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93102Q

NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

New Zealand Scholarship Chemistry, 2004

9.30 am Thursday 11 November 2004

QUESTION BOOKLET

A Periodic Table is printed on page 8 of this booklet.

You should answer ALL the questions in the separate Answer Booklet 93102A

Check that this booklet has pages 2–8 in the correct order.

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

Outcome description

The student will demonstrate the ability to integrate and apply chemical knowledge, principles and skills to a range of situations.

Scholarship Criteria

The student will:

- integrate and apply knowledge, principles and skills from different areas of chemistry.
- analyse and interpret information.

Scholarship with Outstanding Performance Criteria

In addition to meeting the criteria for Scholarship, the student will:

- consistently demonstrate a depth and breadth of knowledge together with insight and flair in the application of chemical principles.

You have three hours to answer the questions in this booklet.

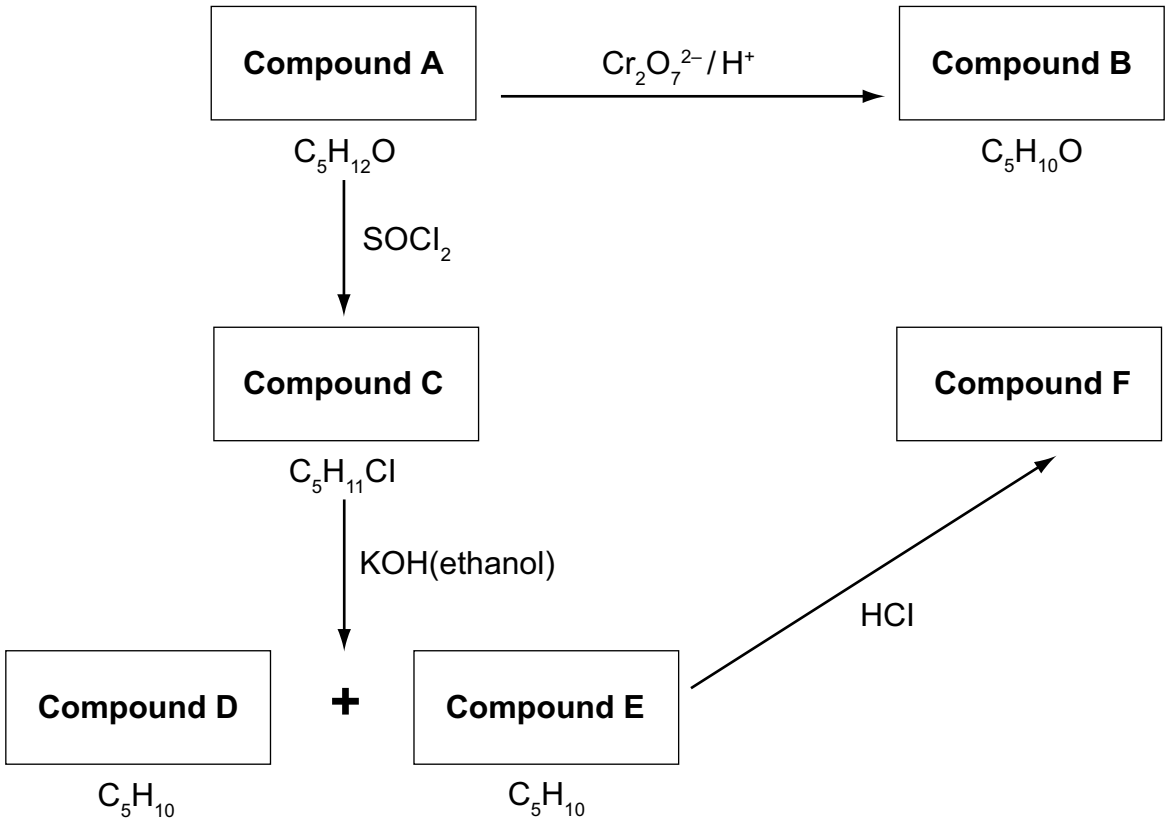
QUESTION ONE: ORGANIC MOLECULES

Suggested time: 30 minutes

(a) Determine the structures of each of the compounds **A** to **F** in the following reaction scheme.

Further information is provided in the box below.

> Compound **A** can exist as enantiomers (optical isomers).
>
> Compound **B** does not react with Tollens' or Fehling's reagents.
>
> Compounds **D** and **E** cannot exist as geometric isomers.
>
> Compound **E** reacts with HCl to produce compound **F** as a major product and also to regenerate Compound **C**.
>
> Compound **F** is a structural isomer of compound **C**.



(b) Compounds **X**, **Y** and **Z** all have the same molecular formula $C_3H_6O_2$.

Compound **X** has neither geometric nor optical isomers. Compound **Y** has geometric isomers only and compound **Z** has optical isomers only.

Draw and name possible structures for each of compounds **X**, **Y** and **Z**.

(c) Account for the variation in boiling points of the amines given in the table below.

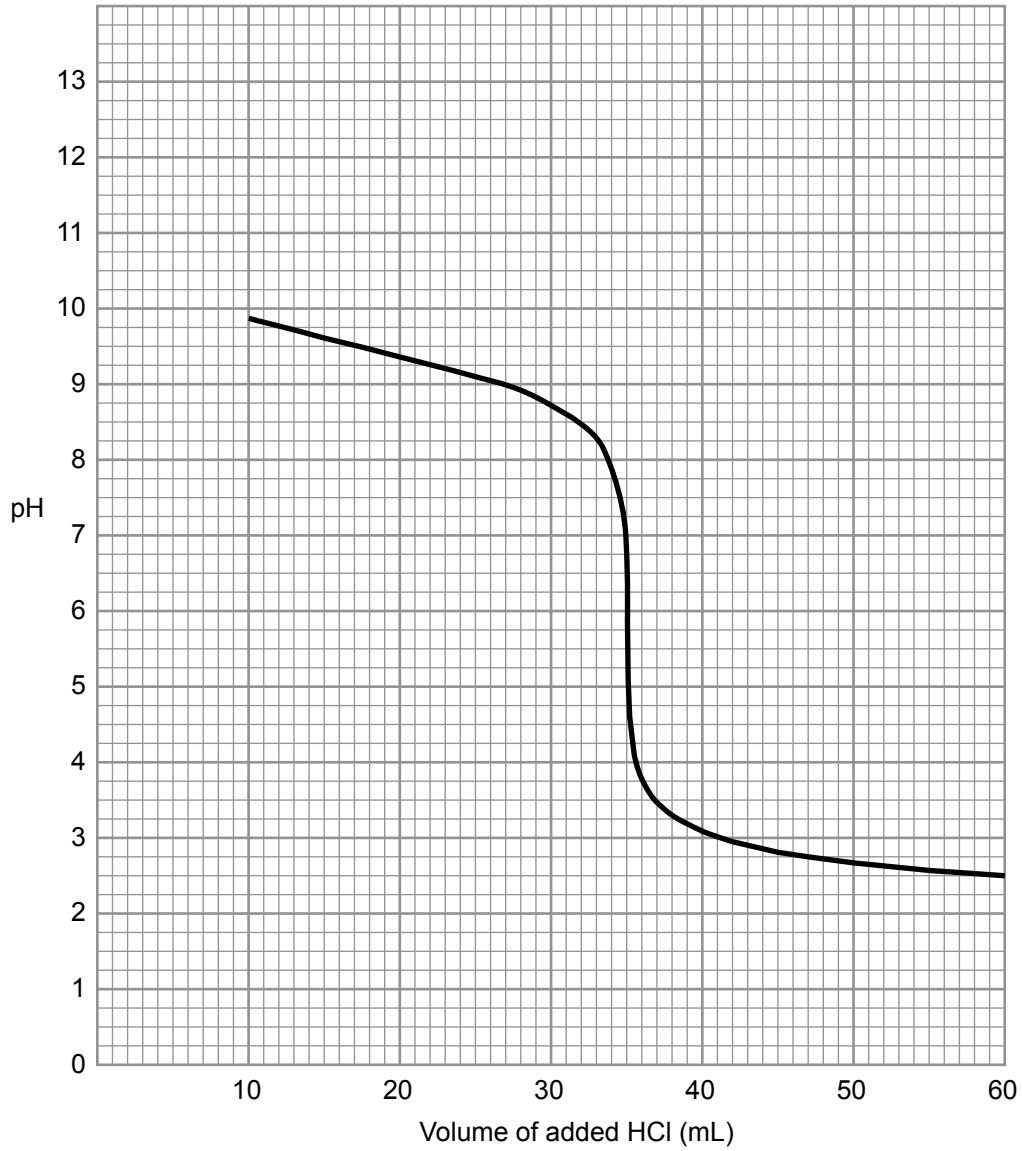
	Name	**Formula**	***M*** **(g mol^{-1})**	**Boiling Point (ºC)**
1	ethyldimethylamine	$(CH_3)_2NCH_2CH_3$	73.1	36.0
2	2-methyl-2-propylamine	$(CH_3)_3CNH_2$	73.1	44.4
3	1-butylamine	$CH_3(CH_2)_3NH_2$	73.1	77.9
4	diethylmethylamine	$(CH_3CH_2)_2NCH_3$	87.2	64

QUESTION TWO: AQUEOUS SOLUTIONS

Suggested time: 30 minutes

(a) The weak base ethanolamine, $HOCH_2CH_2NH_2$, can be titrated with HCl.

The graph below plots the titration of 25.0 mL of a solution of ethanolamine with 0.0107 mol L^{-1} HCl. The portion of the curve from 0 to 10 mL has been left out.



(i) Calculate the pH of the ethanolamine solution.

(ii) Show by calculation that the pH at equivalence point is 5.9.

(iii) Relate the change in pH and the shape of the titration curve to the change in the nature and concentration of the species in the flask as the titration is carried out.

(b) Calculate the pH of a saturated solution of $Hg(OH)_2$. Justify any assumptions made in carrying out the calculation.

$$K_s(Hg(OH)_2) = 3.6 \times 10^{-26}$$

QUESTION THREE: ALCOHOL INVESTIGATIONS

Suggested time: 30 minutes

Alcohol levels in blood samples can be determined by back titration. The alcohol is first removed from the blood by distillation and then heated with a known excess of acidified potassium dichromate solution. Excess potassium iodide is added and the resulting solution is titrated with standard sodium thiosulfate solution. Starch indicator is added near the end point.

Equations for the reactions are:

$$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$$

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

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

(a) Discuss the method described above, justifying the need for each step involved.

(b) A blood sample has been removed from a suspected adult drunk driver.

The alcohol from 10.0 mL blood samples is added to 10.0 mL of acidified 0.0492 mol L^{-1} $K_2Cr_2O_7$ solution and warmed in a water bath. When oxidation is complete, excess KI is added and the sample is titrated with 0.105 mol L^{-1} $Na_2S_2O_3$ solution.

The titre values for four successive 10.0 mL blood samples from the same driver were:
17.94, 17.86, 17.70 and 17.84 mL.

Calculate the concentration of alcohol in the blood and determine if the sample is above the legal limit of 80 mg alcohol per 100 mL of blood.

(c) A student decides to use this analytical method to determine the amount of alcohol present in some home brew. Initial trials of diluted samples of the home brew gave titre values of less than 1 mL.

Explain why the procedure being used is not suitable for quantitative determination of the alcohol in the home brew and outline ways that the method could be adjusted to make it more acceptable.

QUESTION FOUR: COMPARING PROPERTIES

Suggested time: 45 minutes

(a) Discuss, in terms of their structure, the relative sizes of the atoms and ions of the elements O, Mg and S.

(b) Use the data in the table below to deduce which of the two compounds, ethane or ethanol, has the more negative enthalpy of combustion.

	$\Delta_f H°$ (kJ mol^{-1})
CH_3CH_3	–84
CH_3CH_2OH	–235

(c) The K_w for water at room temperature (25°C) is 1 x 10^{-14} and at body temperature (37°C) is 2.5 x 10^{-14}.

Determine the pH of pure water at 37°C and discuss whether this solution is neutral or not.

(d) Oxidation of sugars in our bodies is a long and complicated biochemical process. However, the total energy change for the chemical reaction depends only on initial and final states of the system.

Calculate the standard enthalpy energy change for the combustion of sucrose ($C_{12}H_{22}O_{11}$) and determine the mass in grams of sucrose that would be needed to produce sufficient energy to evaporate exactly one litre of water.

Compound	$\Delta_f H°$ (kJ mol^{-1})
$C_{12}H_{22}O_{11}(s)$	–2222.0
$CO_2(g)$	–393.5
$H_2O(\ell)$	–285.8
$H_2O(g)$	–241.8

QUESTION FIVE: IDENTIFYING WHITE SOLIDS

Suggested time: 30 minutes

A solid which is white and water soluble is known to be one of:

- NaOCl
- NaBr
- KIO_3
- Na_2SO_3.

The identity of the solid can be established using:

(i) red litmus paper

(ii) acidified aqueous I^-.

Formulate a scheme for identifying the solid with reference to the data below.

Provide a comprehensive justification for the steps in the scheme on the basis of the data given.

Acid	**pK_a**
HBr	<0
HOCl	7.54
HIO_3	<0
HSO_3^-	7.20

Couple	***E*°/V (at pH 1)**
$HClO_2/HOCl$	1.67
H_5IO_6/IO_3^-	1.60
$HOCl/Cl^-$	1.51
IO_3^-/I_2	1.20
Br_2/Br^-	1.09
I_2/I^-	0.62
H_2SO_3/S	0.45
HSO_4^-/H_2SO_3	0.17

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**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**									

Lanthanide Series	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
Actinide Series	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** 255