causes an increase in kinetic energy and vibration of molecules. This disrupts the whole range of weak interactions (hydrogen bonds, van der Waals attractions, ionic bonds and disulfide linkages) responsible for maintaining the secondary, tertiary and quaternary structure of Keratin.

OR

- By extreme pH changes
- The extreme pH changes can change the charges on the amino acid residues by protonating or deprotonating the R-groups on the side chain of the proteins (e.g. carboxylic acid group in glutamic acid residue or the amino groups of the side chain in lysine residue). This will disrupt the ionic bonds or hydrogen bonds between the side chains of the protein molecule.

(d) (i)

- $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

<u>OR</u>

$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 6H_2O$

Because of context of question, equations starting from $Cu(OH)_2$ cannot be accepted.

(ii)

- CN^- - Monodentate
  Coordination number = 4

5 **(a)** **(i)**

- The overall 3-dimensional shape of a protein formed by the folding of the secondary structure of the protein to minimize exposure of the hydrophobic groups and expose the hydrophilic groups to water. The folds are held by ionic, disulphide, hydrogen bonding or van der Waals interactions.

(ii)

- Reflux with NaOH(aq) or HC*l* for several hours

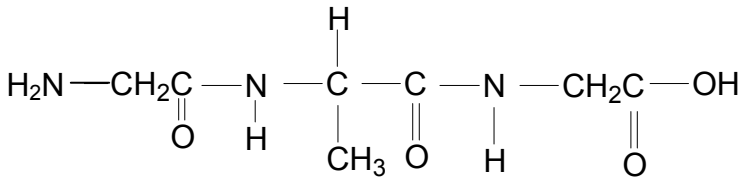
(b) **(i)**

- 6

(ii)

- M_r = 3 × 75 + 2 × 89 + 2 × 165 – 6 × 18
  = 625

(c) **(i)**

- 

(ii)

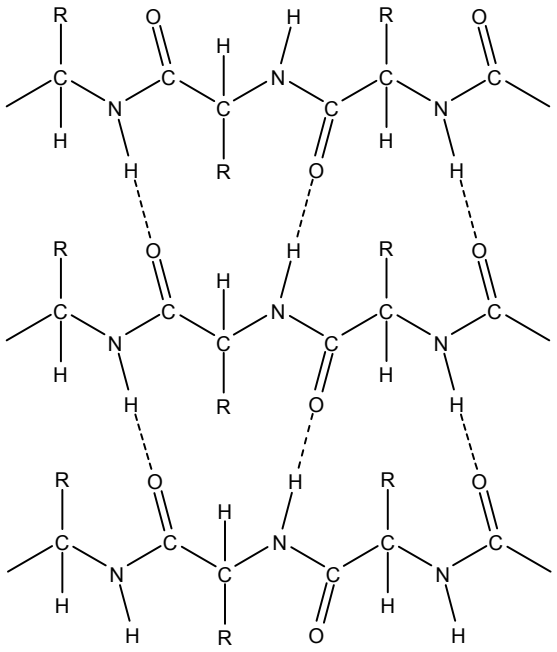
- Condensation

(iii)

- The highly electronegative N and O in the structure is involved in hydrogen bonding to form the secondary and tertiary structures and hence not able to form hydrogen bonds with water molecules.
- The exposed R groups are non-polar and hence silk is hydrophobic.

(iv)

- diagram showing alternating R groups, zig zag shape and hydrogen bonding clearly labelled
- Mention hydrogen bonding in description or in diagram



(d) **(i)**

- Irradiation of Cl_2 results in homolytic cleavage to give Cl radicals which are highly reactive. Reaction starts immediately. When irradiation stops, the
- radicals are still being regenerated and the reaction continues.

•• Mole ratio of 1°, 2° and 3° monochlorinated products 6 : 1 : 1

(iii) $\Delta H = -\Delta H_{RCl} - \Delta H_{HCl} + \Delta H_{RH} + \Delta H_{Cl\text{-}Cl}$

- For 1° Hydrogen $\Delta H = -107$ kJ mol^{-1}
- For 2° Hydrogen $\Delta H = -127$ kJ mol^{-1}
- For 3° Hydrogen $\Delta H = -129$ kJ mol^{-1}

(iv)

- From (iii), the enthalpy change becomes more negative for the substitution of 1° to 3° hydrogen implying that the formation of 2-chloro-2,4-dimethylpentane
- is more spontaneous. A factor that could give rise to this result is the strength of C-H bonds/relative stability of the alkyl radicals.

(v)

- The tertiary hydrogen radical formed is more stable than the secondary hydrogen radical.