Class Adm No

Candidate Name: ____________________

millennia institute

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **18th Sept 2018**

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Section A – Answer **all** questions.

Section B – Answer **one** question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

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

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

The number of marks is given in brackets [ ] at the end of each question or part question.

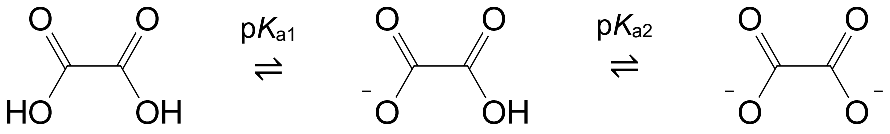
Question	**Section A**			**Section B**		Total
	1	**2**	**3**	**4**	**5**	
Marks	**23**	**20**	**17**	**20**	**20**	**80**

This question paper consists of **11** printed pages and **1** blank page.

Section A

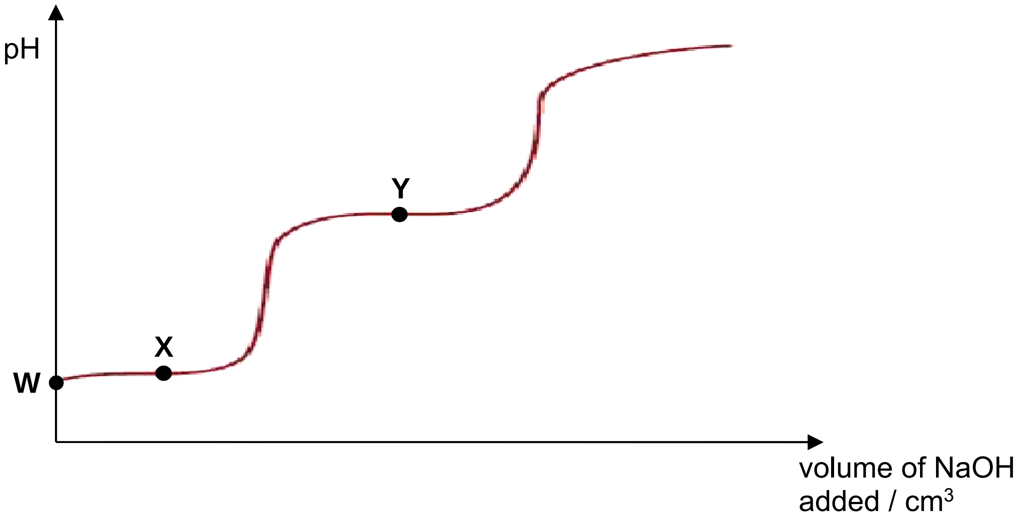
Answer **all** questions from this section.

1 Oxalic acid is a weak diprotic Brønsted acid with $\text{p}K_{a1}$ and $\text{p}K_{a2}$ values of 1.25 and 4.14 respectively.



25 cm^3 of 0.50 mol dm^{-3} oxalic acid was titrated against a solution of 1 mol dm^{-3} of sodium hydroxide. Only 1 to 2 drops of phenolphthalein indicator was used in this titration. It was found that the first colour change occurred at 19.40 cm^3.

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



(a) Suggest why the value of $\text{p}K_{a2}$ is larger than $\text{p}K_{a1}$. [2]

Removal of H^+ for $\text{p}K_{a2}$ is from a negatively charged species while that for $\text{p}K_{a1}$ is from a neutral species, hence dissociation for $\text{p}K_{a2}$ is more difficult / $(COOH)COO^-$ is less acidic than $(COOH)_2$ and the value of $\text{p}K_{a1}$ is larger.

or

The first conjugate base of oxalic acid is stabilised by an intramolecular ion-dipole interaction with the OH group of $(COOH)COO^-$, hence dispersing the negative charge to a greater degree and increasing the acid strength. Thus the first $\text{p}K_a$ value is smaller than the second $\text{p}K_a$ as the second conjugate base formed does not have this extra stability.

(b) **(i)** Calculate the value of pH at point **W**. [1]

$[H^+] = \sqrt{(10^{-1.25})(0.50)}$
$= 0.1677$ mol dm^{-3}
pH = 0.776

(ii) Given that the pH at point **X** is 1.25, calculate the volume of NaOH added at point **X**. [2]

Amount of oxalic acid = 0.50 x $\frac{25}{1000}$
= 0.0125 mol

pH = pK_{a1} + log $\left(\frac{[\text{salt}]}{[\text{acid}]}\right)$

Let x be the amount of salt $(COOH)COO^-$, which is also the amount of NaOH added.

1.25 = 1.25 + $\log\left(\frac{x/V}{(0.0125-x)/V}\right)$

$\frac{x}{0.0125-x}$ = 1

x = 0.00625 mol

vol. of NaOH added = $\frac{0.00625}{1}$
= 6.25 cm^3

or

pH = pK_{a1}, **X** is at MBC, which occurs at HEP(1).

Amount of oxalic acid reacted = 0.0125/2 = 0.00625 mol

= Amount of NaOH added

vol. of NaOH added = $\frac{0.00625}{1}$
= 6.25 cm^3

or

Since pH = pK_{a1}, **X** is at MBC, which occurs at HEP(1).

Since EP(1) vol. of NaOH = $\left(\frac{0.0125}{1}\right)$ = 0.0125 dm^3 = 12.5 cm^3

vol. of NaOH added at HEP(1) = 12.5/2 = 6.25 cm^3

(c) **(i)** Define the term *buffer*. [1]

A buffer is a solution which is able to resist pH changes when small quantities of acid or base are added.

(ii) Write an equation to illustrate how the reaction mixture found at point **Y** can maintain the pH of a solution when a small amount of $OH^-(aq)$ is added. [1]

$(COOH)COO^- + OH^- \rightarrow (COO^-)COO^- + H_2O$

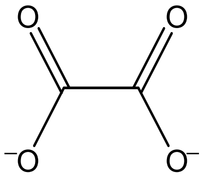
(d) **(i)** Describe how you would recognise the end point of the titration described. [1]

Colourless solution turns pale pink.

(ii) Explain why only 1 or 2 drops of phenolphthalein indicator was used in the titration. [1]

Indicators are weak acids/bases. Addition of more indicator could cause a significant change in the pH of the solution, affecting the accuracy of the titration.

The oxalate ion, $C_2O_4^{2-}$, is known to form complexes with transition metal ions such as platinum(II). The structure of the oxalate ion is as follows.



(e) **(i)** It is observed that a solution of aqueous platinum(II) ions turns universal indicator orange.

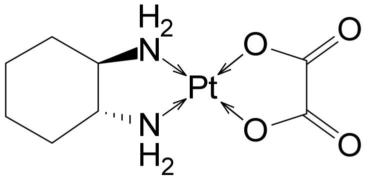
Given that platinum(II) is a transition metal ion known to form **square planar complexes**, explain the observation seen with the aid of a chemical equation. [3]

In water, Pt^{2+} exists as the tetraaqua complex $[Pt(H_2O)_4]^{2+}$

$[Pt(H_2O)_4]^{2+} \rightarrow [Pt(H_2O)_3(OH)]^{+} + H^{+}$

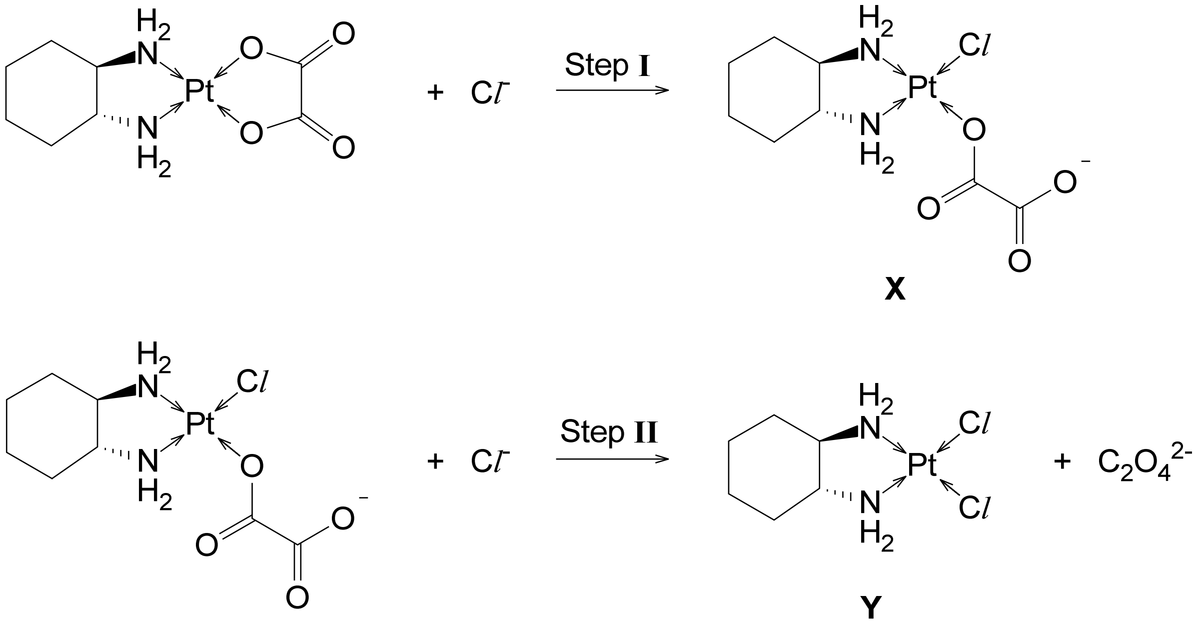
Transition metal ions such as Pt have a <u>high charge density</u> and can polarise the H_2O ligands to release H^+, making the solution <u>acidic</u>.

Oxaliplatin is a platinum(II) based anti-cancer drug used to treat colorectal cancer. It contains one $C_2O_4^{2-}$ ligand.



oxaliplatin

When a **concentrated** Cl^- solution is added to oxaliplatin, ligand exchange occurs and the Cl^- ligands take the place of $C_2O_4^{2-}$ in a two-step reaction.



(ii) By consideration of entropy changes, predict with explanation if Step **I** is likely to be **feasible** if diluted Cl^- solution was used instead. Assume that Cl^- and $C_2O_4^{2-}$ have the same ligand strength.

State the missing numerical data necessary to confirm your prediction. [2]

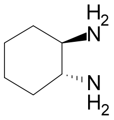
Not feasible, as entropy change of the ligand exchange reaction is negative / reaction is entropically disfavoured due to a decrease in the number of particles.

Enthalpy change of the ligand exchange reaction.

accept ΔG; BE(Pt-Cl) and BE(Pt-O)

(iii) Determine if any the three complexes, oxaliplatin, **X** and/or **Y** can exhibit cis-trans isomerism. Explain your answer. [2]

None of the three complexes can exhibit cis-trans isomerism.

The bidentate  ligand cannot be forced into a trans conformation. *OWTTE*

(iv) Hydrated crystals of complex **Y** have the structural formula $[Pt(C_6H_{14}N_2)Cl_2].2H_2O$.

When excess $AgNO_3$ solution was added to an aqueous solution containing 0.0094 mol of an isomer of $[Pt(C_6H_{14}N_2)Cl_2].2H_2O$, 1.35 g of a white precipitate was obtained.

Determine the structural formula of this isomer. [3]

Amount of $AgCl$ = 1.35 / (107.9+35.5) = 0.009414 mol
= Amount of free Cl^-

∴ 1 mol of isomer contains 1 mol of free Cl^-.

$[Pt(C_6H_{14}N_2)(Cl)(H_2O)]^+Cl^-.H_2O$

(f) **(i)** Determine the number of protons, neutrons and electrons in $^{52}Cr^{3+}$. [1]

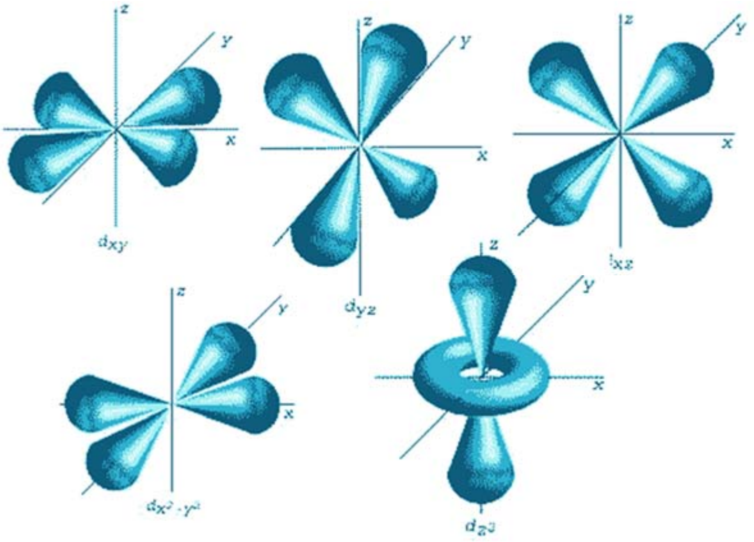
24 protons, 28 neutrons, 21 electrons

(ii) State the full electronic configuration of $^{52}Cr^{3+}$. [1]

$1s^22s^22p^63s^23p^63d^3$

(iii) Draw and label the d orbitals in the valence shell of $^{52}Cr^{3+}$.

You are required to show the orientation of the orbitals with respect to the x, y and z axes. [2]



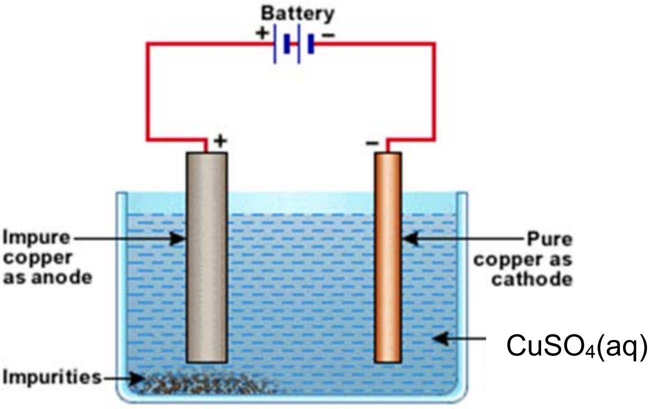
[Total: 23]

2 **(a)** State the relationship between the Faraday constant, *F*, the charge on the electron, *e*, and the Avogadro number, *L*. [1]

$F = Le$

(b) Copper metal containing impurities such as zinc, iron, and silver can be purified via electrolysis.

(i) Draw a **well-labelled** diagram of a suitable set-up for purifying impure copper and state the reaction occurring at the cathode. [3]



Cathode reaction: $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$

A fixed current was passed through the cell for a duration of time to determine the experimental values of *F* and *L*. The following are the results obtained.

current passed through the cell = 0.500 A
duration of time = 30.0 min
change in mass of cathode = 0.299 g

(ii) Use the data above and relevant information from the *Data Booklet* to calculate a value of *L*. [3]

$Q = It = 0.500 \times 30.0 \times 60 = 900C$

Amount of copper deposited = 0.299 / 63.5 = 0.004709 mol
$Cu^{2+} + 2e^- \rightarrow Cu$
Amount of e^- = 0.004709 x 2 = 0.00942 mol
$Q = nF$
$F = 900 / 0.00942 = 95568.5$

$F = Le$
$L = 95568.5 / 1.602 \times 10^{-19} = 5.97 \times 10^{23}$ (3 sf)

(c) Rechargeable lithium ion batteries have been developed in Japan.

The standard electromotive force of a rechargeable lithium ion battery is 3.70 V. During discharge, Li^+ ions flow from the anode to the cathode through the electrolyte.

During the **discharging** process, the ion-electron equation at the cathode is

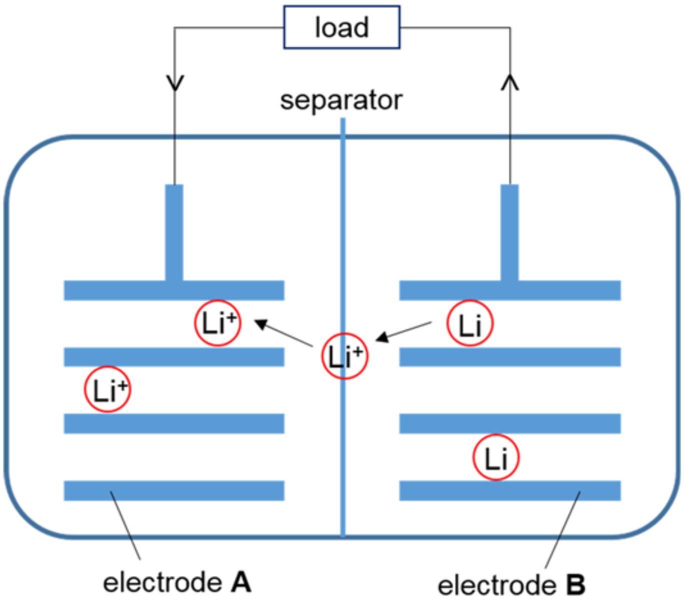
$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2,$$

and the ion-electron equation at the anode is

$$LiC_6 \rightarrow C_6 + Li^+ + e^-$$

where CoO_2 and graphite, C_6, are *layered* solid electrodes which can have Li^+ ions and Li atoms **embedded between their layers** respectively.

A schematic of the rechargeable lithium ion battery **during discharge** is shown below.



(i) By considering the overall equation of the battery during discharge, calculate a value for the standard Gibbs free energy of the reaction in kJ mol^{-1}. [1]

$CoO_2 + Li \rightarrow LiCoO_2$ *or* $CoO_2 + LiC_6 \rightarrow LiCoO_2 + C_6$ [no marks awarded]

$\Delta G = -nFE = -1 \times 96500 \text{ C mol}^{-1} \times 3.70\text{V} = -357 \text{ kJ mol}^{-1}$

(ii) A fully charged battery cell starts with 10.0 g of CoO_2 and 10.0 g of LiC_6.

Calculate the mass of electrode **A** when this cell is fully **discharged**. [3]

Electrode **A** is CoO_2 / $LiCoO_2$.

Amount of CoO_2 (charged) = 10.0 / [58.9 + 2(16.0)]
= 0.1100 mol

Amount of LiC_6 (charged) = 10.0 / [6.9 + 6(12.0)]
= 0.1267 mol
= Amount of Li^+ available

CoO_2 is the limiting reagent / Li^+ is in excess.

Amount of $LiCoO_2$ (discharged) = 0.1100 mol
Mass of $LiCoO_2$ (discharged) = 0.1100 x [6.9 + 58.9 + 2(16.0)] = 10.8 g (3 sf)

(iii) The fully discharged cell is plugged into a power source to recharge it. During the charging process, the direction of electron-flow is reversed.

Determine the mass of electrode **B** when the cell is fully **charged**. [1]

Electrode **B** is C_6 / LiC_6.
Mass of LiC_6 = 10.0 g ;

(iv) Suggest **two** reasons why water cannot be used as the electrolyte solvent in rechargeable lithium ion batteries. [2]

1. Water will undergo electrolysis to produce H_2 and O_2
2. Lithium reacts violently with water

(v) Rechargeable lithium ion batteries tend to perform poorly when used in cold countries. Suggest a reason for this. [1]

Rate of reaction / discharge / flow of ions is lowered when temperature decreases.

(d) Lithium oxide is a white solid that is used to lower the melting point of ceramic glazes.

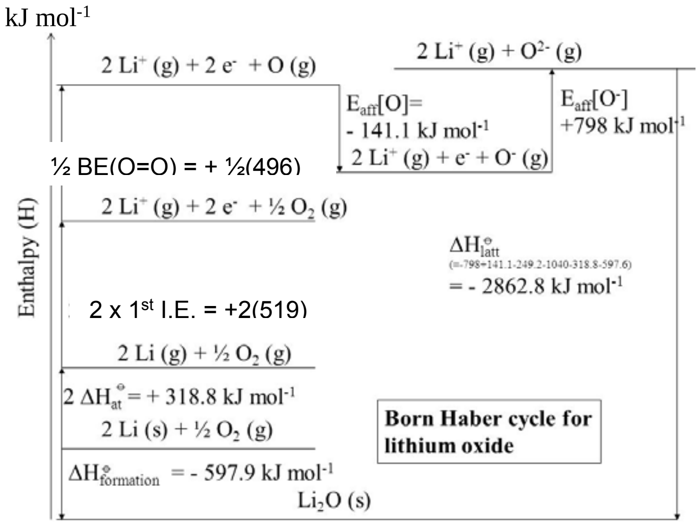
(i) Write an equation, with state symbols, to represent the lattice energy of lithium oxide. [1]

$2Li^+(g) + O^{2-}(g) \rightarrow Li_2O(s)$

(ii) Use the following data, together with appropriate data from the *Data Booklet*, to calculate a value for the lattice energy of lithium oxide.

1st electron affinity of oxygen = -141.1 kJ mol^{-1}
2nd electron affinity of oxygen = +798 kJ mol^{-1}
enthalpy change of atomisation of lithium = +159.4 kJ mol^{-1}
enthalpy change of formation of lithium oxide = -597.9 kJ mol^{-1}

[4]

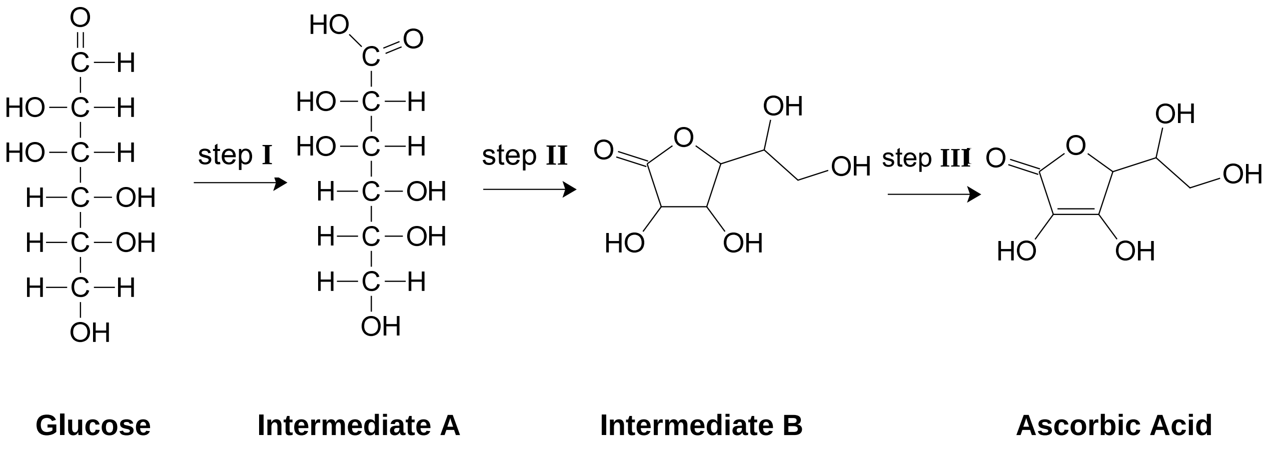


L.E. = -798 – (-141.1) – ½(496) – 2(519) – 2(159.4) + (-597.9)
= -2859.6 kJ mol^{-1}
= -2860 kJ mol^{-1} (3 sf)

[Total: 20]

3 Ascorbic acid, also known as Vitamin C is required for the synthesis of collagen in humans. A vitamin C deficient diet leads to a disease called scurvy. Ascorbic acid is known to be water soluble and is commonly used as a food additive.

The building block for ascorbic acid is the glucose molecule. The following synthetic pathway for the formation of ascorbic acid was proposed.



(a) State the functional groups present in intermediate **B**. [2]

Ester, 2^0 alcohol, 1^0alcohol

(b) State the reagent and conditions required for step **II**. [1]

Conc. H_2SO_4, heat

(c) State the type of reaction for steps **I** and **II**. [2]

Step I: oxidation

Step II: condensation / nucleophilic (acyl) substitution

(d) Identify the type(s) of stereoisomerism shown by ascorbic acid. State the total number of possible stereoisomers. [2]

Enantiomerism.

total number of possible stereoisomers = $2^2 = 4$

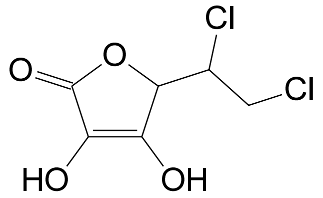
(e) Explain why ascorbic acid is water soluble. [2]

Energy released from the hydrogen bonding between ascorbic acid and water

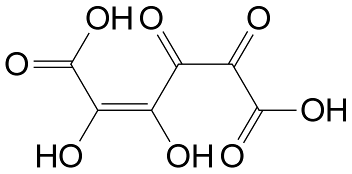
is sufficient to overcome the hydrogen bonding between ascorbic acid molecules and hydrogen bonding between water molecules. Hence, ascorbic acid is water soluble.

(f) Draw the structural formulae of all the organic products formed when ascorbic acid is treated with the following reagents. [3]

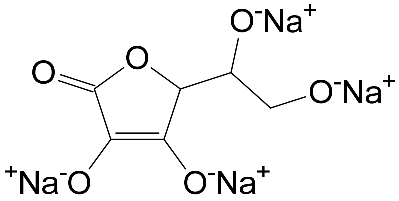
(i) PCl_5



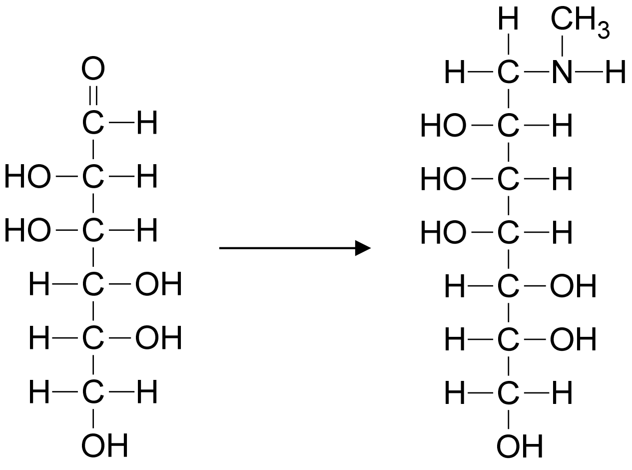
(ii) excess hot acidified $K_2Cr_2O_7$



(iii) Na(s)



(g) Compound **L** can be formed from glucose.



glucose **L**

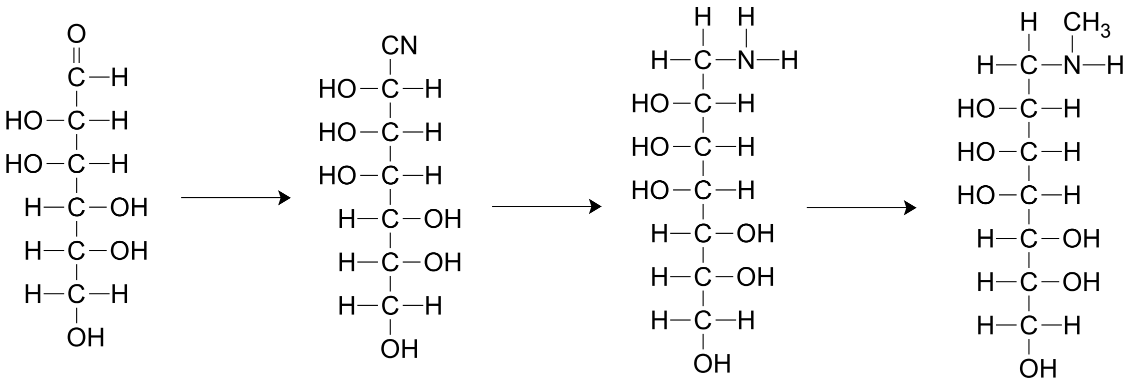
Suggest a synthetic route, involving *not more than three steps*, from **glucose** to **L**.

In your answer, suggest the reagents and conditions involved in each step and draw the structural formulae of the intermediate organic products. You may use R to represent the side chain of the compound that is not involved in the reaction. [5]

Step1: HCN, trace amount of NaOH, cold

Step 2: $LiAlH_4$ in dry ether

Step 3: Limited CH_3Cl, heat



[Total: 17]

Section B

Answer **one** question from this section.

4 In the chlor-alkali industry, 19.8 g impure sample of NaC*l*(s) was dissolved in 150 cm^3 water to form sodium chloride solution. 50 cm^3 of the solution was electrolysed to produce chlorine, sodium hydroxide, and hydrogen.

$$2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH + H_2$$

The pure chlorine gas reacts with hydrogen gas to produce 1.8 g of hydrogen chloride gas in the presence of ultraviolet light.

(a) **(i)** Write an equation to show the production of hydrogen chloride gas. [1]

$Cl_2 + H_2 \rightarrow 2HCl$

(ii) Explain why ultraviolet light is required in the production of hydrogen chloride. [1]

Ultraviolet light provides sufficient energy to break the C*l*-C*l* bond to form the chlorine radicals for the reaction to start.

(iii) State the type of mechanism for the reaction between chlorine gas and hydrogen gas.[1]

Free radical substitution

(iv) Calculate the number of hydrogen chloride molecules produced at room temperature and pressure. [1]

Amount of hydrogen chloride = 1.8/36.5 = 0.0493 mol

Number of hydrogen chloride = 0.0493 x 6.02 x 10^{23} = 2.97 x 10^{22}

(v) Calculate the percentage of sodium chloride present in the impure solid, assuming that all of the chlorine gas and hydrogen gas had reacted. [3]

$HCl : Cl_2 : H_2 : NaCl$

2 : 1 : 1 : 2

Amount of sodium chloride in 50 cm^3 = 0.04931 mol

Amount of sodium chloride in 150 cm^3 = 0.04931 x 3 = 0.1479 mol

Mass of NaC*l* = 0.1479 x (23.0 + 35.5) = 8.654 g

% purity of NaC*l* = 8.654/19.8 x 100% = 43.7% (3 sf)

(b) Hydrogen chloride gas can also be produced by the reaction between concentrated sulfuric acid and dilute hydrochloric acid.

State the role of concentrated sulfuric acid. [1]

Dehydrating agent.

(c) Explain why hydrogen chloride has a lower boiling point than hydrogen bromide. [2]

Both HC*l* and HBr have simple molecular structures. HBr has a larger and more polarisable electron cloud / larger number of electrons compared to HC*l*,

thus more energy is needed to overcome the stronger instantaneous dipole-induced dipole forces of attraction between HBr molecules. Hence, HC*l* has a lower boiling point than HBr.

(d) When an equimolar mixture of gaseous ammonia and gaseous hydrogen chloride at an initial total pressure of 2.5 atm was injected into a chamber maintained at 400 °C, white crystals of ammonium chloride were formed as shown in the following dynamic equilibrium:

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s) \qquad \Delta H > 0$$

It was found that 84% of the gases had dissociated at equilibrium.

(i) Define the term *dynamic equilibrium*. [1]

Dynamic equilibrium refers to a reversible reaction in which the rates of the forward and backward reactions have become equal and there is no net change in the concentrations of the products and reactants.

(ii) Write an expression for the equilibrium constant, K_p, for this reaction. [1]

$$K_p = \frac{1}{P_{NH3}P_{HCl}}$$

(iii) Calculate the value of K_p at 400 °C, giving its units. [2]

100-84 = 16% of each gas remained at equilibrium.

Since V and T are constant, $P \propto n$.

Equilibrium pressure of HC*l* = $NH_3 = \frac{0.16 \times 2.5}{2} = 0.2$ atm

$$K_p = \frac{1}{P_{NH3}P_{HCl}}$$

$$= \frac{1}{(0.2)^2}$$

$$= 25 \text{ atm}^{-2}$$

(iv) State and explain how the partial pressure of the gases and the value of K_p would change if the following changes were made separately:

I. the temperature of the chamber was halved to 200 °C
II. the volume of the chamber was increased (at constant temperature)
III. 2 atm of neon gas is inserted into the chamber [6]

I. By Le Chatelier's Principle, when temperature decreases, the system increases the temperature of the system by favouring the exothermic backward reaction. Position of equilibrium shifts to the left,
partial pressure of the gaseous reactants increases and the value of K_p decreases.

or

When temperature decreases at constant volume, total pressure decreases and partial pressure of the gases decrease. Hence K_p increases.

II. When the volume of the chamber increases, the pressure of the chamber decreases. By Le Chatelier's Principle, the system increases the pressure of the system by favouring the backward reaction to produce more gaseous particles. Position of equilibrium shifts to the left,
partial pressure of the gaseous reactants increases. Value of K_p does not change as temperature is constant.

or

When volume increases at constant temperature, total pressure decreases and partial pressure of the gases decrease. K_p does not change as temperature is constant.

III. When 2 atm of neon gas is inserted, the partial pressure of the gases and K_p remains unchanged
since neon is an inert noble gas and does not react with the other gases in the chamber.

[Total: 20]

5 **(a)** The reaction between propanone, CH_3COCH_3, and bromine, Br_2, in the presence of acid, H^+, is found to have an overall order of reaction of 2.

(i) Given that rate is independent of the bromine concentration, write **three** possible rate expressions for this reaction. [3]

(1) Rate = k $[CH_3COCH_3][H^+]$
(2) Rate = k $[CH_3COCH_3]^2$
(3) Rate = k $[H^+]^2$

(ii) Three separate experiments were carried out. In each experiment, the concentration of one of the three different reactants was doubled respectively.

Predict the effect of doubling the concentration of each reactant on the rate of reaction for the **first** rate expression you have written in **(a)(i)**. [2]

Ecf from rate equation

(1) $[CH_3COCH_3]$ doubles, rate doubles **and** $[H^+]$ doubles, rate doubles
$[Br_2]$ doubles, no effect on rate

(2) $[CH_3COCH_3]$ doubles, rate quadruples
$[Br_2]$ or $[H^+]$ doubles, no effect on rate

(3) $[H^+]$ doubles, rate quadruples
$[CH_3COCH_3]$ or $[Br_2]$ doubles, no effect on rate

(iii) The table below shows how the concentration of propanone changes with time in a reaction.

Time / min	[propanone] / mol dm^{-3}
5.0	1.6
7.0	1.4
9.0	1.2
12.0	1.0
15.0	0.8
18.5	0.6
21.5	0.5
25.0	0.4
28.0	0.3
35.0	0.2

Without plotting a graph, use the data given in the table to confirm that the reaction is first order with respect to propanone. Show your working clearly. [2]

Constant half life

At least two sets of data to justify statement
e.g. [ ] from 1.6 to 0.8 mol dm^{-3} 10 min, 0.8 to 0.4 10min , 0.4 to 0.2 10min

(iv) The overall reaction described in **(a)** is:

$$CH_3COCH_3(aq) + Br_2(aq) \xrightarrow{H^+} CH_3COCH_2Br(aq) + HBr(aq)$$

State **one** dependent variable that you can readily measure in order to follow the progress of the reaction. [1]

Colour intensity / absorbance of aq bromine

(v) State and explain the role of acid in this overall reaction. [2]

Catalyst.

Increases rate of reaction by lowering activation energy.

(b) Similar to bromine, halogens like fluorine and chlorine are not naturally found in their elemental form due to their high reactivity.

(i) State and explain the trend in atomic radius down the halogen group. [2]

Atomic radius increases down Group 17.

Down the group, the number of principal quantum shells increases and the distance between the valence electron and the nucleus increases / effective nuclear charge decreases as the increase in screening effect outweighs the effect of increasing nuclear charge.

(ii) By citing relevant values from the *Data Booklet*, deduce and explain the relative reactivity of the halogens as oxidising agents. [2]

	E^o / V
$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.07

at least 3 values cited

Reactivity (oxidising power) increases in the order $Br_2 < Cl_2 < F_2$

The larger the E^o value, the more likely the halogen is reduced, and the stronger its oxidising power.

(iii) Describe **one** chemical test to illustrate the relative reactivity of any two halogens as oxidising agents. Clearly state any observations seen. [1]

Displacement reaction. Add aqueous chlorine to a solution of bromide ions. The colourless bromide solution turns orange as chlorine has oxidised bromide to bromine.

$Cl_2(aq) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$ $E^\theta_{cell} = +0.29V$ [equation not required]

(iv) Chlorine reacts explosively with hydrogen to form the hydride of chlorine, hydrogen chloride.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

Using your answer in **(b)(ii)** or otherwise, suggest a reason for the general reactivity of the halogens. [1]

In comparison to other substances, the halogens have relatively large positive E^o values. This makes them more reactive as oxidising agents.

(v) Describe and explain the trend in thermal stability of the halogen hydrides. [2]

Order of Thermal Stability: HF(g) > HCl(g) > HBr(g)
at least 3 stated, or trend down the group

Down Group 17, bond energy of the H–X bond decreases. The weaker the H–X bond, the lower the amount of energy required to break it, and the less thermally stable the HX.

(c) Chlorine is able to form an acidic oxide with the formula ClO_2. Another Period 3 element, magnesium, forms a basic oxide with the formula MgO.

(i) Write an equation to show how the oxide ion, O^{2-}, acts as a base in the reaction with water. [1]

$O^{2-} + H_2O \rightarrow 2OH^-$

(ii) Suggest why ClO_2 is not a basic oxide, unlike MgO. [1]

It is a simple covalent oxide and does not dissociate in water to give the oxide ion.

or

It is a non-metal oxide.

[Total: 20]