

New Zealand Chemistry Olympiad Trust

Training Group Selection Examination

Tuesday 3 November 2009

TIME ALLOWED: TWO (2) hours

Answer **ALL** questions on this examination booklet

Calculators may be used

The marks for the **twelve** (12) questions sum to **80**

A periodic table with atomic masses is attached

Name: _____

Question	1	2	3	4	5	6	7	8	9	10	11	12	Total
	/5	/4	/7	/5	/7	/8	/6	/6	/6	/8	/8	/10	/80
Mark													

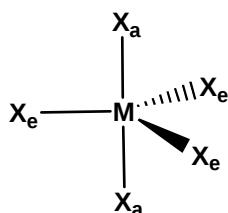
1. [5 marks]

The labels have fallen off three bottles. One of these is known to contain K_2SO_4 ; another contains $\text{Al}_2(\text{SO}_4)_3$; a third contains MgSO_4 . These can be relabelled using a test involving only one reagent. Give the formula for the reagent. Give the observations that you would make that would enable you to identify the contents of the bottles.

Write the balanced equation for any reactions that occur.

2. [4 marks]

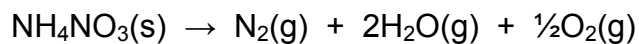
The trigonal bipyramidal geometry for a compound MX_5 , shown below, has two types of positions, X_a and X_e .



Sketch the possible isomers for MA_2X_3 in which two groups are different from the other three.

3. [7 marks]

- a) In April 1947, 2300 tons of ammonium nitrate (with a volume of about 1350 m^3) exploded on a boat in Texas City, U.S.A. The decomposition reaction of ammonium nitrate is:



Calculate the volume of gas formed in the explosion at 25°C and 100 kPa pressure, assuming the ammonium nitrate on the boat was 100% ammonium nitrate.

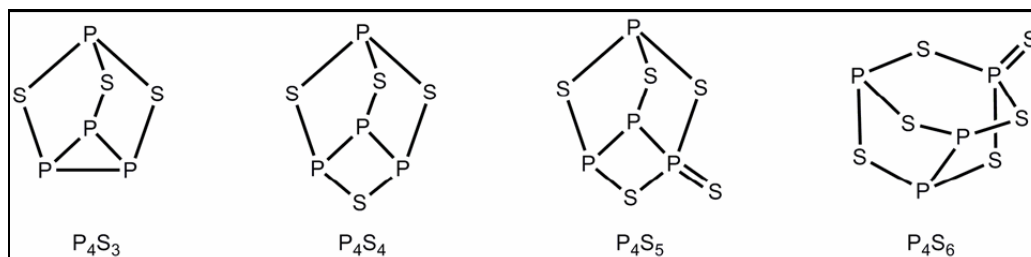
At 25°C and 100 kPa pressure the one mole of a gas occupies 0.02479 m^3 .

$1 \text{ ton} = 1016.05 \text{ kg}$; $M(\text{NH}_4\text{NO}_3) = 80.0 \text{ g mol}^{-1}$

- b) Describe what forces must be overcome to decompose NH_4NO_3 .

4. [5 marks]

Phosphorus sulfides can be made by heating white phosphorus with sulfur. When this reaction is carried out at low temperature a range of products from P_4S_3 to P_4S_{10} are produced. ^{31}P -NMR spectroscopy has been used to determine the structures of many of the phosphorus sulfides:



In ^{31}P -NMR spectroscopy, the number of peaks seen corresponds to the number of different P environments, for example P_4S_3 has two different P environments so shows two peaks in the ^{31}P -NMR spectrum.

- a) Using the structures above, predict how many peaks would be seen in the ^{31}P -NMR spectrum of:

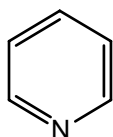


P_4S_4 has, in fact, been shown to exist in two different isomeric forms. You are given the structure of one isomer above. The second isomer shows only one peak in the ^{31}P -NMR spectrum.

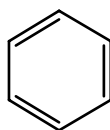
- b) Suggest a structure for the second isomer of P_4S_4 .

5. [7 marks]

Approximately two-thirds of all known molecules can be classified as heterocyclic. Such compounds contain a ring that has at least one atom other than carbon, such as nitrogen or oxygen. An example is pyridine, which exists in molecules such as nicotine and vitamin B₆.



pyridine



benzene

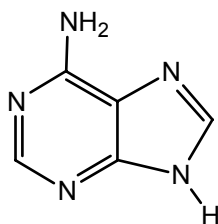
Pyridine has a six-membered ring, like benzene, containing one nitrogen atom.

(a) There are three isomers of the corresponding compounds that contain two nitrogen atoms. Draw these isomers.

(b) How many isomers would there be for such compounds containing three nitrogen atoms? Draw them.

QUESTION 5 Continued

One important heterocyclic compound is adenine, shown below, which is a component of DNA.

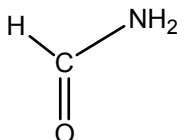


(c) What is the molecular formula of adenine?

Adenine can be formed from hydrogen cyanide.

(d) How many molecules of HCN would be required for this?

Adenine can be more efficiently prepared from methamide (formamide):



(e) What would be the other product from this reaction?

(f) Write a balanced equation for the reaction of methamide (formamide) to give adenine.

6. [8 marks]

Hydrocarbon **A** has the formula C_6H_{12} and exists as *cis-trans* (E-Z) isomers. Each of these isomers reacts with HCl to form two different monochlorides. The two isomers each react with H_2/Pd to give C_6H_{14} (**B**). **B** reacts with chlorine in the presence of light to give **four** different monochlorides.

- a) Draw the possible structure(s) and give the name(s) of B.
- b) Draw the possible structure(s) of an alkene C_6H_{12} which could form B by reacting with H_2/Pd .

7. [6 marks]

- a) N_2O_3 is a blue liquid formed by reaction of NO_2 and NO . Explain why this reaction can be referred to as a redox reaction.
- b) Draw a Lewis structure for the N_2O_3 molecule.
- c) Predict the O-N-O and N-N-O bond angles and compare with the bond angle in NO_2^+ . Explain your answer.

8. [6 marks]

When ammonium dichromate is added gradually to molten ammonium thiocyanate, NH_4SCN , Reinecke's salt is formed. It has the formula $\text{NH}_4[\text{Cr}(\text{SCN})_x(\text{NH}_3)_y]$ and the following percentage composition by mass:

Cr	15.5%
S	38.15%
N	29.2%

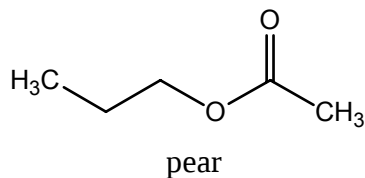
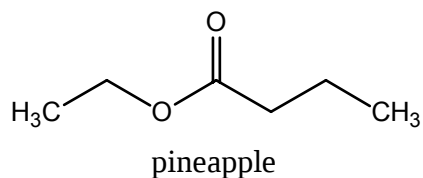
a) Calculate the values of x and y in the above formula.

b) Calculate the oxidation number of chromium in the complex.

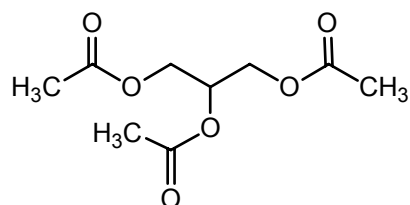
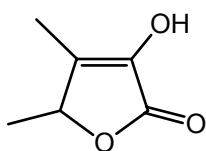
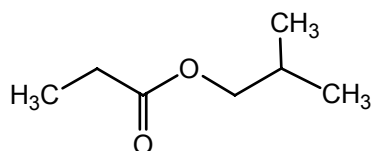
9. [6 marks]

Esters ($\text{RCO}_2\text{R}'$) are sweet smelling volatile compounds that are formed from reaction between a carboxylic acid (RCO_2H) and an alcohol ($\text{R}'\text{OH}$).

(a) Draw the structures of the acid and alcohol combinations which would lead to the following flavourings?

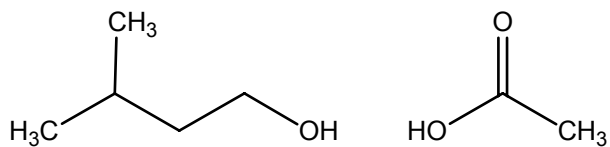


(b) Esters can be hydrolysed back to acids and alcohols. Draw the structures which would be produced by hydrolysis of the following compounds?



QUESTION 9 Continued

- (c) Hydrolysis of an ester produces the two compounds shown below. What is the structure of the ester, and what is its name?



10. [8 marks]

Hydroxylamine, NH_2OH , is a base and a reducing agent; it reacts with hydrochloric acid to form the salt hydroxylammonium chloride, $\text{NH}_3\text{OH}^+\text{Cl}^-$, and with Fe^{3+} ions to produce Fe^{2+} .

1.00 g of hydroxylammonium chloride was dissolved in distilled water and made up to a total volume of 250 cm^3 . A 25.0 cm^3 aliquot of this solution was added to a solution containing an excess of both iron(III) ions and sulfuric acid. The mixture was then boiled and allowed to cool. It was then titrated against a solution of $0.0200\text{ mol dm}^{-3}$ potassium manganate(VII), KMnO_4 , which oxidizes the Fe^{2+} ions back to Fe^{3+} and is itself reduced to Mn^{2+} ions; 28.9 cm^3 of the potassium manganate(VII) solution was required.

(a) Draw the structure for hydroxylammonium chloride, $\text{NH}_3\text{OH}^+\text{Cl}^-$. Include on your diagram the approximate values of the bond angles.

(b) Calculate the ratio of the number of moles of Fe^{3+} ions to the number of moles of hydroxylammonium chloride which have reacted together.

QUESTION 10 Continued

- (c) Calculate the oxidation number of the nitrogen in hydroxylammonium chloride and hence in the product.
- (d) Suggest which of the following is the nitrogen-containing product formed from the hydroxylammonium chloride: N_2 , NO , N_2O , N_2O_4 , NH_3 .
- (e) Write a balanced equation for the reaction between hydroxylammonium chloride and iron(III) ions.

11. [8 marks]

Primary chloroalkane molecules undergo substitution of the Cl^- by CN^- when warmed with potassium cyanide in ethanol. The organic molecule formed can then be warmed with dilute sulfuric acid to convert it into a carboxylic acid.



Compound **A**, $\text{C}_4\text{H}_9\text{OCl}$, is an organic molecule with no branching in the carbon chain.

When compound **A** is reacted with concentrated sulfuric acid it produces Compounds **B**, **C** and **D** ($\text{C}_4\text{H}_7\text{Cl}$). Compound **B** does not have geometric isomers, but Compound **C** and Compound **D** are geometric isomers of one another.

Compound **B** reacts with aqueous NaOH to produce Compound **E** ($\text{C}_4\text{H}_8\text{O}$)

Compound **A** is reacted with potassium cyanide in ethanol to produce an organic compound that is warmed with dilute sulfuric acid to give compound **F** ($\text{C}_5\text{H}_{10}\text{O}_3$).

Compound **E** reacts with Compound **F** in the presence of sulfuric acid to produce a sweet smelling Compound **G** ($\text{C}_9\text{H}_{16}\text{O}_2$)

QUESTION 11 Continued

Draw the structural formulae for compounds **A – G**, and name Compounds **A** to **F**

12. [10 marks]

An anhydrous homogeneous mixture contains three salts: barium chloride, magnesium chloride and barium nitrate. Two identical 5.000 g samples of the mixture were weighed out.

The first sample was dissolved in distilled water and an excess of dilute sulfuric acid was added. The resulting precipitate was filtered, washed and dried. It weighed 3.927 g.

The second sample was made up to 250.0 cm³ with distilled water in a volumetric flask. 25.00 cm³ aliquots were titrated with 0.2312 mol dm⁻³ silver nitrate solution. The average titre was 21.24 cm³.

What was the percentage composition by mass of the mixture?

Periodic Table

1 H 1.008																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.8	6 C 12.01	7 N 14.01	8 O 16.00	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 39.9
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 69.7	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 (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71 see below	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 see below	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110	111	112						
			57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
			89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.1	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (245)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)