CHEMISTRY

DATE: 4 June 2008 (afternoon)

DURATION OF THE EXAM :

3 hours (180 minutes)

PERMITTED MATERIAL :

Calculator (not graphical and not programmable)

INSTRUCTIONS :

Answer two A questions and two B questions.

Indicate which four questions you have answered by putting crosses in the appropriate place on the sheet supplied.

Use a separate answer sheet for each of the four main questions.

Question A1

Page 1/2 | Marks

a) i. Copy and complete the following equations and give the acid-base conjugate pairs for each reaction. — 3 marks

$$CH_3{-}NH_2(aq) + H_2O(l) \rightleftharpoons$$
$$CO_3^{2-}(aq) + H_3O^+(aq) \rightleftharpoons$$
$$HCO_3^-(aq) + CH_3{-}NH_2(aq) \rightleftharpoons$$

Given:

Acid	pK_a
$H_3O^+(aq)$	–1.74
$HCO_3^-(aq)$	10.3
$CH_3{-}NH_3^+(aq)$	10.6
$H_2O(l)$	15.7

ii. Classify all the bases in the three reactions in order of decreasing strength and justify the order. — 2 marks

iii. Identify the species (from the equations above) which show amphoteric behaviour and explain your answer. — 2 marks

b) The following information is given for aqueous solutions at 25 ^oC:

1.00×10^{-2} mol dm^{-3} methylamine solution, CH_3-$NH_2(aq)$, has a pH of 11.2.

1.00×10^{-2} mol dm^{-3} ammonia solution, $NH_3(aq)$, has a pH of 10.6.

i. Use the pH values given above to show that methylamine and ammonia are weak bases. — 2 marks

ii. Which of the two bases has the lowest K_b value? Explain your answer. — 1 mark

iii. Calculate the value of K_b for ammonia, NH_3. — 2 marks

c) 150 cm^3 of 1.00×10^{-2} mol dm^{-3} ammonia solution, $NH_3(aq)$, was mixed with 50.0 cm^3 of 1.50×10^{-2} mol dm^{-3} hydrochloric acid solution, HCl(aq). This produced a buffer solution with a pH of 9.24.

i. Write an equation for the reaction that occurs when the ammonia and hydrochloric acid solutions are mixed. — 1 mark

ii. Determine the amount of NH_3 (in moles) and the amount of its conjugate acid (in moles) present in the buffer solution. — 2 marks

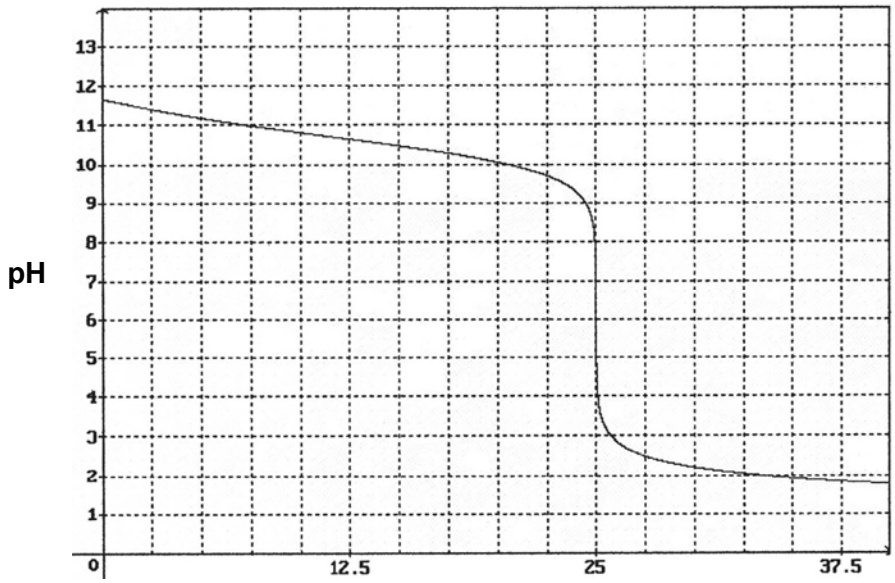
iii. Calculate the pK_a value for the conjugate acid of NH_3. — 1 mark

Question A1

Marks

d) A known mass of methylamine, CH_3-NH_2, was dissolved in water at 25 ^oC.

50.0 cm^3 of this solution was taken and titrated with 1.00 x 10^{-1} mol dm^{-3} hydrochloric acid solution, HCl(aq). The change in pH as an increasing volume of hydrochloric acid was added is shown in the graph below:



i. Use the graph to determine the pH at the equivalence point and determine the volume of hydrochloric acid added to reach the equivalence point. — 2 marks

ii. Write the equation for the reaction that explains the pH at the equivalence point. — 2 marks

iii. Calculate the initial concentration of the methylamine solution. — 2 marks

iv. Estimate the pK_b of methylamine, using data obtained from the graph. — 2 marks

v. Choose the best indicator to use for the titration from the list below. Explain your choice. — 1 mark

Indicator	pK_a
phenolphthalein	9.4
bromocresol red	6.3

Question A2

	Marks
Chlorine gas, $Cl_2(g)$, is a very important raw material in the chemical industry.	
a) In the laboratory, chlorine gas can be obtained by the action of hydrochloric acid on the MnO_4^- ion according to the following unbalanced equation: $\mathbf{MnO_4^-\,(aq) + Cl^-\,(aq) + H^+\,(aq) \rightarrow Mn^{2+}\,(aq) + H_2O\,(l) + Cl_2\,(g)}$	
i. State the oxidation numbers of all the elements and balance the equation.	3 marks
ii. The following experimental facts have been noted about halogens: Chlorine gas has no effect on a solution of sodium fluoride. Chlorine gas reacts with a solution of sodium iodide forming iodine, I_2. Chlorine gas reacts with a solution of sodium bromide forming bromine, Br_2. Iodine, I_2, has no effect on a solution of sodium bromide. From the information given above classify these halogens in order of their increasing oxidising ability. Explain your answer.	3 marks
b) Chlorine gas can also be obtained in the laboratory by electrolysis. The electrolysis of a solution of zinc chloride, $ZnCl_2(aq)$, is carried out in a U-tube. The power supply connected to the graphite electrodes generates a constant current of 5.00×10^{-1} A for 10.0 minutes	
i. Using the table below, indicate all the species that could react at the positive electrode (anode) and write the corresponding half-equations.	2 marks
ii. Is the release of chlorine gas that is observed at this electrode expected according to the potentials given below? Explain your answer.	2 marks
iii. Using the table below, indicate all the species that could react at the negative electrode (cathode) and write the corresponding half-equations.	2 marks
iv. Calculate the mass of the metal obtained at the negative electrode (cathode). **Given:** Molar atomic mass (g mol^{-1}): H = 1.01; Zn = 65.4 1 Faraday = 9.65×10^4 C mol^{-1} (Redox table on the following page)	2 marks

Question A2

Marks

Given:

Redox couples	$E^{\ominus}$ / V
$H_2O(l) / H_2(g), OH^-(aq)$	− 0.83
$Zn^{2+}(aq) / Zn(s)$	− 0.76
$O_2(g), H^+(aq) / H_2O(l)$	+ 1.23
$Cl_2(g) / Cl^-(aq)$	+1.36

c) Chlorine gas reacts with a warm solution of concentrated sodium hydroxide solution according to the following unbalanced equation: — 3 marks

$$\mathbf{Cl_2\ (g) + OH^-\ (aq) \rightarrow Cl^-\ (aq) + ClO_3^-\ (aq) + H_2O\ (l)}$$

Use oxidation numbers to balance this equation.

d) The compound sodium chlorate(V), $NaClO_3(s)$, can be used as a weed killer. The following method is used to determine the percentage by mass of this compound in an herbicide powder.

First, an excess of a solution of iron(II) ions is added so that all the chlorate(V) ions react according to the following equation:

Reaction 1:

$$\mathbf{ClO_3^-(aq) + 6\ Fe^{2+}(aq) + 6\ H^+(aq) \rightarrow 6\ Fe^{3+}(aq) + Cl^-\ (aq) + 3\ H_2O(l)}$$

The excess iron(II) ions are then reacted with an acidified solution of dichromate(VI), $Cr_2O_7^{2-}(aq)$, ions according to the following equation:

Reaction 2:

$$\mathbf{Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ Fe^{2+}(aq) \rightarrow 2\ Cr^{3+}(aq) + 6\ Fe^{3+}(aq) + 7\ H_2O(l)}$$

12.0 g of a herbicide powder were dissolved in distilled water to give a final volume of 1.00 dm^3. 20.0 cm^3 of this solution was removed and placed in a flask. Excess acid was added and then 100 cm^3 of 5.00×10^{-1} mol dm^{-3} solution of iron(II) ions was added.

When **reaction 1** was complete, a solution of dichromate(VI) ions with a concentration of 2.50×10^{-1} mol dm^{-3} was progressively added. 28.0 cm^3 of this solution were required to complete **reaction 2**.

Calculate:

i. The amount (in moles) of $Fe^{2+}(aq)$ ions that reacted with the $Cr_2O_7^{2-}(aq)$ ions. — 2 marks

Question A2

Page 3/3	Marks
ii. The amount (in moles) of $Fe^{2+}(aq)$ ions that reacted with the $ClO_3^-(aq)$ ions.	2 marks
iii. The molar concentration of $ClO_3^-(aq)$ ions in the herbicide powder solution.	2 marks
iv. The percentage by mass of $NaClO_3(s)$ in the herbicide powder.	2 marks
Given: Molar atomic mass ($g\ mol^{-1}$): O = 16.0; Na = 23.0; Cl = 35.5	

Question A3

Page 1/2 | Marks

a) Air contains mainly oxygen, O_2 (g), and nitrogen, N_2 (g). Under normal conditions they do not react together. However, in car engines and in domestic heating devices, nitrogen monoxide, NO(g), is formed. At lower temperatures, this gas can react with oxygen to form nitrogen dioxide, NO_2(g).

i. Give the equations for both reactions: one for the formation of nitrogen monoxide and the other for nitrogen dioxide. — 4 marks

Both of these nitrogen oxides are hazardous to organisms and to the environment. These oxides can be removed from exhaust fumes. This can be achieved by reacting these gases with gaseous ammonia, NH_3(g), in the presence of a catalyst. Water and nitrogen are formed by this reaction.

ii. Give the equation for the reaction of nitrogen monoxide with ammonia. — 3 marks

iii. Give the name of this type of reaction and explain your answer. — 2 marks

iv. Calculate the mass of ammonia needed to react with one ton (10^3 kg) of nitrogen monoxide. — 3 marks

Given: Molar atomic mass (g mol^{-1}): H = 1.01; N = 14.0; O = 16.0

In the exhaust pipes of cars the catalytic converter eliminates the nitrogen monoxide present in the fumes by reacting with carbon monoxide, CO(g), producing nitrogen as one of the products.

v. Give the equation for this reaction. — 2 marks

b) One of the damaging effects of the nitrogen oxides is caused by them forming acid rain. This also occurs with the gaseous oxides of sulphur: sulphur dioxide and sulphur trioxide. Sulphur dioxide reacts with water to form sulphurous acid, H_2SO_3(aq). The pK_a values at 25 °C are given below. The solubility of sulphur dioxide is 33.9 dm^3 of gas per 1.00 dm^3 of liquid water at 25 °C.

$$H_2SO_3(aq) + H_2O(l) \rightleftharpoons HSO_3^-(aq) + H_3O^+(aq) \quad pK_{a1} = 1.97 \quad (1)$$

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons SO_3^{2-}(aq) + H_3O^+(aq) \quad pK_{a2} = 7.18 \quad (2)$$

i. Calculate the pH of the solution considering only step **(1).** Assume that the solution is saturated and that SO_2 is totally converted into H_2SO_3(aq) and that there is no volume change when the SO_2 dissolves in the water. — 5 marks

Given:

Molar volume of a gas at 25 °C = 24.5 dm^3 mol^{-1}

Question A3

Page 2/2	Marks
Petrol contains small quantities of sulphur as an impurity. During the combustion of petrol, sulphur dioxide and sulphur trioxide are formed. If the air is humid then sulphuric acid, $H_2SO_4(aq)$, is formed. This acid rain not only damages plants but also minerals are eroded by the acid. An example of a mineral which can be eroded is calcium carbonate, $CaCO_3(s)$, present in the soil and in buildings.	
ii. Give an equation for the reaction of calcium carbonate with excess sulphuric acid.	2 marks
If an aqueous solution of sulphur dioxide is treated with excess bromine, $Br_2(aq)$, sulphate ions, $SO_4^{2-}(aq)$ are formed.	
iii. Explain, using an equation, why the pH decreases when the reaction proceeds.	4 marks

Question B1

	Page 1/1	Marks
a)	Give the simplified structural formulae of three primary alcohols which are isomers of pentan-1-ol, $C_5H_{11}OH$, and give the IUPAC name for one of them.	4 marks
b)	Do you expect the boiling points of the isomers in part a) to be higher or lower than that of pentan-1-ol? Explain your answer.	2 marks
c)	Dehydration of pentan-1-ol can yield two different products.	
	i. Using simplified structural formulae, write equations for the two reactions referred to above. Name a catalyst used in both reactions.	3 marks
	ii. Name the class of organic compounds to which each of the products in the above two reactions belongs.	2 marks
d)	The two compounds **X** and **Y** shown below are among those secreted by insects to attract other members of the same species. **$CH_3CH_2CH_2CH_2COOH$** **$CH_3COOCH_2CH_2CH_2CH_2CH_3$** **X** **Y** Such compounds are used to control insects. They are made synthetically. One of the starting materials used for their synthesis is pentan-1-ol.	
	i. Give the name and formula of an oxidising agent used to convert pentan-1-ol into compound **X**. Give the simplified structural formula and IUPAC name for any other organic product that might be obtained.	4 marks
	ii. Name the reagent and the catalyst used with pentan-1-ol to synthesise compound **Y**.	2 marks
	iii. Assuming that the pentan-1-ol is totally labelled using ^{18}O what would be the molecular molar mass of compound **Y**? Explain your answer by outlining the mechanism for the reaction leading to the synthesis of compound **Y**.	4 marks
	iv. Compare the solubility of ethanoic acid and compound **X** in water. Explain the difference.	2 marks
	v. Write the equation of the complete combustion of compound **Y**.	2 marks
	Given: Molar atomic mass (g mol^{-1}): H = 1.01; C = 12.0; O = 16.0	

Question B2

Page 1/2 | Marks

Consider the following organic compounds **A**, **B**, **C**, **D**:

A: C_6H_{11}-NH_2 (cyclohexylamine)

B: C_6H_5-NH_2 (phenylamine)

C: C_6H_{11}-NH-CH_3 (N-methylcyclohexylamine)

D: C_6H_5-NH-C_6H_5 (N,N-diphenylamine)

a) i. State and explain which structural feature makes these compounds Brønsted bases. — 2 marks

ii. Give the structural formula of the conjugate acid of compound **D**. — 1 mark

iii. The pK_b values of these compounds are:
9.6, 3.2, 3.4, 9.4 (in random order).
Assign the correct pK_b value to each of the four compounds **A**, **B**, **C**, **D**. Explain your answer. — 4 marks

iv. Between which two of these values does the pK_b of ammonia, NH_3, lie? Explain your answer. — 2 marks

b) An experiment is carried out using compound **B**. Two labelled test tubes are placed in an ice-water bath and contain:

Tube 1: Hydrochloric acid, crystals of sodium nitrite, $NaNO_2$(s), and a few of drops of compound **B**.

Tube 2: Sodium hydroxide solution, NaOH(aq), and a few drops of compound **B**.

i. Give the structural formula of the organic cation (positive ion) present in tube 1. — 2 marks

ii. If the contents of tubes 1 and 2 are now mixed, a precipitate called 'aniline yellow' is obtained. Write the structural formula of 'aniline yellow'. — 2 marks

c) Compound **B** was used to manufacture the pain-relieving medicine acetanilide, C_6H_5-NH-CO- CH_3.

i. Name the organic functional group present in acetanilide. — 1 mark

This functional group is also present in polypeptides and nylons.

ii. Write the simplified structural formulae of all the dipeptides that can be obtained from the reaction between 2-aminoethanoic acid (glycine) and 2-aminopropanoic acid (alanine). — 2 marks

iii. 1,6-diaminohexane condenses with hexane-1,6-dioic acid to form nylon 6,6. Give the simplified structural formula for the repeating unit in nylon 6,6 — 2 marks

Question B2

Page 2/2	Marks
iv. Give the simplified structural formula of the organic compound **E**, which must be reacted with **B** to synthesise acetanilide.	1 mark
v. The yield of this synthesis relative to compound **B** is 60 %. Calculate the mass of acetanilide obtained from 10.0 g of **B**.	4 marks
Compound **E** can be used to synthesise another pain-relieving medicine, paracetamol, $HO\text{-}C_6H_4\text{-}NH\text{-}CO\text{-}CH_3$.	
vi. Give the structural formula of the other organic compound which must be reacted with compound **E** to obtain paracetamol.	2 marks
Given:	
Molar atomic mass ($g\ mol^{-1}$): H = 1.01; C = 12.0; O = 16.0; N = 14.0	

Question B3

Page 1/2 | Marks

a) Sometimes when a bottle of wine is opened it is undrinkable because it tastes like vinegar. To prevent this, tablets of potassium hydrogensulphite, $KHSO_3(s)$ can be added. This substance kills bacteria and reacts with aldehydes forming tasteless compounds. Excessive use of these tablets could cause health problems and the World Health Organisation has put a limit of 0.7 mg intake of potassium hydrogensulphite per kg of body mass.

i. Using structural formulae, write the half-equation to illustrate the partial oxidation of ethanol to form an aldehyde. — 2 marks

ii. Using structural formulae, write the half-equation for the complete oxidation of ethanol in aqueous solution to illustrate how the wine becomes acidic. — 2 marks

iii. Potassium hydrogensulphite reacts with aldehydes in a 1:1 molar ratio. A particular wine contains 35.0 mg dm^{-3} of ethanal. Calculate the minimum mass of potassium hydrogensulphite needed to eliminate the ethanal present in a bottle (750 cm^3) of this wine. — 3 marks

Given: Molar atomic mass (g mol^{-1}):

H = 1.01; C= 12.0; O = 16.0; S= 32.1; K = 39.1

iv. State whether this intake of potassium hydrogensulphite is within the safety limits, if a 75.0 kg person drinks a whole bottle of this wine. Explain your answer. — 2 marks

b) Good wine still contains some carboxylic acids but as long as these are less than 5.00×10^{-1} g dm^{-3} the wine will taste good. Ethanoic acid is not the only carboxylic acid present in wine. Other acids include 2,3-dihydroxybutandioic acid, 2-hydroxybutandioic acid and 2-hydroxypropanoic acid.

i. Draw the structural formulae of these three carboxylic acids. — 3 marks

The carboxyl group of 2-hydroxypropanoic acid can be reduced in two steps, producing compound **A** and then compound **B**.

ii. An acidified solution of product **A** reacts with a solution of potassium cyanide, KCN(aq). Give the mechanism for this reaction. — 3 marks

iii. The boiling point of product **B** is much higher than that of propan-1-ol. Give two reasons which explain this difference. — 2 marks

Several esterification reactions can occur in a mixture of product **B** and 2-hydroxypropanoic acid.

iv. Draw the structural formulae of three possible products that can be formed. — 3 marks

Question B3

Page 2/2	Marks
c) Aromatic alcohols are more acidic than aliphatic ones. For example hydroxybenzene (phenol) has a pK_a of 10 whereas ethanol has a pK_a of 16.	
i. Using structural formulae explain why phenol is a stronger acid than ethanol.	3 marks
ii. Write an equation to illustrate the acidity of phenol.	2 marks