New Zealand Chemistry Olympiad Trust

Training Group Selection Examination

Thursday 3 November 2011

TIME ALLOWED: 120 minutes

Answer **ALL** questions on this examination booklet

Calculators may be used

The marks for the **eight** (8) questions sum to **80**

A periodic table with atomic masses is also provided

STUDENT'S NAME:________________________________

SCHOOL:______________________________________

Question	**1 /10**	**2 /12**	**3 /10**	**4 /10**	**5 /6**	**6 /14**	**7 /7**	**8 /11**	**Total /80**
Mark									

1) Water [10 marks]

a) Water is a very interesting chemical substance. In your own words explain the following properties of water: [1 mark each]

i. Ice cubes float in liquid water

ii. Water is a good solvent for ionic substances

iii. Washing hung on a line at temperatures below 0 ˚C still becomes dry

iv. A burn from steam at 100 ˚C is more serious than a burn from liquid water at 100 ˚C, or a burn from ethanol vapour at 100 ˚C

v. Very pure water has a high electrical resistivity (18 MΩ cm) but still conducts electricity very slightly

b) Calculate the pH of a solution made from mixing each of the following solutions.
[Use $K_w = 10^{-14}$ at 25 ˚C] [5 marks]

i. 25 mL of 0.15 mol L^{-1} NaOH with 10 mL of 0.1 mol L^{-1} H_2SO_4

ii. 10 mL of 0.15 mol L^{-1} HCl with 25 mL of 0.2 mol L^{-1} HCl

2) Molecular shapes [12 marks]

a) Draw Lewis diagrams of the following molecules. Use these to draw the three-dimensional shapes of the molecules, mark any non-bonding lone pairs, and estimate all bond angles. If a molecule is polar, mark the slightly positive end. [2 marks each]

i. NH_3

ii. BF_3

iii. NO_2

iv. ClO_2^-

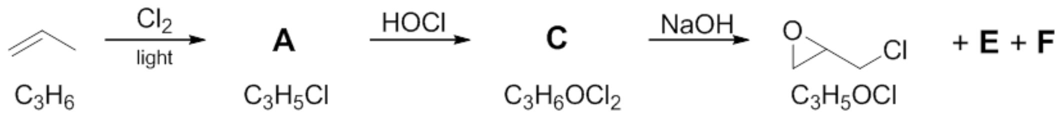
b) The last of these is an ion used to make chlorine dioxide gas, ClO_2. This ClO_2 gas is an important bleach used in timber treatment that was first obtained by the very hazardous disproportionation of chloric acid, $HClO_3$. The other products of this disproportionation reaction are water and perchloric acid, $HClO_4$.

i. Give the oxidation states of chlorine in ClO_2, $HClO_3$ and $HClO_4$. [1.5 marks]

ii. Using these oxidation states, or otherwise, write a balanced equation for the formation of ClO_2 from $HClO_3$. [2.5 marks]

3) Synthesis of epoxy resins [10 marks]

The synthesis of epoxy resins is a multi-billion dollar industry worldwide. The product of the scheme is epichlorohydrin, an intermediate in the synthesis of one type of epoxy resin that is a high-performance adhesive.



a) Draw the structure for **A**. [1 mark]

b) Formation of **A** also gives rise to an inorganic product **B**. Give the formula for **B**. [1 mark]

c) Give the type of the reaction occurring in formation of **A** from C_3H_6. [1 mark]

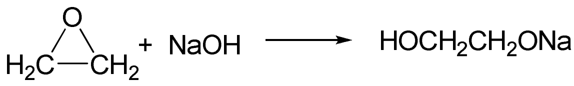
d) Draw the structure for **C.** [1 mark]

e) Give the type of reaction occurring in formation of **C** from **A.** [1 mark]

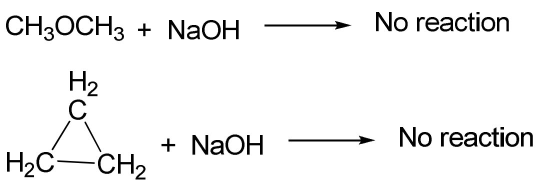
f) What is the role played by NaOH in formation of epichlorohydrin from **C**? *Justify your answer.* [1 mark]

g) What are the products **E** and **F**? [2 marks]

h) The oxygen-containing functional group in *epi*-chlorohydrin is known as an epoxide. Epoxides are compounds that have an oxygen in a three-membered ring. Epoxides are susceptible to a ring-opening reaction in which one of the carbon-oxygen bonds is broken.



As show below, a similar reaction does not occur if the oxygen is not in the ring OR for ring compounds that do not contain oxygen.



Give reasons for these differences in reactivity. [2 marks]

4) Organic isomers [10 marks]

There are three isomeric compounds having the formula $C_6H_{14}O$ that do not react with acidified potassium dichromate.

a) Draw the structures of the three $C_6H_{14}O$ isomers that fit this description.[3 marks]

One of these isomers (**A**) reacts with concentrated sulfuric acid to give a mixture of two compounds (**B** and **C**) which have the formula C_6H_{12}. **B** exists as cis-trans isomers. **C** does not.

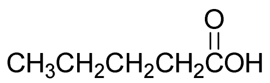
b) Which of these is **A**? Justify your choice including drawing structures for **B** and **C** and explaining why one of these can exist as *cis-trans* isomers while the other can not. [3 marks]

c) **B** and **C** react with aqueous H_2SO_4 to give **A** as the major product along with **D** and **E**, compounds that are isomers of **A**. Draw **D** and **E**. [2 marks]

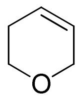
d) Which of these could be converted to **F**, a compound which is isomeric with **B** and **C**? Write the equation for the reaction including the reagent. [2 marks]

5) Organic molecule identification [6 marks]

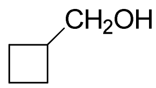
These four compounds below **(A-D)** are in bottles from which the labels have fallen off.



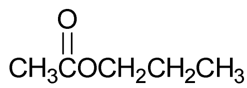
A



B



C



D

a) Devise a scheme, using test-tube reactions, to identify the contents of the bottles. You may choose any appropriate reagents to use in the identification.
Your scheme should indicate the sequence in which the test tube reactions are done and the reasons for your sequence.
Write equations for any reactions that occur. [4 marks]

b) ^{13}C NMR spectroscopy is a technique that is used to deduce the structure of unknown organic compounds. In ^{13}C NMR a peak is observed for each carbon in a molecule that is in a different bonding environment. In some cases the number of bonding environments is equal to the number of carbons; in other cases symmetry in the structure results in the number of bonding environments being fewer than the number of carbon atoms.

Which of the structures above has the fewest bonding environments for carbon? Justify your answer. [2 marks]

6) Gas Equilibrium [14 marks]

The equilibrium $2NO_2(gas) \rightleftharpoons N_2O_4(gas)$ is established at 25 ˚C in a glass piston.

The enthalpy change for the forward reaction is $\Delta_r H$ = –57.2 kJ/mol.

a) Predict, with reasoning, what will happen to the *equilibrium constant* and the *amount in moles of **N_2O_4** compared to the original system* in the piston when equilibrium is re-established after the following changes. (Apart from change (ii) the volume of the piston is constant): [1 mark each]

i. The temperature is increased to 100 ˚C

ii. The piston is pushed in, halving the volume available to the gas

iii. An additional amount of NO_2 gas is added to the reaction mixture

iv. An additional amount of N_2O_4 gas is added to the reaction mixture

v. A catalyst is added to the reaction mixture

vi. Argon gas is added to the reaction mixture, doubling the total pressure in the piston

b) N_2O_4 gas is colourless, while NO_2 is a reddy-orange colour. This fact can be used to determine the concentration of NO_2 in the reaction mixture through the use of *Beer's Law* ($A = \varepsilon cl$) which relates the amount of light absorbed (A, no units) to the concentration of NO_2 (c, mol L^{-1}), the length of the cell through which the light is passed (*l*, often 1cm) and a molar absorptivity coefficient ε which has units L mol^{-1} cm^{-1}.

6.42×10^{-3} mol of pure NO_2 gas is introduced to a 10.0 mL glass piston with a 1 cm path length at 25 ˚C, and the absorbance of the gas is immediately measured to be A = 0.845. After the gas has reached equilibrium the absorbance in the same cell is measured to be only A = 0.0546.

i. Use the information above to determine ε for NO_2 . State any assumptions necessary. [2 marks]

ii. Calculate K_c for the $2NO_2(gas) \rightleftharpoons N_2O_4(gas)$ equilibrium at 25 ˚C. [3 marks]

c) Calculate the heat given off (in J) when the 6.42×10^{-3} mol of pure NO_2 gas is allowed to reach equilibrium at 25 ˚C in the situation above. If you have not managed to calculate K_c in the previous part, you may use K_c = 170.0. [3 marks]

7) Superconductors [7 marks]

Yttrium oxide, barium carbonate and copper oxide react in a solid state reaction at high temperature (900 °C) to form the superconductor **A** which contains 13.4 % Y, 41.2 % Ba and 28.6 % Cu by mass percentage.

a) Assuming that the only element unaccounted for in **A** is oxygen, determine the empirical formula of **A**. [3 marks]

b) Given that the oxidation state of yttrium is +3 and barium is +2, calculate the average oxidation state of copper. (If you could not determine the empirical formula of compound A, use $\mathbf{Y_2BaCu_3O_8}$) [1 mark]

c) Reduction of **A** at 200 °C in hydrogen reduces all the Cu^{3+} in the material to Cu^{2+} and produces compound **B** and water vapour. All the other elements remain in the same oxidation state. Given that the starting mass of the material was 84.2 mg, what would be the mass of the remaining compound **B** after reduction? (Hint: consider the difference in oxygen content for the two different compounds, A and B)
[3 marks]

8. Razor blades (11 marks)

Razor blades are made from an alloy of iron and chromium. A piece of a razor blade with a mass of 0.1331 g is allowed to react with an excess of dilute sulfuric acid to form a pale green solution containing Fe^{2+} ions. When the solution is titrated with acidified potassium permanganate of unknown concentration, 20.08 mL of the permanganate solution is consumed. The Cr^{3+} ions formed when the Cr metal dissolves in sulfuric acid do not react with the permanganate under these conditions.

A 10.00 mL aliquot of a 0.0500 mol L^{-1} oxalic acid solution ($H_2C_2O_4$) is acidified with sulfuric acid, and the solution is titrated with the **same** permanganate solution. 9.76 mL of the permanganate solution is consumed. The oxalic acid is oxidised to CO_2.

a) **Write** balanced chemical equations for:

i) the reaction between Fe and sulfuric acid. [2 marks]

ii) the reaction that takes place in the titration of the sample solution with permanganate ions. [2 marks]

iii) the reaction between oxalic acid and permanganate ions. [2 marks]

b) **Calculate** the concentration of the permanganate solution. [2 marks]

c) **Calculate** the mass percent of iron in the razor blade. [3 marks]

PERIODIC TABLE OF THE ELEMENTS

Atomic Number — 1 **H** 1.0 — Molar Mass / g mol^{-1}

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
																	2 **He** 4.0
3 **Li** 6.9	4 **Be** 9.0											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											13 **Al** 27.0	14 **Si** 28.1	15 **P** 31.0	16 **S** 32.1	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** 63.5	30 **Zn** 65.4	31 **Ga** 69.	32 **Ge** 72.6	33 **As** 74.9	34 **Se** 79.0	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** 98.9	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	57−71 Lantha	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	89−103 Actini	104 **Rf** 261	105 **Db** 262	106 **Sg** 263	107 **Bh** 262	108 **Hs** 265	109 **Mt** 266									

Lanthanide Series	57 **La** 139	58 **Ce** 140	59 **Pr** 141	60 **Nd** 144	61 **Pm** 145	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	71 **Lu** 175
Actinide Series	89 **Ac** 227	90 **Th** 232	91 **Pa** 231	92 **U** 238	93 **Np** 237	94 **Pu** 244	95 **Am** 243	96 **Cm** 247	97 **Bk** 247	98 **Cf** 251	99 **Es** 252	100 **Fm** 257	101 **Md** 258	102 **No** 255	103 **Lr** 262