SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CHEMISTRY 9647/02

Preliminary Examination
Paper 2 Structured Questions (SPA)
Suggested Solutions

1 (a) <u>Planning</u>

In the presence of hydrogen ions, H^+, bromate(V) ions, BrO_3^- , oxidise bromide ions, Br^-, to bromine, Br_2.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

The reaction is relatively slow and can be followed by adding aqueous phenol and the indicator methyl orange to the reaction mixture. As bromine is formed, it reacts rapidly with the phenol present until the latter is used up. The free bromine now in solution bleaches the methyl orange indicator.

The initial rate of the reaction can be investigated by measuring the time taken to bleach the methyl orange indicator.

You are to plan a series of experiments, to determine the order of reaction with respect to the bromide ion.

In addition to the standard apparatus present in a laboratory, you are provided with the following:

FA 1 0.01 mol dm^{-3} aqueous KBr.
FA 2 1.0 mol dm^{-3} potassium bromate(V), $KBrO_3$.
FA 3 1.0 mol dm^{-3} sulfuric acid, H_2SO_4.
Aqueous phenol containing methyl orange indicator
Distilled water

(i) Complete the table below and outline, by means of a series of numbered steps,

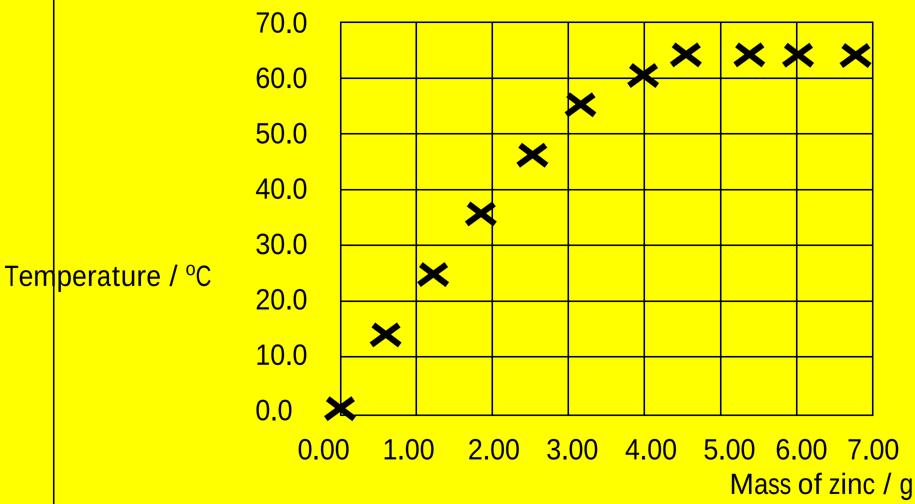
- the apparatus to be used
- the experimental procedure
- the measurements to be taken, to collect the required data.

Expt.	Volume of phenol/methyl orange indicator solution / cm^3	Volume of **FA1** / cm^3	Volume of **FA2** / cm^3	Volume of **FA3** / cm^3	Volume of distilled water / cm^3
1	20.0	50.0	50.0	20.0	0.0
2	20.0	40.0	**50.0**	**20.0**	**10.0**
3	20.0	30.0	**50.0**	**20.0**	**20.0**
4	20.0	20.0	**50.0**	**20.0**	**30.0**
5	20.0	10.0	**50.0**	**20.0**	**40.0**

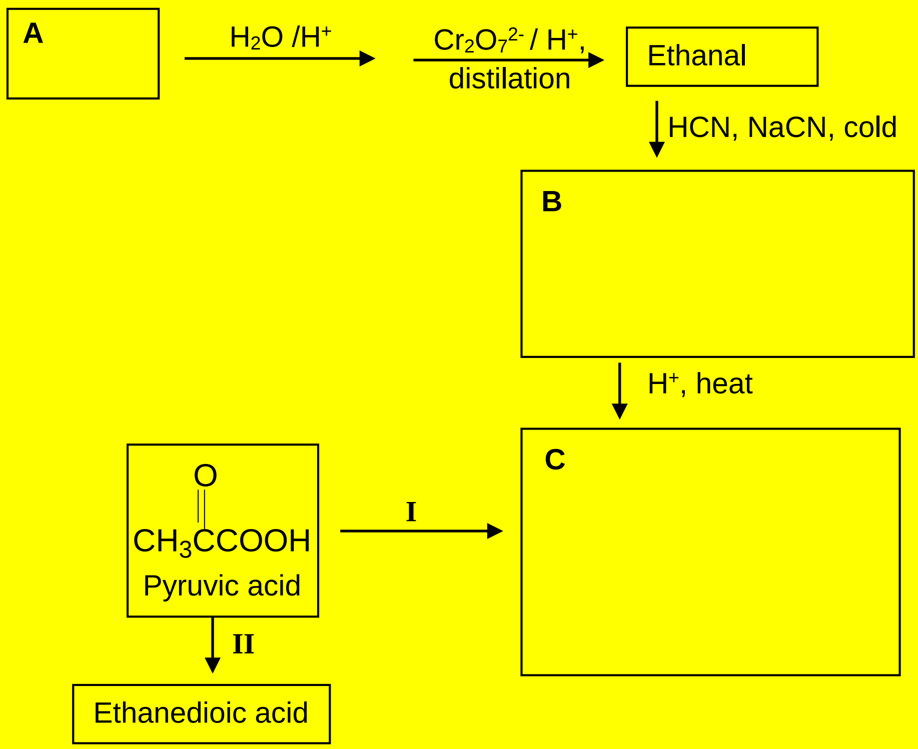
1. Using a measuring cylinder, add 20.0 cm^3 of the phenol/indicator solution into a clean, dry conical flask.
2. Using different measuring cylinders, place 50.0 cm^3 of FA 1 and 20.0 cm^3 of FA 3 into the conical flask.
3. Place the conical flask on a white tile.
4. From another measuring cylinder, measure 50.0 cm^3 of FA 2.
5. Add FA 2 into the conical flask, simultaneously starting the stopwatch.

   Swirl the conical flask carefully.
6. Stop the stopwatch when the colour of the indicator just disappears to leave a colourless solution. Record the time taken.
7. Repeat procedure 1 to 6 for experiments 2 to 5.

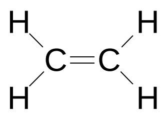
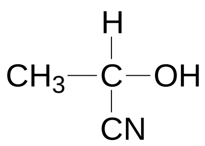
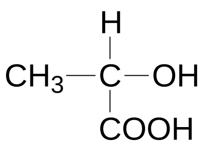
		(ii)	In order to find the order of reaction with respect to bromide, a graph of $\log_{10}(\frac{1}{t})$ against $\log_{10}$(volume of KBr(aq)) can be plotted. Use the rate equation to derive a relationship between $\log_{10}(\frac{1}{t})$ and $\log_{10}$(volume of KBr(aq)). Hence, explain how the order of reaction with respect to bromide can be found from the plotted graph.
			In these experiments, the total volume has been kept constant and only the concentration of **FA 1** in the reaction mixture has been changed. The rate equation, where ***n*** is the rate order with respect to **FA 1**, can be simplified to rate = $k'[Br^-]^n$ (where $k' = k[BrO_3^-]^m[H^+]^n$) · taking logarithms of the factors in this equation gives $lg(\text{rate}) = n \times lg([Br^-]) + lg(k)$ Hence, by finding the **<u>gradient</u>** of the plotted graph, order of reaction wrt Br^- can be found.
		(iii)	The concentration of the phenol used in the experiment is very low. Suggest why this is so. **[7]**
			If too much phenol was present, it is possible that the **<u>reaction could have taken longer</u>** OR if a large amount of phenol was added the **<u>mixture may not have decolourised at all as all the bromine formed would have reacted with the phenol present</u>**.

	(b)	An experiment was carried out to measure the enthalpy change for the reaction of zinc with aqueous copper (II) sulfate. The equation for the reaction is: Zn (s) + $CuSO_4$ (aq) à $ZnSO_4$ (aq) + Cu (s) · A measuring cylinder was used to transfer separate 50 cm^3 samples of 1.25 mol dm^{-3} copper (II) sulfate solution into polystyrene cups. · Different weighed amounts of zinc powder were added to each sample of copper (II) sulfate. · Each mixture was stirred thoroughly and the temperature rise noted. The results of the experiments are summarised on the graph below. 	
		(i)	Explain why the graph shows an initial rise in temperature and then levels off.
			Initially <u>**$CuSO_4$ in excess so amount of reaction depends on amount of Zn**</u> Or <u>**more $CuSO_4$ reacts (as more Zn added)**</u> Graph levels off because <u>**all $CuSO_4$ used up**</u> (reject just ' Reaction is complete ')
		(ii)	Using the data from the graph, calculate the $\Delta H_{reaction}$.
			Q = 50 x <u>63.5</u> x 4.18 =13271.5 J Amount of $CuSO_4$ = 50 x $\frac{1.25}{1000}$ = 0.0625 mol ΔH = - $\frac{13271.5}{0.0625}$ = <u>**- 212 x 10^3 J mol^{-1}**</u>
		(iii)	Suggest a simple practical change to the **method** that will make the experiment more accurate. **[5]**
			<u>**Use a lid on the cup (to reduce heat loss), extra insulation for cup, weigh $CuSO_4$ solution, use burette/pipette to measure volumes**</u> (Reject Repeat experiments OR use more accurate balance OR Smaller mass intervals)
			Total 12 marks

2 (a) Pyruvic acid is an important component in living cells as it is involved in the aerobic process of supplying energy. The flow chart shows a series of reactions starting with compound **A**, which has an empirical formula of CH_2.



(i) Draw the structures of compounds **A, B** and **C** in the boxes above.

A	B	C
		

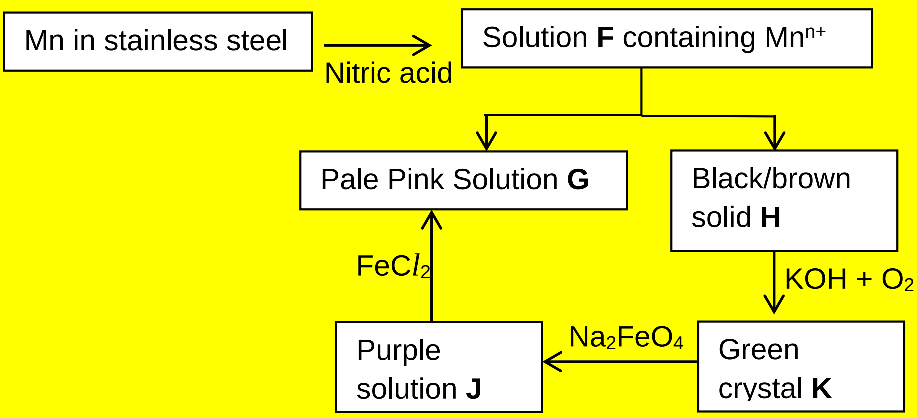
(ii) State the reagents and conditions for Steps **I** and **II**.

[5]

Step **I**: **<u>methanolic $NaBH_4$ or H_2 nickel catalyst, heat or H_2 platinum, rtp</u>**

Step **II**: **<u>I_2 (aq), NaOH (aq), warm, followed by H^+(aq)</u>**

	(b)	Element **D** can form two different chlorides. The two chlorides of element **D** is commonly used in Organic Chemistry qualitative analysis to test for a specific functional group. When dissolved in a solution containing methyl orange, chlorides of element **D** turn the solution red. 10 cm^3 of liquid organic compound **E**, $C_nH_{2n+2}O$, is vaporised and burnt in excess oxygen. After the reaction is cooled to 25 ^oC, a contraction of 20 cm^3 in the gas volume was observed. When the resultant gases from the combustion was passed through aqueous sodium hydroxide, the gas volume decreased a further 20 cm^3. The vapour of **E** is also observed to react with the same reagents and conditions of step **II** mentioned in **(a)**.	
		(i)	State the identities of element **D** and organic compound **E**.
			D is phosphorus. **E** is ethanol. (Since 10 cm^3 of vapour **E** combusted to give 20 cm^3 of CO_2, by Avogadro's and volume ratio, n =2 è C_2H_6O
		(ii)	Hence, write an equation, if any, between one of the chlorides of element **D** and organic compound **E**.
			$CH_3CH_2OH + PCl_5$ à $CH_3CH_2Cl + POCl_3 + HCl$ **or** $3CH_3CH_2OH + PCl_3$ à $3CH_3CH_2Cl + H_3PO_3$
			Total 8 marks

3	**(a)**	**(i)**	Both strontium and manganese are silvery metals. Write the electronic configurations of manganese and strontium.
			Mn: [Ar]$3d^5 4s^2$ Sr: [Kr]$5s^2$
		(ii)	Manganese and strontium both contribute two electrons into the sea of delocalised electrons. Suggest if strontium or manganese has a higher melting point.
			Cationic radius of manganese is smaller as compared to strontium ions. **Electrostatic forces of attraction b/w the cations and sea of delocalised electrons(metallic bonding) is stronger in Mn than in Sr**. Thus **more energy** is required to overcome these forces of attraction. **Mn has a higher melting point than Sr**. (For your information m.p. of strontium is 777°C and manganese is 1246°C)
		(iii)	Manganese is particularly important in the manufacturing of stainless steel. Below shows a reaction schematic of manganese containing compounds. **F** undergoes a reaction to form **G** and **H**.  Using the information provided, state the oxidation number of manganese in **F** and **K**. (All Mn and its compounds have different oxidation state).
			F: +3 **K**: +6
		(iv)	Suggest the formula of purple solution **J**.
			$NaMnO_4$

(v) Suggest the type of reaction when **F** forms **G** and **H**.
Write a balanced chemical equation, including state symbols, for this reaction.

[10]

<u>Disproportionation reaction</u>

Reduction: $Mn^{3+} + e \rightarrow Mn^{2+}$

Oxidation: $2H_2O + Mn^{3+} \rightarrow MnO_2 + 4H^+ + e$

Overall: **<u>Mn^{3+} (aq) + $2H_2O$ (*l*) $\rightarrow$ Mn^{2+} (aq) + MnO_2 (s) + $4H^+$ (aq)</u>**

(b) Strontium compounds such as SrF_2 and $SrSO_4$ are sparingly soluble in water. Their solubility products at 298 K are given in the table below:

Strontium compound	**Numerical value of K_{sp}**
SrF_2	2.5×10^{-9}
$SrSO_4$	3.2×10^{-7}

(i) Suggest, using quantitative calculations, which of the two compounds is less soluble in water at 298 K.

SrF_2 (s) $\rightleftharpoons$ Sr^{2+} (aq) + $2F^-$ (aq)
$K_{sp}(SrF_2) = [Sr^{2+}][F^-]^2$

$2.5 \times 10^{-9} = (s)(2s)^2$
$s = 8.55 \times 10^{-4}$ mol dm^{-3}

$SrSO_4$ (s) $\rightleftharpoons$ Sr^{2+} (aq) + SO_4^{2-} (aq)

$K_{sp}(SrSO_4) = [Sr^{2+}][SO_4^{2-}]$

$3.2 \times 10^{-7} = (s)^2$
$s = 5.66 \times 10^{-4}$ mol dm^{-3}

Based on the calculated solubilities, **<u>$SrSO_4$ is less soluble</u>** than SrF_2.

(ii) A sample of strontium(II) fluoride is dissolved in a solution of sodium fluoride. Predict qualitatively the effect (if any) on the solubility and solubility product of strontium(II) fluoride.

[4]

SrF_2 (s) $\rightleftharpoons$ Sr^{2+} (aq) + $2F^-$ (aq)

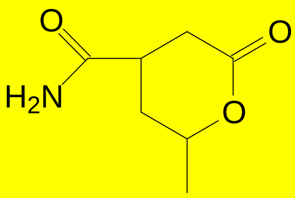
NaF (s) $\rightarrow$ Na^+ (aq) + F^- (aq)

There will be **<u>common ion effect</u>** due to the increase in $[F^-]$.

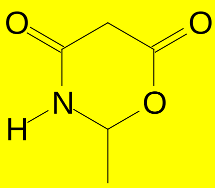
By Le Chatelier's Principle, **<u>position of equilibrium</u>** will shift to the **<u>left</u>** to **<u>decrease $[F^-]$</u>**. The solubility of SrF_2 is **<u>reduced.</u>**

The solubility product of SrF_2 is **<u>not affected</u>** as it is only dependent on temperature.

(c) Propose chemical test(s) to differentiate the following organic compounds. You are to state clearly in your answer the reagents and conditions used and observations made. Write chemical equation(s) for any reactions that have occurred.



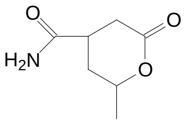
and



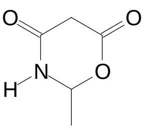
[4]

Test: Add NaOH (aq), heat

Observation:

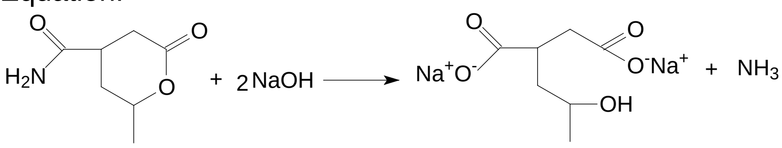


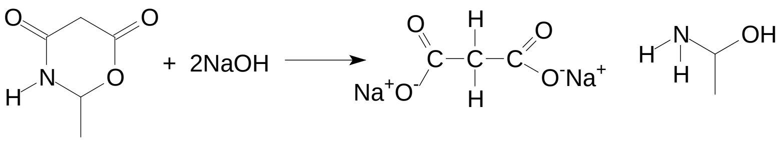
: effervescence



: No effervescence

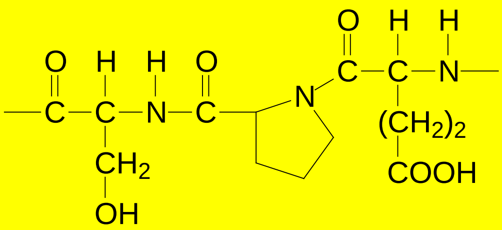
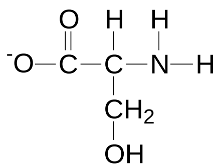
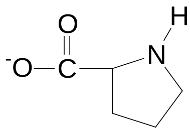
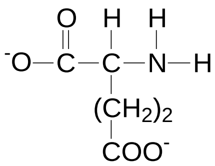
Equation:

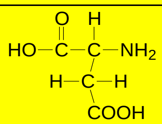
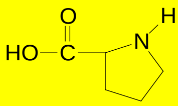
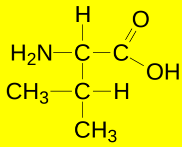




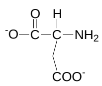
(Test for NH_3: Moist red litmus paper turns blue)

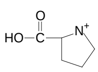
Total 18 marks

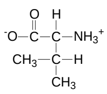
4(a)	Amino acids serve as the building blocks of proteins. They can be linked together in varying sequences to form a vast variety of proteins. An example of a segment of a protein is shown below. 	
	(i)	In the space provided below, draw the structural formulae of the amino acids formed from the hydrolysis of the above protein with aqueous sodium hydroxide.
		  
	(ii)	Amino acids from can be separated using electrophoresis. With reference to the isoelectric point of the amino acids provided, indicate the positions of the amino acid on the gel at a pH of 5.96.

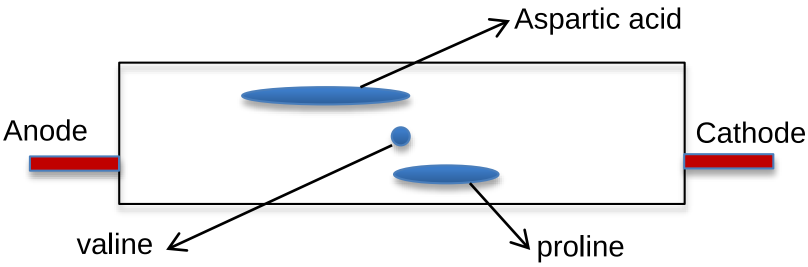
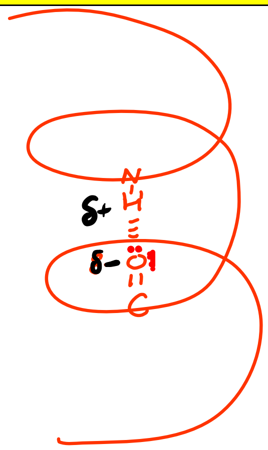
Amino acid	**Structure**	**Isoelectric point**
Aspartic acid		2.77
Proline		6.30
Valine		5.96

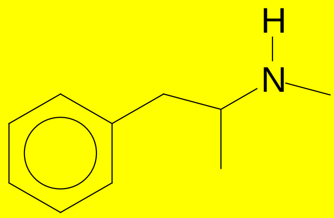
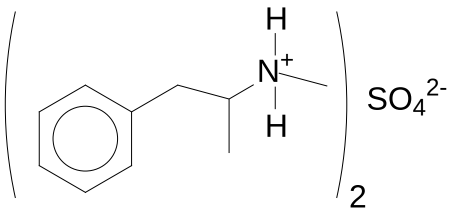
Analysis :Species at 5.96 for respective amino acids:

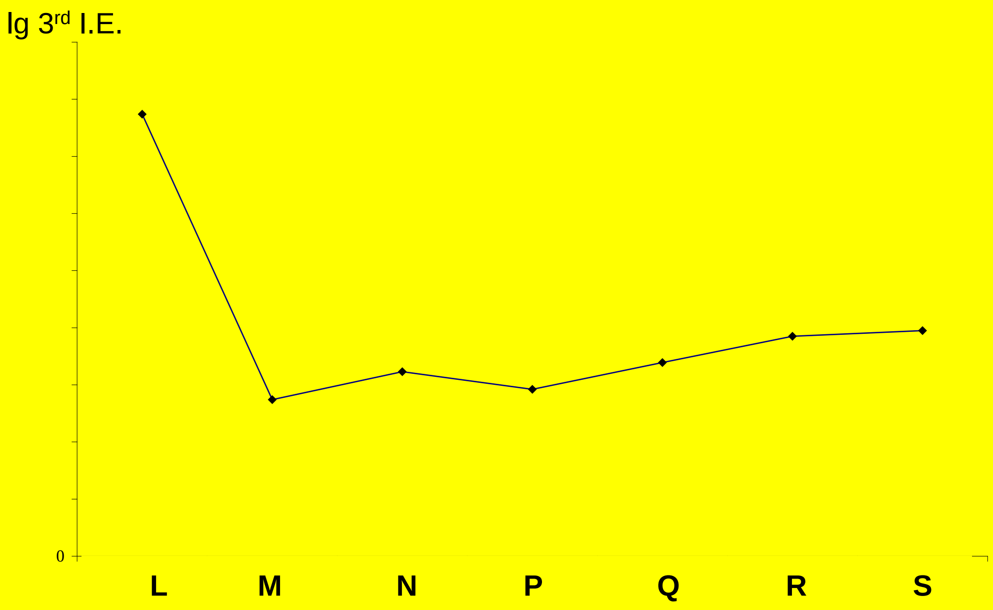
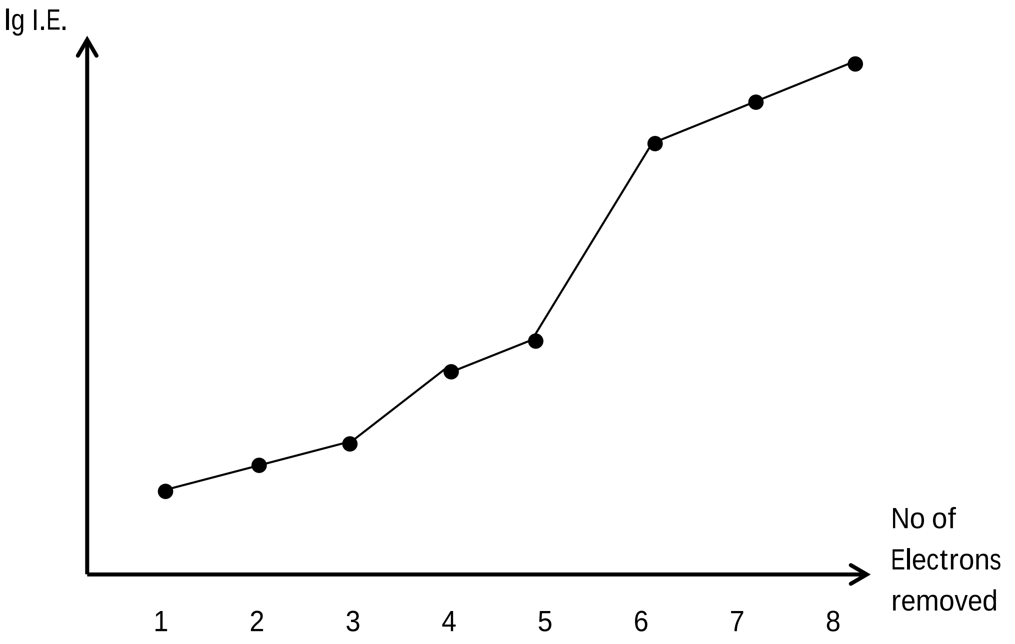
For aspartic acid:  è shift towards anode

For proline:  è shift towards cathode

For valine:  è remains in the middle

		
	(iii)	A common secondary structure of proteins is the alpha helix. With the aid of a diagram and your knowledge in chemical bonding, describe the alpha helix structure.
		[7]
		 **On diagram:** **1) 2 lone pair of electrons** on O atom **2)** dipoles (**δ+ and δ-)** and **3) hydrogen bond** (IIIIIIII) must be shown Hydrogen bonds formed between O atom of (-C=O $^{\delta-}$) group for C_1 and the H atom of (-N-H$^{\delta+}$) group of the **fourth** peptide bond for **C_4** down the same protein chain which stabilises the structure.

(b)	**(i)**	Methamphetamine, $C_{10}H_{15}N$, is a psychostimulant. It has high potential for abuse and addiction. In high doses, it can induce euphoria and anxiety. Under the Misuse of Drugs Act in Singapore, a person who carries 500 grams of methamphetamine will be sentenced to the Mandatory Death Penalty. Its structure is as shown:  A 25.0 cm^3 sample of 0.500 mol dm^{-3} methamphetamine was titrated with aqueous hydrochloric acid of the same concentration. Would you expect the equivalence point to be above 7 or below 7? Explain your answer.
		Due to **salt hydrolysis** pH of equivalence point should be **below 7**.
	(ii)	State the formula of the organic product formed when methamphetamine was reacted with sulfuric acid instead of hydrochloric acid. **[3]**
		
		Total 10 marks

5	Elements **L** to **S** are consecutive Period 3 elements with proton number less than 20. The following graph shows the third ionisation energies of these elements. [**L** to **S** are not specific elements from the Periodic Table]. 	
	(a)	Identify the group that element **P** belongs to.
		[1]
		Group V
	(b)	Sketch a graph to show the successive ionisation energies of element **P** when the first eight electrons are removed from it.
		[1]
		

	(c)	Explain the drop in the third ionisation energy from element **N** to **P**.
		[2]
		N^{2+}: $1s^2 2s^2 2p^6 3s^2$ **P**$^{2+}$: $1s^2 2s^2 2p^6 3s^2 3p^1$ The **<u>3p electron</u>** to be removed from P^{2+} is **<u>further away</u>** from the nucleus than the **<u>3s electron</u>** to be removed from N^{2+}. The **<u>3p electron</u>** experiences **<u>weaker electrostatic forces of attraction</u>** than the 3s electron and requires less energy to remove. Thus there is a drop in third ionisation energy from element **N** to **P**.
	(d)	Write down the equations for the reaction of the oxide of **M** with aqueous hydrochloric acid and aqueous sodium hydroxide.
		[2]
		M_2O_3(s) + 6 **HC*l* (aq)** à 2 MCl_3(aq) + 3 H_2O (*l*) M_2O_3(s) + 2 **NaOH(aq)** + 3 H_2O(*l*) à 2 Na[$M(OH)_4$] (aq)
	(e)	Describe the reactions, if any, of the chlorides of element **M** and **P** with water, suggesting the pH of the resulting solutions and writing equations, where appropriate.
		[6]
		M undergoes **hydrolysis** as it has **<u>high charge density</u>**, able to **<u>polarise</u>** and weaken O-H bond in H_2O of $[B(H_2O)_6]^{3+}$ (aq) to release acidic H^+ and give an **acidic** solution. **M**Cl_3 (s) + 6 H_2O (*l*) à [**M**$(H_2O)_6]^{3+}$ (aq) + 3 Cl^- (aq) [**M**$(H_2O)_6]^{3+}$(aq) à [**M**$(H_2O)_5(OH)]^{2+}$ (aq) + H^+ (aq) pH of solution = 3 **P**Cl_3 (*l*) + 3 H_2O (*l*) à H_3**P**O_3 (aq) + 3 HC*l* (aq) Or **P**Cl_5 (*l*) + 4 H_2O (*l*) à H_3**P**O_4 (aq) + 5 HC*l* (aq) pH of solution = 2 [**L** to **S** are not specific elements from the Periodic Table]
		Total 12 marks

6	**(a)**	Nitrogen monoxide in the air can be converted to nitric acid, which results in acid rain. Both nitrogen monoxide and nitrogen dioxide participate in ozone layer depletion. One way of forming nitrogen monoxide is through the dissociation of nitrogen dioxide. $2NO_2\ (g) \rightleftharpoons 2NO\ (g) + O_2\ (g)$ At 494 °C, the value of K_p for the above reaction is 36.9 kPa. When a certain partial pressure of nitrogen dioxide is put into an empty vessel at 494 °C, equilibrium is reached when 45% of the original nitrogen dioxide has decomposed.	
		(i)	Write an expression for the equilibrium constant, K_p, for the reaction.
			$K_p = \dfrac{P_{NO}{}^2\, P_{O_2}}{P_{NO_2}{}^2}$
		(ii)	What is the original partial pressure of nitrogen dioxide before any dissociation occurred?
			[3]

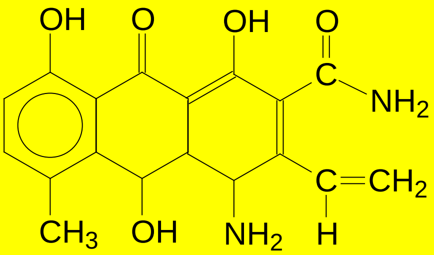
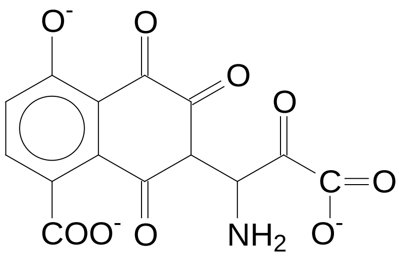
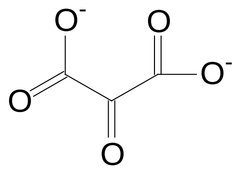
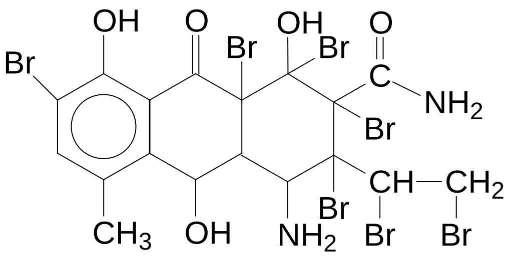
Let the initial pressure of NO_2 be ***x*** mol.

	$2\ NO_2\ (g) \rightleftharpoons$	$2\ NO\ (g)$ +	$O_2\ (g)$
Initial pressure (kPa)	***x***	0	0
Change in Presure	-0.45***x***	+0.45***x***	+0.225***x***
Equilibrium pressure (kPa)	0.55***x***	0.45***x***	0.225***x***

$$K_p = \frac{(0.225x)(0.45x)^2}{(0.55x)^2} = 36.9$$

x = 244 kPa

Hence, initial pressure of NO_2 = 244 kPa

	(b)	Draw the structural formula of the organic products formed when compound **T** reacts with the following reagents.  Compound **T**	
		(i)	Alkaline aqueous $KMnO_4$, heat
			 
		(ii)	Br_2 in CCl_4, absence of UV light
			[5]
			

(c) Compound **U** has the molecular formula $C_9H_{12}O$.

It reacts with chlorine gas in the presence of light to form compound **V**, $C_9H_{11}OCl$, which is optically active.

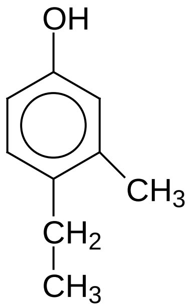
On addition of bromine water at room temperature, **U** forms a white precipitate **W**, $C_9H_{10}OBr_2$.

When treated with acidified potassium manganate(VII) under reflux, **U** forms compound **X**, $C_8H_6O_5$. 1 mole of **X** reacts with 2 mole of thionyl chloride.

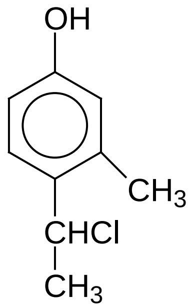
Draw the structures for compounds **U** to **X.**

[4]

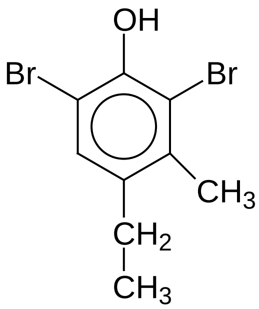
U:



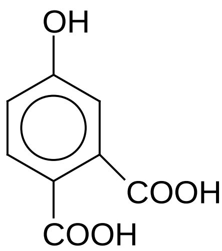
V:



W:



X:



Total 12 marks

END