Victoria Junior College
2011 H2 Chemistry Prelim Exam 9647/2
Suggested Answers

1 Planning

An acid can be represented by the general formula, H_xA, where *x* represents the basicity of the acid.

A bottle of a dilute aqueous solution of an acid, either monobasic or dibasic, was found. However, the label on the bottle had been damaged. Only the concentration of the acid, 1.00 mol dm^{-3} was readable.

A student was given a 1.00 mol dm^{-3} sodium hydroxide solution. She was asked to determine the basicity of the acid in the bottle by mixing different volumes of the acid and sodium hydroxide.

(a) (i) Write an equation to represent the molar enthalpy change of neutralization between sodium hydroxide and H_xA.

$$\frac{1}{x}\ \mathbf{H_xA + NaOH \rightarrow \frac{1}{x}Na_xA + H_2O}$$ [1]

(ii) A student determined the basicity of the acid by performing the following experiments:

Experiment 1: 30 cm^3 of H_xA(aq) was added to 60 cm^3 of NaOH(aq)
Experiment 2: 60 cm^3 of H_xA(aq) was added to 30 cm^3 of NaOH(aq)

The changes in temperature of the mixture were measured for Experiment 1 and Experiment 2 as ΔT_1 and ΔT_2 respectively.

Suggest and explain the basicity of H_xA if $\Delta T_1 = 2 \times \Delta T_2$

Heat is released when water is formed in the neutralization process. The amount of heat released in Experiment 1 is twice that in Experiment 2. Since total volume of mixture remained unchanged, therefore, the number of moles of water formed in Experiment 1 is twice that in Experiment 2. H_xA is a dibasic acid because in Experiment 1, all the acid and alkali are reacted while in Experiment 2, the alkali is the limiting reagent. [2]

Alternatively

If x = 1
$HA + NaOH \rightarrow NaA + H_2O$

Experiment	H_xA	NaOH	η_{H2O}
1	30 (limiting)	60 (excess)	y
2	60 (excess)	30 (limiting)	y

Both experiments will produce same amount of water.
Hence $\Delta T_1 = \Delta T_2$ (since total volume of mixture is fixed)

Experiment	H_xA	NaOH	η_{H2O}
1	30 (limiting)	60 (limiting)	$2y$
2	60 (excess)	30 (limiting)	y

If x = 2
$H_2A + 2\ NaOH \rightarrow Na_2A + 2\ H_2O$
Experiment 1 will produce twice the amount of H_2O.
Hence $\Delta T_1 = 2\Delta T_2$ (since total volume of mixture is fixed)
$\therefore$ x = 2 dibasic acid

(b) For this part, you may assume that the acid in the bottle is a monobasic acid, HA.

A student decided to determine whether the acid, HA, is a strong or weak acid by performing a series of experiments involving mixing of hydrochloric acid with sodium hydroxide and HA with sodium hydroxide.
Explain how, from the suggested experiment, the student might be able to determine whether HA is a strong or weak acid.

If HA is a weak acid, some of the heat evolve during neutralization is absorbed to dissociate the weak acid, HA, fully. Hence $\Delta T_{(HA/NaOH)} < \Delta T_{(HCl/NaOH)}$. If HA is a strong acid, full dissociation occurs like HCl, $\Delta T_{(HA/NaOH)} = \Delta T_{(HCl/NaOH)}$ [2]

FA 1 is a solution of sodium hydroxide of unknown concentration.
FA 2 is 1.0 mol dm^{-3} hydrochloric acid.

Since neutralization reaction is exothermic, a series of experiments can be performed by mixing different volumes of **FA 1** and **FA 2** to determine the concentration of sodium hydroxide.

(c) (i) Write a procedure to determine the temperature changes for the series of reactions between **FA 1** and **FA 2**.

Your answers should include choice of apparatus to measure the volume and temperature of the solutions. Give suitable headings for the columns numbered **1** to **5** as part of the plan of the experiment.

Volume of **FA 1** /cm^3	Volume of **FA 2** /cm^3	1	2	3	4	5
30.00	40.00					
33.00	37.00					
36.00	34.00					
40.00	30.00					
44.00	26.00					
48.00	22.00					
50.00	20.00					

Headings for

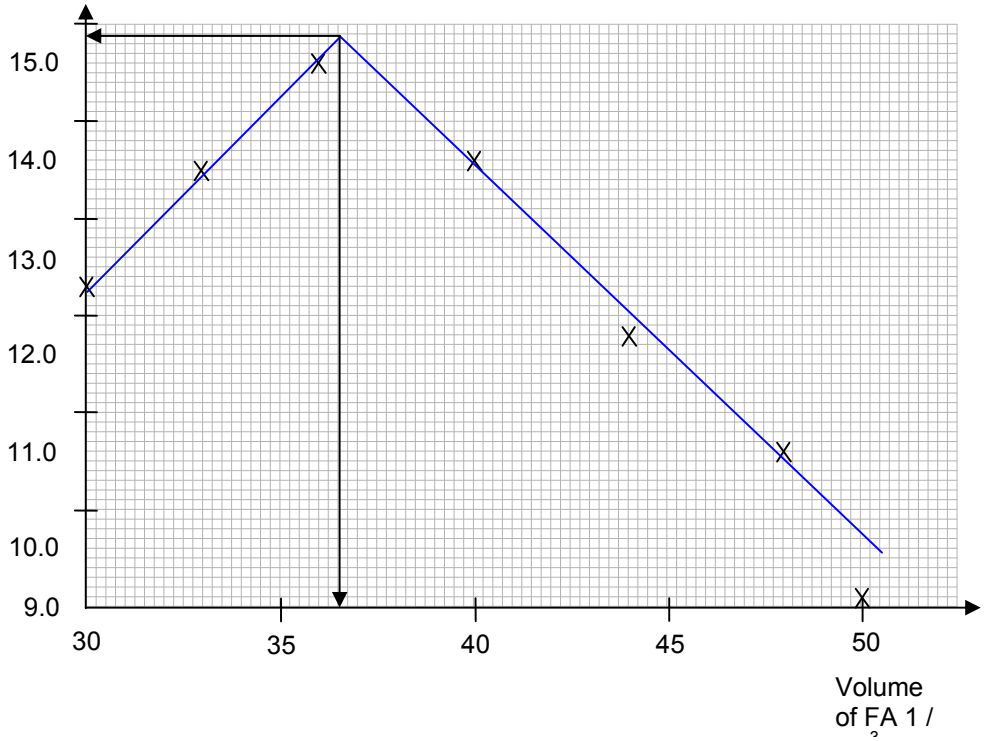
1. **Temperature of FA 1 /^oC**
2. **Temperature of FA 2 /^oC**
3. **Average temperature of solutions before mixing /^oC**
4. **Final temperature of solution after mixing /^oC**
5. **Temperature change /^oC**

Procedure

1. **Use a burette to transfer 30.00 cm^3 of FA 1 into the Styrofoam cup labeled FA 1. Place the cup in a 250 cm^3 beaker to prevent it from tipping over.**
2. **Use another burette to transfer 40.00 cm^3 of FA 2 into the styrofoam cup labeled FA 2.**
3. **Use two thermometers to stir and measure the temperature of the FA 1 and FA 2 solution.**
4. **Calculate the average temperature of the solutions.**
5. **Add the contents of FA 2 cup to the FA 1 cup. Use the thermometer to stir the mixture and measure the maximum temperature of the mixture.**
6. **Wash and carefully dry both the FA 1 and FA 2 styrofoam cups.**
7. **Repeat steps 1 to 5 using 40.00 cm^3 and 50.00 cm^3 of FA 1, each time using the appropriate volume of FA 2 so that the total volume of reacting mixture is 70.00 cm^3.**

[4]

(ii) The following points were plotted on a grid after an experiment. Draw a suitable graph through the plotted points.



[1]

(iii) By using the graph in **(ii)**, calculate the concentration of sodium hydroxide in the experiment. [2]

Volume of FA 1 used when temperature change is max
= 36.5 cm^3
No. of moles of FA 2 (hydrochloric acid) used
= (70–36.5) / 1000 × 1.0
= 0.0335 mol
Concentration of FA 1
= 0.0335 / (36.5 / 1000)
= 0.918 mol dm^{-3}

[Total: 12]

2 Oxoanions of Group VII elements have the general formula XO_m^-, where m = 1, 2, 3 or 4. These oxoanions are strong oxidizing agents.

(a) Explain why fluorine does not form oxoanions.

Fluorine is the most electronegative element, and is unable to form a compound in which it has a positive oxidation number. In addition, fluorine is in Period 2 of the Periodic Table, thus unable to expand its octet structure to form more than 1 covalent bond.

[2]

(b) 1.25 x 10^{-3} mol of an aqueous bromate salt containing the BrO_m^- anion was added to excess potassium iodide. The resulting mixture was washed with chloroform to dissolve the iodine, and the aqueous and organic layers were separated. Silver nitrate solution was added to the aqueous layer, and a mixture of two precipitates was obtained.

(i) Identify the two precipitates formed.

AgBr (redox product) and AgI (excess KI) [1]

(ii) The iodine collected in the organic layer was titrated against 0.500 mol dm^{-3} sodium thiosulfate. 14.90 cm^3 of titrant was required to discharge the blue-black colour of the starch indicator. Calculate the value of ***m***.

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

$n_{thiosulfate}$ = $\frac{14.90}{1000} \times 0.500$ **= 7.45 x 10^{-3} mol**

n_{iodine} = ½ $n_{thiosulfate}$ = 3.725 x 10^{-3} mol

$\frac{n_{iodine}}{n_{bromate}} = \frac{3.725 \times 10^{-3}}{1.25 \times 10^{-3}} = 3$ **(nearest whole number)**

$I_2 + 2e^- \rightarrow 2I^-$

6 mol of electrons were transferred

Original oxidation state of Br in BrO_m^- = -1 + 6 = +5

5 + m(-2) = -1

m = 3

[3]

(iii) The two precipitates can be separated by addition of concentrated aqueous ammonia, followed by filtration. Describe what you expect to observe and explain the chemical principles behind this method.

The cream ppt dissolves, while yellow ppt is obtained as the residue.

High $[NH_3]$ causes formation of soluble $[Ag(NH_3)_2]^+$ complex, lowering $[Ag^+]$.
As a result, the equilibrium

$$Ag^+(aq) + Br^-(aq) \rightleftharpoons AgBr(s)$$

shifts to the left. The ionic product $[Ag^+][Br^-]$ falls below Ksp and hence the salt dissolves.
The Ksp of AgI is so low that even at high $[NH_3]$, the ionic product $[Ag^+][I^-]$ is still higher than Ksp.

[4, max 3]

(c) 0.500 g of a Group II iodate(V) salt, $M(IO_3)_2$, was heated and decomposed to give a white solid, a purple gas, and a colourless gas that rekindles a glowing splint.

(i) Identify the 3 decomposition products.

Metal oxide, iodine and oxygen gas

(ii) Write a balanced equation for the decomposition reaction, including state symbols.

$2M(IO_3)_2(s) \rightarrow 2MO(s) + 2I_2(g) + 5O_2(g)$

(iii) Given that 0.0532 g of the white solid was collected, calculate the relative atomic mass of the metal, and hence deduce its identity.

$$n_{salt} = n_{oxide}$$

$$\frac{0.500}{A_r + 2(127.0 + 3\times16.0)} = \frac{0.0532}{A_r + 16.0}$$

$$A_r = 23.8$$

M is magnesium.

[4]

(d) Predict how the thermal decomposition of barium iodate(V) differs from that of $M(IO_3)_2$. Explain your reasoning.

Barium iodate(V) decomposes at a slower rate / requires a higher temperature for thermal decomposition.
Ba^{2+} has a larger ionic radius than Mg^{2+}, thus a lower charge density, and poorer polarizing power. It distorts the IO_3^- anion cloud to a lower extent, thus $Ba(IO_3)_2$ is more stable to heat.

[3]
[Total: 16]

3 The two most abundant atmospheric gases react to a small extent at 298 K in the presence of a catalyst to achieve dynamic equilibrium as shown:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_p = 0.30$$

(a) Explain the term *dynamic equilibrium*. [1]

It refers to a state of the system where the rate of forward reaction is the same as the rate of the backward reaction.

(b) Atmospheric oxygen and nitrogen, each at a partial pressure of 0.780 atm, are put into a 1 dm^3 evacuated flask at 298 K with a catalyst and equilibrium is established after 30 minutes. Calculate the equilibrium partial pressure for each of the three components at 298 K. [3]

	$N_2(g)$	$O_2(g)$	$2NO(g)$
Initial P/ atm	**0.780**	**0.780**	**0**
Change P/ atm	**-x**	**-x**	**+2x**
Eqm P / atm	**0.78-x**	**0.780-x**	**2x**

$K_p = (P_{NO})^2 / (P_{N2})(P_{O2})$

$0.30 = 4x^2 / (0.78-x)^2$

$x = 12.14$ (reject) or 0.1677

$P_{O2} = P_{N2} = 0.78 - 0.1677 =$ 0.612 atm

$P_{NO} = 2 \times 0.1677 =$ 0.335 atm

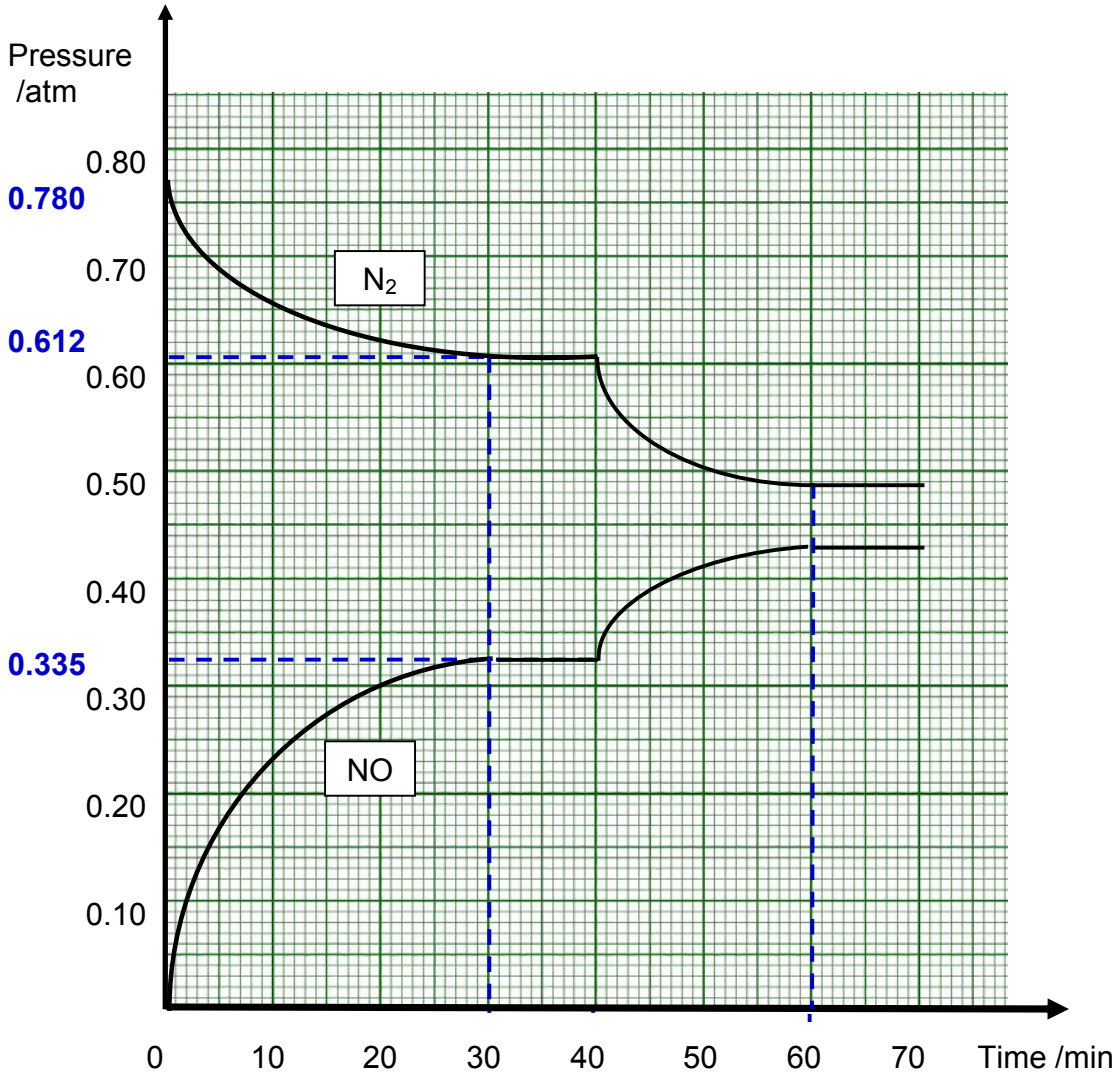
(c) What is the total pressure in the container at equilibrium? [1]

Total pressure = 0.612 + 0.612 + 0.335 = 1.56 atm

(d) Find K_c for this reaction at 298 K. [1]

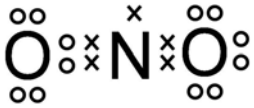
Since total number of moles of gaseous reactants and products is the same.
$K_c = K_p =$ 0.30

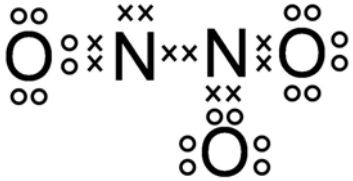
(e) On the grid below, sketch pressure versus time curves for N_2 and NO under the conditions as described in **(b)** at 298 K from 0 to 40 minutes. Label the curves and indicate significant values on the axes. [2]



(f) The temperature of the system was raised to 350 K at 40 min.
Given that the reaction is endothermic and equilibrium is re-established at 60 min, sketch on the axes above, the pressure versus time curves for N_2 and NO from 40 min to 70 min. [2]

(g) NO is readily oxidised to reddish-brown NO_2. Both NO and NO_2 chemically combine to form N_2O_3.
Draw dot-and-cross diagrams to show the bonding in NO_2 and N_2O_3. [2]



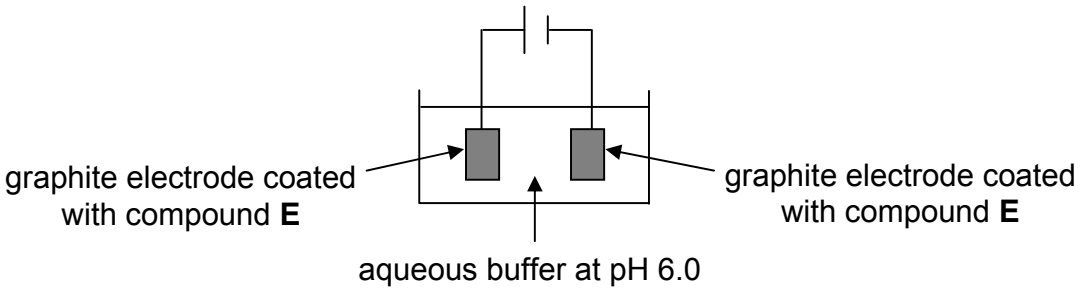


(h) Explain in terms of structure and bonding, why N_2O_4 has a higher boiling point than NO_2. [2]

Both NO_2 and N_2O_4 have simple molecular structure consisting of simple discrete molecules held together by van der Waals' / dispersion forces However, N_2O_4 has a larger relative molecular mass, hence it has more electrons leading to stronger van der Waals' forces. So, a larger amount of heat energy is needed to separate the molecules, leading to a higher boiling point.

[Total: 14]

4 The electrolysis of organic compounds has been well studied since 1970s. For instance, Kolbe studied the electrolysis of a series of aromatic organic compounds. Compound **E** with the molecular formula, C_6H_7NO is a **1,4-disubstituted aromatic compound** studied using the experimental set up as shown.



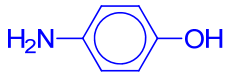
(a)(i) Compound **E** dissolves in both aqueous hydrochloric acid and aqueous sodium hydroxide. However, it does not dissolve in aqueous sodium carbonate. Deduce the structure of compound **E**.

Compound E could contain *basic* –NH_2 group which can react with HCl.

Compound E has acidic phenolic –OH group which is capable of reacting with NaOH.

Phenol is <u>not sufficiently acidic</u> to react with Na_2CO_3, unlike carboxylic acid.

Structure of compound E



[2]

(ii) Compound **E** is oxidised to compound **F**, C_6H_5NO at the anode.

A series of chemical tests was performed on compound **F.** When 2,4-dinitrophenylhydrazine was added, an orange precipitate was observed. No silver mirror was obtained when warmed with aqueous $Ag(NH_3)_2^+$ solution. One mole of compound **F** reacts with excess hydrogen gas in the presence of platinum catalyst to yield compound **G** with molecular formula $C_6H_{13}NO$.

Deduce the structures of compounds **F** and **G**.

Orange ppt with 2,4 DNPH implies that carbonyl (<u>aldehyde or ketone</u>) is present.

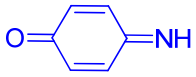
No silver mirror with aqueous $Ag(NH_3)_2^+$ implies that <u>aldehyde is absent (or ketone is present).</u>

Catalytic reduction adds <u>8 hydrogen atoms to 1 molecule of compound F.</u>

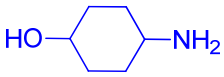
1 molecule of H_2 is used to reduce the ketone.

The remaining 3 molecules of H_2 must be used to reduce 3 double bonds.

Structure of compound F



Structure of compound G



[4, max 3]

(b)(i) Compound **F** is reduced at the cathode back to compound **E**. Write the half equation for this reduction using the molecular formulae.

Cathode: $C_6H_5NO + 2H^+ + 2e \rightarrow C_6H_7NO$

[1]

(ii) Using relevant $E^{\ominus}$ data from the *Data Booklet*, explain whether the standard reduction potential of the half equation in **(b)(i)** has a positive or negative value.

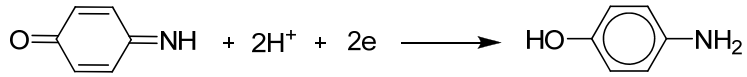
$2H^+ + 2e \rightleftharpoons H_2$ $E^{\ominus} = 0.00$ V
Since compound F is preferentially reduced at the cathode over H^+ ions, the standard reduction potential of the half equation in a(iii) should be positive.

[Note: Quoting $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ $E^{\ominus} = -0.83$ V is not acceptable as it cannot be used to judge whether the standard reduction potential of compound F is positive or negative.]

[1]

(iii) A current of 2.0 A is supplied to the experimental set-up. Using the half equation in **(b)(i)**, calculate, in mg/min, the average rate of mass gain at the cathode, given that the molecular mass of compound **E** is 109.0.

Quantity of charge per minute = 2 x 1 x 60 = 120 C

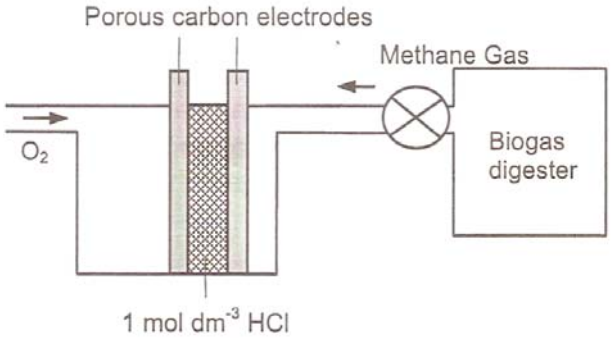


No. of moles of compound E formed at cathode per minute
= 0.5 x no of moles of electrons
= 0.5 x (120 / 96500) = 6.22×10^{-4} mol

Average rate of mass gain
= 6.22×10^{-4} x 109.0 x 1000
= 67.8 mg/min

[2]

(c) Tonnes of organic waste are dumped into rivers annually in the rural areas of China. Environmental scientists have warned of the danger of dead seas forming in a few decades due to eutrophication (depletion of oxygen in water bodies). To encourage the reduction of disposal of organic waste into the rivers, the Chinese government built biogas tanks in the rural areas where the inhabitants can obtain electricity from the **combustion of methane gas** generated from the organic waste. One such biogas tank is shown below:



(i) With reference to methane, eefine standard enthalpy change of combustion.

The enthalpy change when 1 mole of methane is completely burnt in excess oxygen under standard conditions of 298K and 1 atm.

[1]

(ii) It was found that 10 kg of organic waste on the average generates 035 kg of methane gas in a biogas tank Using relevant data from the *Data Booklet*, estimate the average amount of energy released from 505 kg of organic waste deposited into the biogas tank

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Bond	Energy / kJ mol^{-1}
C-H	410
O=O	496
C=O	740
O-H	460

ΔH_c^{θ} (methane) = (4 x 410) + (2 x 496) – (2 x 740) – (4 x 460)
= –688 kJ mol^{-1}

No. of moles of CH_4 generated from 505 kg of organic waste

$$= \frac{\frac{50.5}{10} \times 0.35 \times 1000}{16.0}$$

= 1105 mol

Average amount of energy released = 1105 x 688
= 760 x 10^4 kJ

[3]

(iii) Write the ionic half equations for the reaction occurring at the anode and cathode of the biogas tank.

Anode: $CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e$
Cathode: $O_2 + 4H^+ + 4e \rightarrow 2H_2O$

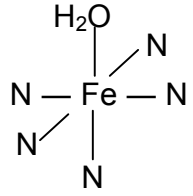
[2]
[Total: 15]

5(a) A study by a Dutch research firm tested the efficacy of using pig's blood to filter the harmful chemicals normally ingested by humans when smoking It was found that pig haemoglobin, when used in cigarette filters, rendered them more effective at trapping harmful chemicals which are thus prevented from entering a smoker's lungs
The basic structure of this new choice filter is similar to that of any carbon based cigarette filter, but contains haemoglobin absorbed in the activated carbon These two substances in combination work as a highly efficient scavenger of the harmful gaseous compounds present in cigarette smoke

(i) Describe the *quaternary* structure of haemoglobin

Haemoglobin consists of 4 separate polypeptide chains of two types, namely 2 α chains and 2 β chains.
Each polypeptide carries a haem group containing Fe^{2+} to form a subunit.
Each subunit folds and coils into a compact globular shape through interactions between the R groups such as ionic bonds, hydrogen bonds and van der waals forces.
The subunits are also held together by R group interactions to form a larger precise 3-dimensional structure.
In the folding of the polypeptide chain, the hydrophobic R groups are directed inwards to the centre of the structure while the hydrophilic R groups are directed outwards the surface of the structure, making it soluble in water.

(ii) The iron atom in the haemoglobin molecule contains six 3d electrons and it is surrounded by six ligand atoms as shown below Five of these are nitrogen atoms from the protein, and one is an oxygen atom from a water molecule



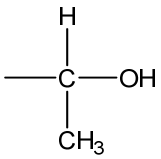
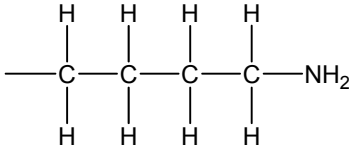
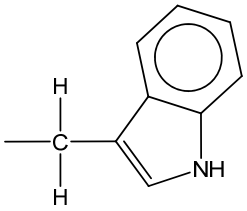
Predict how haemoglobin is able to function as an efficient scavenger of the harmful carbon monoxide gas present in cigarette smoke

Carbon monoxide will displace water or oxygen molecule in the above structure to form a more stable compound via a ligand-exchange reaction

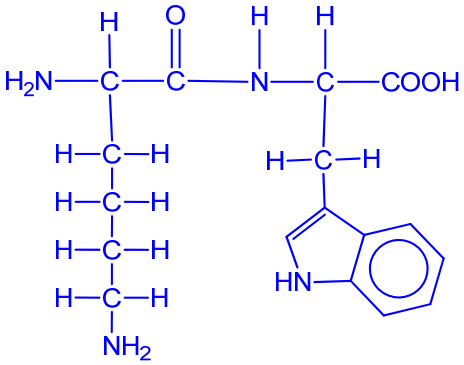
[4]

Optimum amino acid balance is important to maximize growth and efficiency in pigs Diets are routinely formulated to meet the threonine:lysine and tryptophan:lysine ratio requirement in pig feed

Information of the three amino acids in pig feed is listed below

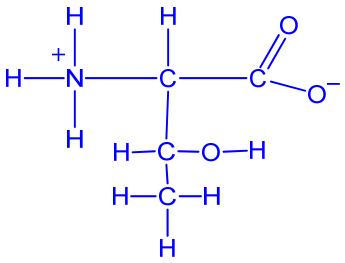
Amino acid	Formula of side chain (R' in $R'CH(NH_2)CO_2H$)	Isoelectric point
Threonine (Thr)		560
Lysine (Lys)		960
Tryptophan (Trp)		589

(b) Draw the structural formula of the dipeptide, lys-trp



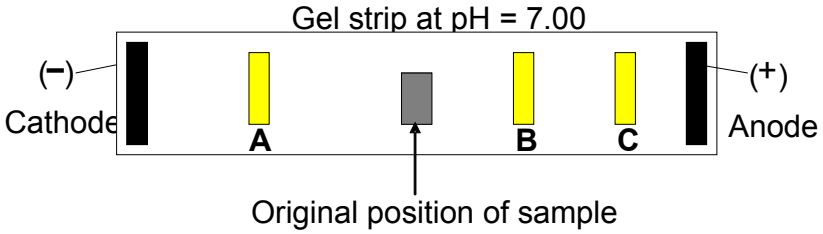
[1]

(c) Draw the structure of threonine at pH = 560

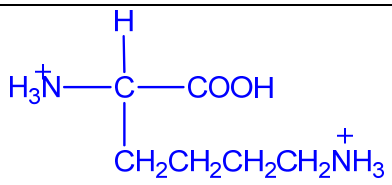


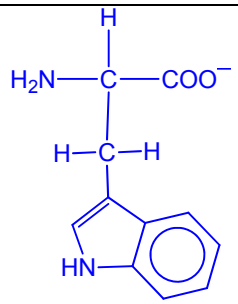
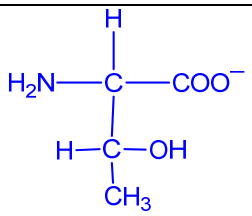
[1]

(d) The technique known as electrophoresis can be used to separate the amino acids This technique involves placing a solution of different amino acids at the centre of an agarose gel placed in an aqueous solution of a known pH An electric potential is then applied through electrodes which are connected to the two ends of the gel strip
An electrophoresis experiment is run on a solution containing the 3 amino acids mentioned above at pH 700 and the relative positions of the amino acids are obtained as shown in the diagram



Draw the structural formulae of the species found at positions **A**, **B** and **C** at the end of the experiment

Position	Structure at pH = 700
A	

B	
C	

[3]

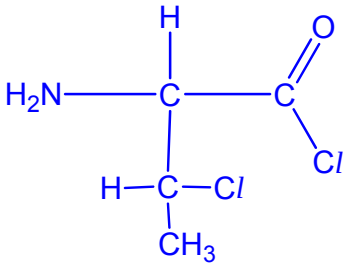
(e) State and explain the relative basicities of tryptophan and lysine

Try is a weaker base than lys
For Try, overlap of nitrogen p-orbital and π–orbital of phenyl ring results in delocalization of nitrogen lone pair into the aromatic ring
Thus, the nitrogen lone pair on side chain of Try is less available for donation to an acid than that of lys, where the nitrogen lone pair is more available for donation due to absence of delocalisation effect

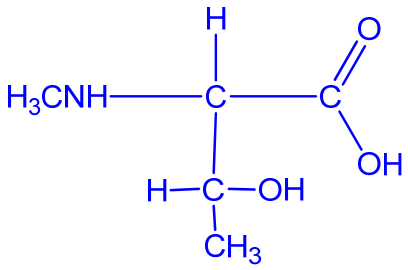
[3]

(f) Draw the structural formula of the organic products when

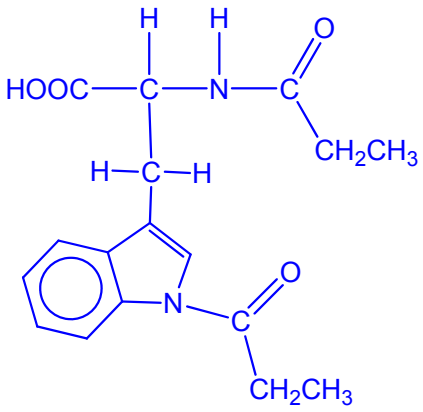
(i) PCl_5 is added to threonine (thr);



(ii) chloromethane is added to threonine (thr);



(iii) propanoyl chloride is added to tryptophan (trp)



[3]
[Total: 15]