

New Zealand Chemistry Olympiad Trust

Training Group Selection Examination

Wednesday 1 November 2006

TIME ALLOWED: TWO (2) hours

Answer **ALL** questions on this examination booklet

Calculators may be used

The marks for the **thirteen** (13) questions sum to **80**

A periodic table is attached

Name: _____

[illegible]

1. [3 marks]

State one way in which H is similar to each of the following elements.

(a) Li

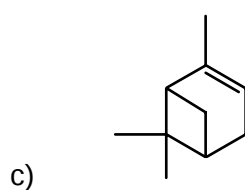
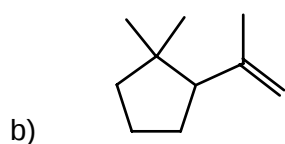
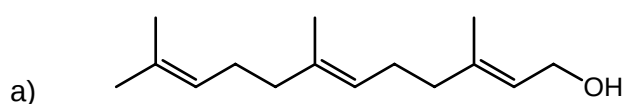
(b) C

(c) F

2. [6 marks]

Natural rubber is a polymer composed of isoprene (2-methyl-1,3-butadiene). Isoprene can be found not only in rubber but in a wide range of natural products called terpenes, most of which have carbon skeletons made up of isoprene units **joined head-to-tail**. Recognition of this fact - the isoprene rule - has been a great help in working out structures and determining the biosynthetic origin of terpenes.

Identify the isoprene units in the following terpenoid natural products.



3. [8 marks]

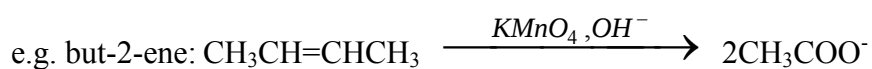
A 0.200 g sample containing only CaCO_3 and MgCO_3 is titrated with 0.200 mol L^{-1} HCl . 20.75 mL is required to reach the methyl orange end-point, when all the carbonate has been converted to H_2CO_3 .

a) What would be the titre if the sample was pure CaCO_3 ?

b) Calculate the mass of CaCO_3 in the sample.

4. [7 marks]

Alkenes are oxidatively cleaved to salts of carboxylic acids by hot permanganate solutions.



When an alkene A is hydrogenated, the alkane formed contains 83.62% C.

- a) Determine the formula of the alkene A. Assume there is only one double bond in the alkene.
- b) Draw possible structure(s) of the alkene if the salt of more than one different carboxylic acid is formed upon treatment with hot permanganate solution.
- c) What compounds would produce the following products after reaction with **hot** permanganate?
- i) butanoate ($\text{C}_3\text{H}_7\text{COO}^-$) and ethanoate (CH_3COO^-) ions.
- ii) $^-\text{OOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^-$ only.

5. [5 marks]

The first step in nitric acid synthesis is the conversion of NH_3 to NO at about 900°C :



Explain the effect on the position of the equilibrium for this reaction upon:

- a) decreasing the temperature.

- b) using air rather than pure oxygen, while keeping the total pressure constant at 8 atmospheres.

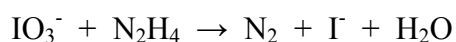
- c) not using a Pt/Rh catalyst.

The yield of NO depends upon both the position of the equilibrium and the rate of the reaction.

- d) **Explain** what you would expect the effect to be of decreasing the temperature on the yield of NO .

6. [3 marks]

Using half equations for the oxidation and reduction reactions, balance the equation for the following redox equation under acidic conditions:



7. [6 marks]

According to a widely accepted model, the universe began about 15 billion years ago in a big bang and has been expanding ever since. The temperature of the expanding universe can be estimated using:

$$T = 10^{10}/t^{1/2}$$

where T is the average temperature of the universe in Kelvin (K) and t is the age of the universe in seconds.

- a) Estimate the age of the universe (in years) when the temperature was 1000 K, sufficiently low to allow atoms in molecules to remain bonded.

- b) The average temperature now is about the same as the cosmic microwave background, 3 K. For what fraction of the history of the universe has the temperature of the universe been low enough for molecules to remain bonded.

8. [12 marks]

The following table shows what happens when each of three positive ions (K^+ , Cu^{2+} , and Ag^+) is put into water with any of three negative ions (Br^- , SO_4^{2-} and NO_3^-) and ammonia (NH_3).

	Br^-	SO_4^{2-}	NO_3^-	NH_3
K^+	colourless solution	colourless solution	colourless solution	colourless solution
Ni^{2+}	green solution	green solution	green solution	Green solid which dissolves in excess NH_3
Ag^+	Pale yellow precipitate	White precipitate	colourless solution	White solid, which turns brown and dissolves in excess NH_3

Five solutions contain: KBr , $NiSO_4$, $Ni(NO_3)_2$, $AgNO_3$ and NH_3 ,

Explain how you would distinguish each solution **using just these five solutions**.

You may find it useful to fill in the following table:

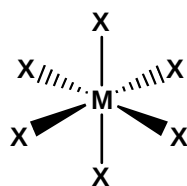
	KBr	$NiSO_4$	$Ni(NO_3)_2$	$AgNO_3$	NH_3
KBr					
$NiSO_4$					
$Ni(NO_3)_2$					
$AgNO_3$					
NH_3					

Question 8 continued on next page

Working Space for Question 8

9. [4 marks]

The octahedral geometry for a compound MX_6 , shown below, has six equivalent positions.



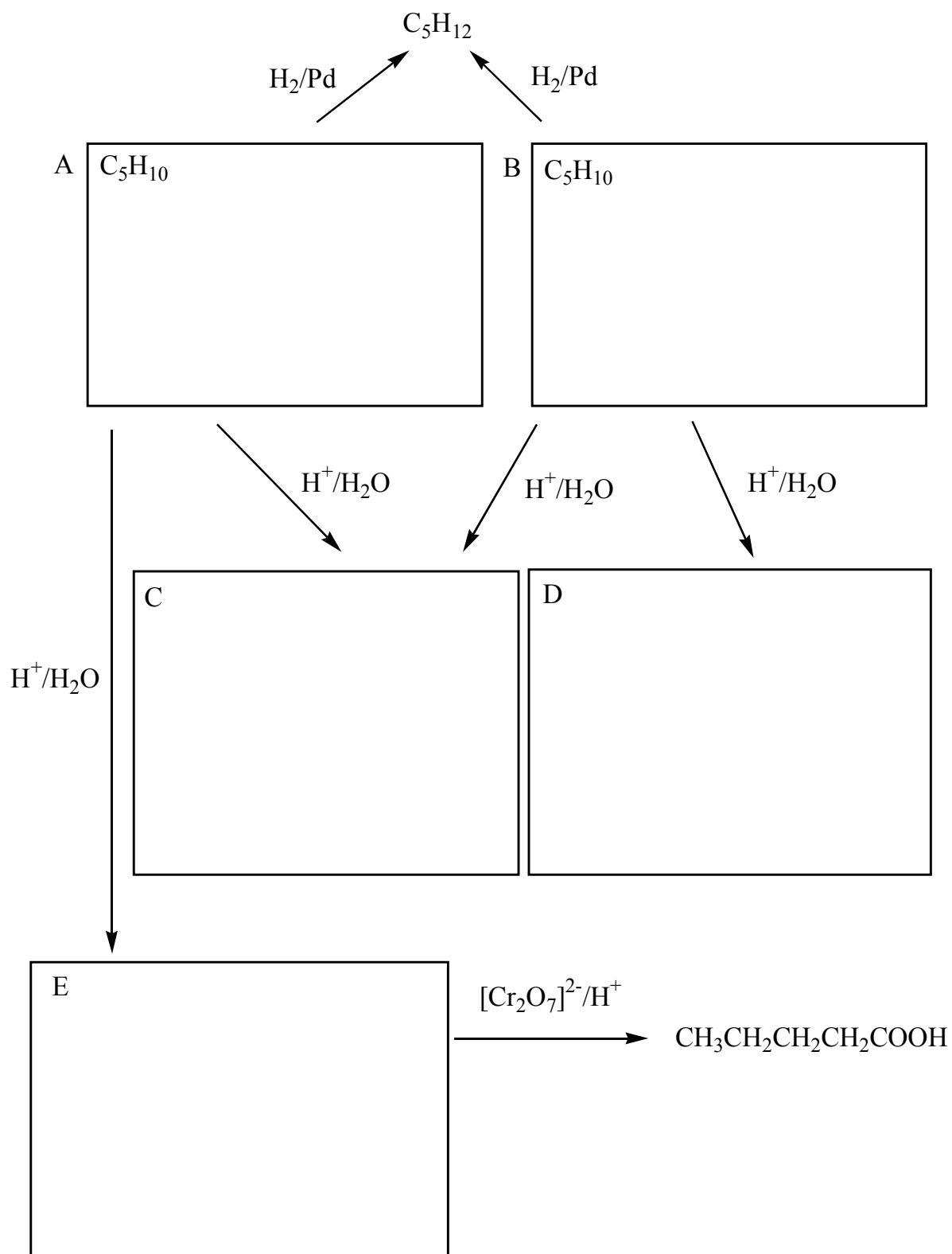
- (a) Sketch the possible isomers for MA_2X_4 in which two groups are different from the other four.
- (b) Sketch the possible isomers for MA_3X_3 in which three groups are different from the other three.

10. [5 marks]

- a) Nitrogen combines with bromine to form a molecule. What is the shape of the molecule?
- b) Four reasons for answers to part a) are given below. For each reason, state whether it is a valid reason, and if not, **explain** why it is invalid.
- i) Nitrogen forms three bonds which equally repel each other to form a trigonal planar shape,
- ii) The tetrahedral arrangement of the bonding and non-bonding electron pairs around nitrogen results in the shape of the molecule.
- iii) The polarity of the nitrogen-bromine bonds determines the shape of the molecule.
- iv) The difference in electronegativity values for bromine and nitrogen determine the shape of the molecule.

11. [7 marks]

Complete the diagram by drawing **structural formulae** and writing **IUPAC (systematic) names** for the compounds A-E.



12. [8 marks]

(a) Draw a Lewis structure for **cyclic** O_3 .

(b) Draw two equivalent Lewis structures for non-cyclic O-O-O .

(c) What is the approximate O-O-O bond angle for non-cyclic O-O-O ?

(d) For one of your equivalent structures from part (b), calculate the formal charge on each O atom (i.e. the number of valence electrons in the atom, minus twice the number of lone pairs, minus the number of bonds to the atom).

- (e) Draw the Lewis diagram of oxygen difluoride, OF_2 .
- (f) Ozone, O_3 , has the non-cyclic structure and has a boiling point of -112°C . Polar OF_2 has a greater molecular mass than ozone, but it has a lower boiling point at -145°C . **Explain** this observation.

13. [6 marks]

The average chemical formula for common diesel fuel is $\text{C}_{12}\text{H}_{26}$. Dodecane ($\text{C}_{12}\text{H}_{26}$) has an enthalpy of combustion of $-8072 \text{ kJ mol}^{-1}$ and a density of 0.745 g cm^{-3} . The enthalpy of combustion for a given substance is defined as the enthalpy change for the reaction of one mole of the substance with oxygen to form $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$.

- a) Write down a balanced equation for the combustion of dodecane.
- b) Calculate the energy density, expressed as kJ of heat given off in combustion per litre of fuel (kJ/L) for dodecane.

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
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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)
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