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93102Q

NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

Scholarship 2005
Chemistry

9.30 am Wednesday 7 December 2005
Time allowed: Three hours
Total Marks: 94

QUESTION BOOKLET

You should write ALL your answers in the Answer Booklet 93102A.

A Periodic Table is printed on page 2 of this booklet.

Show ALL working. Start each question on a NEW page. Number each question carefully.

Check that this booklet has pages 2–7 in the correct order.

Question	Number of Marks	Suggested Time
One	22	40 minutes
Two	14	25 minutes
Three	14	25 minutes
Four	14	25 minutes
Five	14	25 minutes
Six	16	25 minutes

YOU MAY KEEP THIS BOOKLET AT THE END OF THE EXAMINATION.

PERIODIC TABLE OF THE ELEMENTS

1	*2*											*13*	*14*	*15*	*16*	*17*	*18*
																	2 **He** 4.0
3 **Li** 6.9	4 **Be** 9.0							Atomic Number 1 **H** 1.0 Atomic Mass				5 **B** 10.8	6 **C** 12.0	7 **N** 14.0	8 **O** 16.0	9 **F** 19.0	10 **Ne** 20.2
11 **Na** 23.0	12 **Mg** 24.3	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	13 **Al** 27.0	14 **Si** 28.1	15 **P** 31.0	16 **S** 32.0	17 **Cl** 35.5	18 **Ar** 40.0
19 **K** 39.1	20 **Ca** 40.1	21 **Sc** 45.0	22 **Ti** 47.9	23 **V** 50.9	24 **Cr** 52.0	25 **Mn** 54.9	26 **Fe** 55.9	27 **Co** 58.9	28 **Ni** 58.7	29 **Cu** 63.6	30 **Zn** 65.4	31 **Ga** 69.7	32 **Ge** 72.6	33 **As** 74.9	34 **Se** 78.9	35 **Br** 79.9	36 **Kr** 83.8
37 **Rb** 85.5	38 **Sr** 87.6	39 **Y** 88.9	40 **Zr** 91.2	41 **Nb** 92.9	42 **Mo** 95.9	43 **Tc** (98)	44 **Ru** 101	45 **Rh** 103	46 **Pd** 106	47 **Ag** 108	48 **Cd** 112	49 **In** 115	50 **Sn** 119	51 **Sb** 122	52 **Te** 128	53 **I** 127	54 **Xe** 131
55 **Cs** 133	56 **Ba** 137	71 **Lu** 175	72 **Hf** 179	73 **Ta** 181	74 **W** 184	75 **Re** 186	76 **Os** 190	77 **Ir** 192	78 **Pt** 195	79 **Au** 197	80 **Hg** 201	81 **Tl** 204	82 **Pb** 207	83 **Bi** 209	84 **Po** 210	85 **At** 210	86 **Rn** 222
87 **Fr** 223	88 **Ra** 226	103 **Lr** 262	104 **Rf** 261	105 **Db** 262	106 **Sg** 263	107 **Bh** 262	108 **Hs** 265	109 **Mt** 266									

57 **La** 139	58 **Ce** 140	59 **Pr** 141	60 **Nd** 144	61 **Pm** 147	62 **Sm** 150	63 **Eu** 152	64 **Gd** 157	65 **Tb** 159	66 **Dy** 163	67 **Ho** 165	68 **Er** 167	69 **Tm** 169	70 **Yb** 173
89 **Ac** 227	90 **Th** 232	91 **Pa** 231	92 **U** 238	93 **Np** 237	94 **Pu** 239	95 **Am** 241	96 **Cm** 247	97 **Bk** 249	98 **Cf** 251	99 **Es** 254	100 **Fm** 257	101 **Md** 258	102 **No** 256

QUESTION ONE (22 marks)

(a) The boiling points of three compounds are: CH_3OH, 65°C; CH_3Cl, −24°C; CH_3Br, 4°C

Discuss the relative strengths of the intermolecular forces in liquid samples of these three compounds.

(b) Heavy metal ions such as silver and lead are toxic to human systems.

Show by calculation whether the addition of 5 mg of silver nitrate or the addition of 5 mg of lead nitrate to 9 L of blood (the average human blood volume) will result in the greater mass of metal ion remaining in solution in the blood.

$[Cl^-]$ in blood = 3.65 g L^{-1}.
$K_s(AgCl)$ = 1.6×10^{-10}
$K_s(PbCl_2)$ = 2.4×10^{-4}
$M(AgNO_3)$ = 170 g mol^{-1}
$M(Pb(NO_3)_2)$ = 331 g mol^{-1}

(c) The shape of the tetrafluoride molecule ZF_4 depends on the group in the periodic table in which the atom Z is found. ZF_4 molecules may have shapes described as tetrahedral, seesaw (distorted tetrahedral) or square planar. Only one of these shapes will give rise to a polar molecule.

Discuss the above information. Choose molecules to illustrate each of the shapes described and justify your choice.

QUESTION TWO (14 marks)

(a) Hydrogen carbonate ions, HCO_3^- play a major role in maintaining the pH of blood plasma. HCO_3^- is a member of two acid-base conjugate pairs:

$$H_2CO_3 / HCO_3^- \ (pK_a(H_2CO_3) = 6.38)$$
$$HCO_3^- / CO_3^{2-} \ (pK_a(HCO_3^-) = 10.32)$$

The pH of arterial blood is 7.4.

Show by calculation which conjugate acid-base pair is more important at this pH. Comment on the relative abilities of this system to buffer against added acid and against added base.

(b) Account for the observation that platinum metal reacts with aqua regia (a mixture of hydrochloric and nitric acids) but not with concentrated hydrochloric or nitric acid individually.

$Pt^{2+} + 2e^- \rightarrow Pt$ $\quad E° = 1.18$ V

$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$ $\quad E° = 0.96$ V

$PtCl_4^{2-} + 2e^- \rightarrow Pt + 4Cl^-$ $\quad E° = 0.76$ V

$PtCl_6^{2-} + 2e^- \rightarrow PtCl_4^{2-} + 2Cl^-$ $\quad E° = 0.68$ V

$2H^+ + 2e^- \rightarrow H_2$ $\quad E° = 0.00$ V

QUESTION THREE (14 marks)

Hydroxylammonium chloride ($^+NH_3OH\,Cl^-$) reacts with Fe^{3+} ions to produce Fe^{2+}.

1.00 g of hydroxylammonium chloride was dissolved in distilled water and diluted to 250.0 mL. 25.00 mL of this solution was added to a solution containing an excess of iron(III) ions and sulfuric acid. The mixture was boiled. After cooling it was then titrated with a solution of 0.0200 mol L^{-1} potassium permanganate. 28.90 mL was needed to reach the equivalence point.

(a) Determine which of N_2, NO, N_2O, N_2O_4 or NH_3 is the nitrogen-containing product of the reaction between the hydroxylammonium chloride and iron(III) by:

(i) calculating the ratio of the amount in moles of Fe^{3+} ions to the amount in moles of hydroxylammonium chloride that have reacted

(ii) considering the oxidation number of nitrogen in the reactant and possible products.

(b) Write a balanced equation for the reaction of iron(III) with hydroxylammonium chloride.

QUESTION FOUR (14 marks)

A classic system used in equilibrium studies involves the reaction of ethanol with ethanoic acid to produce ethyl ethanoate and water.

$$CH_3COOH(\ell) + CH_3CH_2OH(\ell) \rightleftharpoons CH_3COOCH_2CH_3(\ell) + H_2O(\ell)$$

(a) In experiment **(1)**, a mixture of 1.00 mol ethanoic acid and 0.500 mol of ethanol was allowed to stand until analysis showed that the composition was constant. The equilibrium mixture was then analysed by titration. The acid in one hundredth of the reaction mixture was completely consumed by 30.74 mL of 0.0940 mol L^{-1} $Ba(OH)_2$.

In experiment **(2)**, the above procedure was repeated using 0.500 mol of ethanoic acid and 0.500 mol of ethanol.

(i) Calculate the equilibrium constant, *K*, for the reaction, and the % yield of the ester, using the information from experiment **(1)**. (Note that the only water in the reaction mixture is produced in the reaction.)

(ii) Discuss, with reference to the *K* expression, how the equilibrium concentrations of each component of the mixture in experiment **(2)** differ from the concentrations in experiment **(1)**.

(b) In the preparation of organic compounds, reaction conditions are manipulated to maximise the % yield and the purity of the product. The following procedure has been used to prepare the ester, ethyl ethanoate.

INSTRUCTIONS FOR PREPARING THE ESTER, ETHYL ETHANOATE

1. Mix 5 mL of ethanol with 5 mL of ethanoic acid in a **dry**, pear-shaped flask.
2. Carefully **add**, with mixing, **1 mL of concentrated sulfuric acid**.
3. Add one or two boiling chips and gently **reflux the mixture** for 10 minutes.
4. **Distil the product mixture.**
5. Transfer the distillate to a separating funnel, and **add 3 mL of 30% sodium carbonate solution**. Stopper the funnel and shake carefully. Make sure you periodically invert the funnel and open the tap.
6. Separate the two layers. **Add some anhydrous calcium chloride to the liquid from the upper layer**. Stir well, then allow to stand.
7. Decant the ethyl ethanoate into a small, dry flask and **distil, collecting the fraction that boils between 74 – 79°C**.

Discuss how each of the actions given in **bold** (in the above instructions) affects the % yield or the purity of the product.

The boiling point of ethyl ethanoate is 77.1°C.

QUESTION FIVE (14 marks)

Alcohols having five carbons are widely used in the flavour industry. One of these is used in the preparation of a wasp attractant. This compound has one –OH group, is saturated and has at least one carbon branch and no ring.

(a) Draw structures for all compounds fitting this description.

(b) Devise a method based on the chemical reactivity and properties of the isomers that would identify which of the alcohols is the one used in the preparation of the wasp attractant.

Discuss the structural basis for the different observations that would be made at each step in this method.

Assume that:

- any compound that has a stereocentre is present as a single enantiomer and the presence of optical activity in a molecule can be detected with a polarimeter
- reaction products can be isolated so that their functional groups can be identified
- the following reagents are available: Br_2, acidified $K_2Cr_2O_7$, $SOCl_2$, $NaHCO_3(aq)$, KOH in ethanol.

QUESTION SIX (16 marks)

Some automatic titrators used in modern analytical laboratories measure the electrical conductivity of the solution in the flask as the titration proceeds. The equivalence point is determined by monitoring changes in the conductivity of the solution. These changes depend on the concentration and the relative conductivities of the ions in solution.

The relative conductivities of some ionic species are shown in the table below.

Ionic species	**Relative conductivity**
Na^+, Cl^-, CH_3COO^-	1
OH^-	3
H_3O^+	5

(a) Sketch the plot of conductivity of the titration mixture against the volume of NaOH added for the titration of 1.00 mol L^{-1} HCl with 1.00 mol L^{-1} NaOH. (See hint below.)

Justify your answer by showing how significant points on the graph were determined ***OR*** by discussing the reasons for the changing conductivity.

(b) Show on the graph drawn in (a) how the shape will change if 1.00 mol L^{-1} CH_3COOH is used in the titration instead of HCl. Justify your answer.

Hint: It may be useful to construct a table to identify the ions present and their relative concentrations and conductivities at different stages in the titration, including a point after the equivalence point. It can be assumed that the total conductivity in a solution is the sum of conductivities of the ions present.