New Zealand Chemistry Olympiad Trust

Training Group Selection Examination

Wednesday 29 October 2014

TIME ALLOWED: 120 minutes

Answer **ALL** questions on this examination booklet

Calculators may be used

The marks for the **twelve** (12) questions sum to **100**

A periodic table with atomic masses is also provided

STUDENT'S NAME:____

STUDENT'S EMAIL:____

SCHOOL:____

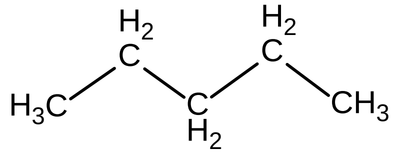
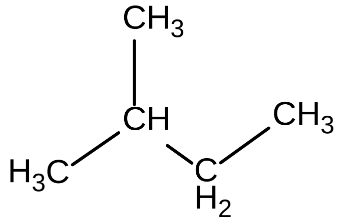
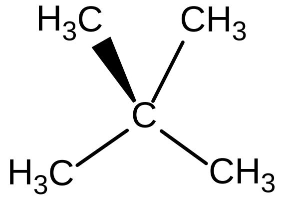
Question	1 /8	2 /4	3 /12	4 /5	5 /12	6 /10	7 /7	8 /6	9 /5	10 /12	11 /13	12 /6	Total /100
Mark													

QUESTION ONE (8 marks) ***Change to 9 marks total***

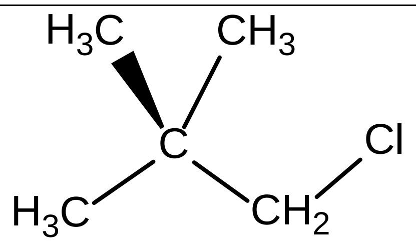
Do not penalise if structures not shown as 3D. Allow condensed structural formulae

There are three isomers of C_5H_{12}.

(a) Draw the structure of each isomer. *1 mark each*

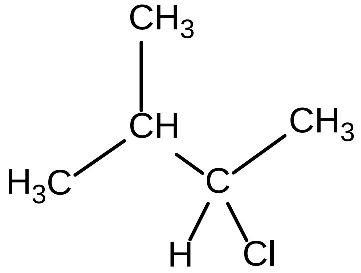
(b) One of the alkane isomers from part (a) reacts with Cl_2 in the presence of light to give a single monohalogenated organic product. Draw the structure of that product.



1 mark

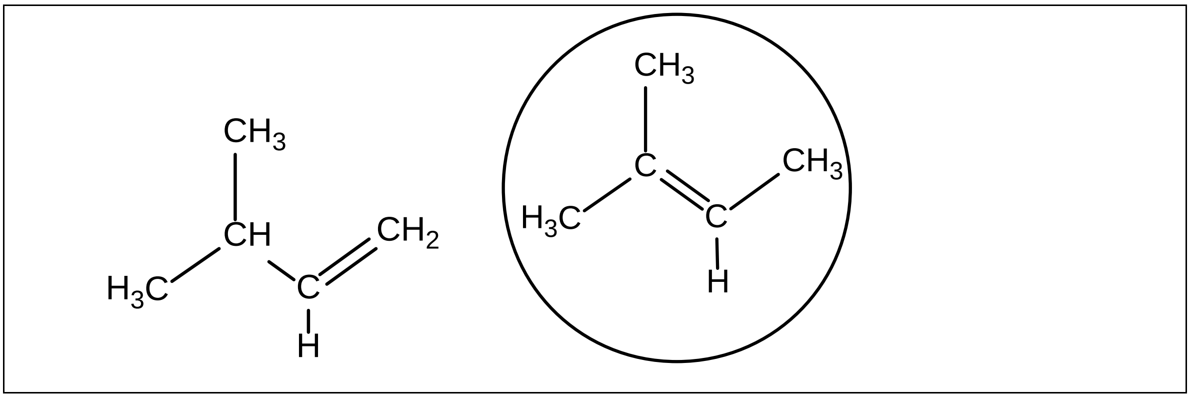
(c) Another one of the isomers from part (a) reacts with Cl_2 in the presence of light to give four different monochloro alkanes. One of these is a secondary chloroalkane.

(i) Draw the structure of this chloroalkane.



1 mark

(ii) Draw the structures of alkenes produced when the secondary chloroalkane from part (i) reacts with KOH in ethanol.



2 marks

(iii) Circle the alkene from part (ii) above that is formed in the greatest amount. Justify your answer.

The H is removed from the C atom (adjacent to the C carrying the OH) with the least number of H atoms attached

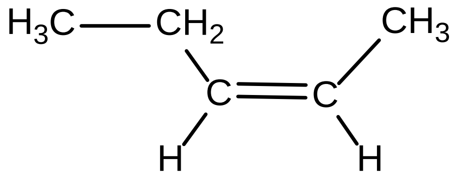
1 mark for selecting correct isomer

1 mark for explanation BUT second mark only possible if correct isomer circled

QUESTION TWO (4 marks)

There are five C_5H_{10} constitutional (structural) isomers that are alkenes.

(a) One of the five alkenes exists as *cis-trans* stereoisomers. Draw the structure of the cis isomer of this alkene.



1 mark

(b) Explain why the alkene in part (a) exists as *cis-trans* isomers whereas the isomeric alkene that has the same carbon skeleton does not.

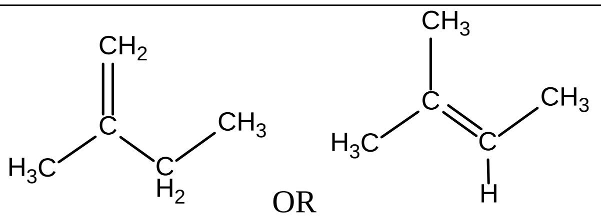
Both alkenes have a double bond which limits the rotation around the bond. *½ mark*

The alkene above has 2 different groups attached the C atom at each end of the double bond whereas the pent-1-ene isomer has 2 H atoms on the atom at one end of the double bond

1/2 mark

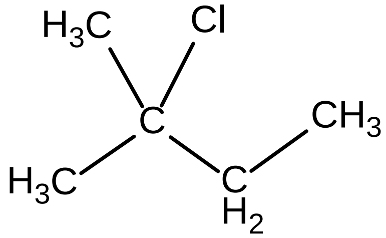
(c) Two C_5H_{10} alkenes have the same carbon skeleton, but neither exists as *cis-trans* isomers. One of these reacts with HCl to form a tertiary chloroalkane as the major product.

(i) Draw the structure of this alkene;



1 mark

(ii) Draw the structure of the chloroalkane described above.



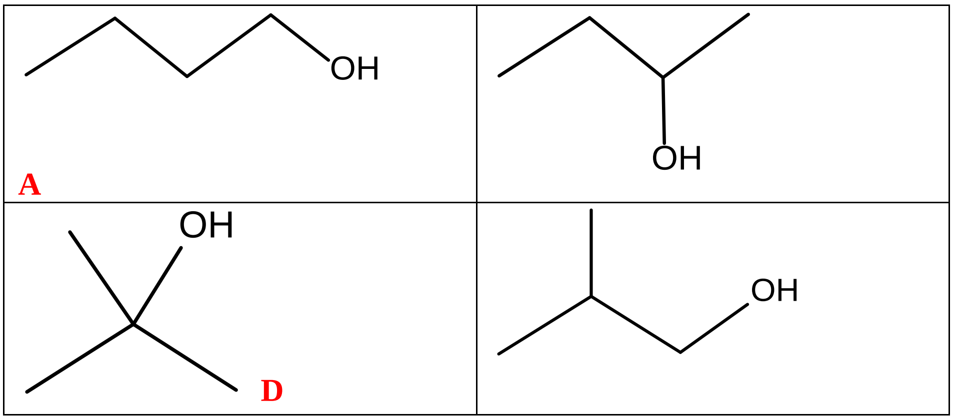
1 mark

QUESTION THREE (12 marks)

This question is concerned with four alcohols and their physical and chemical properties. These alcohols have the formula $C_4H_{10}O$ and their boiling points are given in the table below.

Isomer	Boiling point	Reaction with $Cr_2O_7^{2-}$?
A	117 °C	Yes
B	102 °C	Yes
C	98 °C	Yes
D	82 °C	No

(a) (4 marks) Draw the structures of each of the four isomers.



4 marks – 1 mark each structure. Can be condensed structural isomer

(b) (2 marks) On the basis of your structures and the information given above, how does branching affect the attractive forces between the molecules? *Justify your answer.*

Branching means the molecules cannot pack as closely together and this reduces the attractive forces between the particles leading to a lower boiling point

2 marks

(c) (4 marks) Identify isomers **A** and **D** in your answer to part (a) above. *Justify your answer.*

A (identified above) is a straight chain alcohol and since the molecules can pack closely together it will have the strongest intermolecular forces and therefore the highest boiling point.

1 mark for correctly identifying A and 1 mark for justification linking straight chain to stronger intermolecular forces

D is a tertiary alcohol and therefore will not undergo oxidation with dichromate.

1 mark for identifying D and 1 mark for linking to fact tertiary alcohols are not oxidized.

(d) (2 marks) What additional information would you need to identify isomers **B** and **C**?

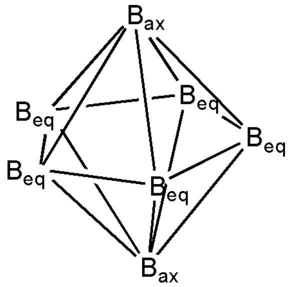
The primary alcohol is oxidised to an aldehyde that reacts with Tollens or Benedicts etc /or is oxidised to a carboxylic acid that turns blue litmus pink

The secondary alcohol is oxidised to a ketone that will not react according to any of the tests above

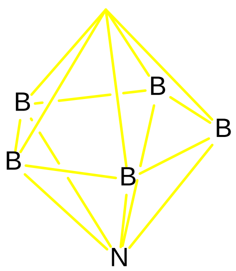
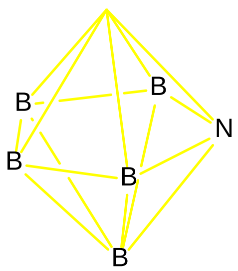
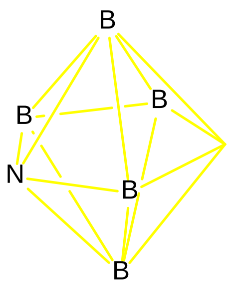
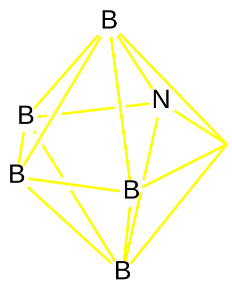
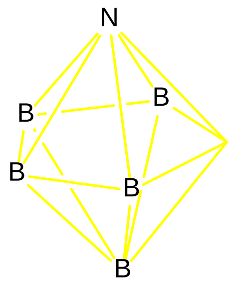
1 mark for linking to products of oxidation and 1 for valid test.

QUESTION FOUR (5 marks)

$[B_7H_7]^{2-}$ is a **pentagonal bipyramid** (shown below without the H atoms) with ten triangular faces. It has two types of B atoms; two axial (ax) and five equatorial (eq). A ***nido*-pentagonal bipyramid** is missing one of these vertices/atoms.



The cluster $[B_5NH_6]^{2-}$, in which one of the B atoms has been replaced by an N atom, is predicted to be a *nido*-pentagonal bipyramid. Sketch the possible isomers for this ion by writing B or N over the appropriate vertices in the polyhedra given below. You may not need to use all of the polyhedra to show all of the isomers.

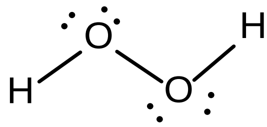
			
			

5 marks – 1 mark each
Deduct at most 1 mark if there are any repeats of an existing structure that is oriented in another way

QUESTION FIVE (12 marks)

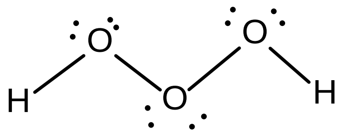
(a) Draw ONE Lewis structure and the 3-dimensional molecular shape for each of the following molecules:

(i) Hydrogen peroxide (H_2O_2);



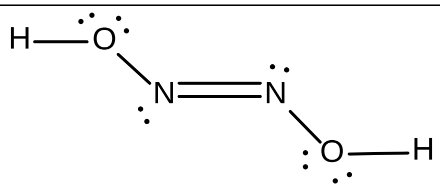
1 mark

(ii) Trioxidane (H_2O_3);



1 mark

(b) (i) Draw ONE Lewis structure and the 3-dimensional molecular shape for hyponitrous acid (a symmetric molecule with formula $N_2(OH)_2$);



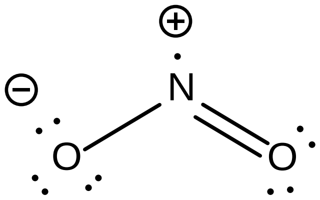
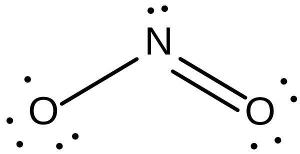
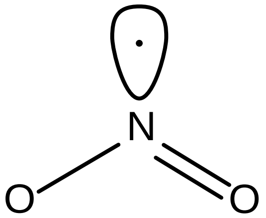
1 mark for Lewis structure (any shape but must show correct number of es and obey octet rule)
1 mark for shape – may be cis or trans

(ii) Hyponitrous acid can be synthesised as both the *cis* and *trans* isomers, but the *trans* isomer is the most stable. Give a reason in terms of electron pair repulsion theory to explain this.

Lone-pair to lone-pair repulsion is greater than lone-pair to bonding-pair repulsion. The *trans* isomer minimises lone-pair to lone-pair repulsion between the N atoms.

2 marks- 1 for each statement or equivalent

(c) (i) Draw TWO Lewis structures for nitrogen dioxide (NO_2) and the 3-dimensional molecular shape for one of these.

 *1 mark – any shape*	 *1 mark any shape*	V-shape  *1 mark – does not need to show single electron on N*

(ii) The "formal charge" is the number of valence electrons in the atom, minus the number of lone pair electrons at that atom in the Lewis structure, minus the number of bonds to the atom in the Lewis structure. Formal charge can be used to help explain where electrons are likely to be found on atoms in a molecule. Identify your structure in part (i) that formal charge suggests is most likely.

The <u>second structure</u> (with zero formal charges is most likely on this basis)

1 mark - correct structure identified (does not need to justify)

(iii) The O-N-O bond angle is actually 134.3°. Does this value support your proposed Lewis structure? Justify your answer.

<u>No.</u> The <u>second structure should have a bond angle less than 120°</u> whereas the <u>first structure should have a bond angle much greater than 120°</u> because of the <u>lower electron-electron repulsion between the unpaired electron and the N–O bonding electrons</u>.

1 mark for No,

1 mark for comparing bond angles

1 mark for linking to lower repulsion between unpaired e and bonded pairs (compared to non-bonding pair and bonded pairs)

QUESTION SIX (10 marks)

Silver nitrate is used in volumetric analysis to determine the concentration of chloride ions in an aqueous solution. Because of the high cost of $AgNO_3$, a student uses an available supply of 0.0500 mol L^{-1} $AgNO_3$ solution and some solid $AgNO_3$ to prepare 100.0 mL of 0.0750 mol L^{-1} $AgNO_3$. She prepares the solution by:

(i) pipetting exactly 50.00 mL of the 0.0500 mol L^{-1} $AgNO_3$ solution into a 100.0 mL volumetric flask;

(ii) adding an appropriate mass of $AgNO_3$;

(iii) diluting the solution to exactly 100.0 mL.

(a) What mass of $AgNO_3$ should be added in step (ii)? [$M(AgNO_3)$ = 169.9 g mol^{-1}]

$n(Ag^+)$ in final solution = 0.100 L x 0.075 mol L^{-1} = 0.00750 mol ***1 mark***

$n(Ag^+)$ pipetted = 0.0500 L x 0.0500 mol L^{-1} = 0.00250 mol ***1 mark***

$n(AgNO_3)$ needing to be added = 0.00750 mol – 0.00250 mol = 0.00500 mol ***1 mark***

$m(AgNO_3)$ = 0.00500 mol x 169.9 g mol^{-1} = 0.8495 g ***1 mark***

(b) Solid $MgCl_2$ (0.100 g) was then added to the solution. Assuming no change in the total volume, what is the concentration of each of the following species?
[$M(MgCl_2)$ = 95.2 g mol^{-1}]

(i) $Mg^{2+}{}_{(aq)}$

$n(Mg^{2+})$ = 0.1 g/95.2 g mol^{-1} = 0.00105 mol Mg^{2+} ***1 mark***

$[Mg^{2+}]$ = 0.00105 mol/0.1 L = 0.0105 mol L^{-1} ***1 mark***

(ii) $Ag^+{}_{(aq)}$

$n(Cl^-)$ = 0.0021 mol ***1 mark***
$n(Ag^+)$ = (0.075 x 0.1) – 0.0021 = 0.0054 mol ***1 mark***
$[Ag^+]$ = 0.0054/0.1 = 0.054 mol L^{-1}

(iii) $NO_3^-{}_{(aq)}$

0.075 mol L^{-1}

QUESTION SEVEN (7 marks)
The Kjeldahl method can be used to determine the percentage of nitrogen in meat and other organic products. A 0.0986 g sample was heated with concentrated sulfuric acid for two hours to oxidise organic matter and convert all nitrogen to ammonium ions. The solution was then made strongly basic by adding excess sodium hydroxide solution producing ammonia. The ammonia was then distilled into 50.00 mL of 0.1010 mol L^{-1} HNO_3. Exactly 23.45 mL of 0.1500 mol L^{-1} NaOH was required to neutralise the excess acid.

Calculate the amount (moles) of NH_3 that was distilled into the HNO_3 and hence determine the percentage of N in the original sample.

n(HNO_3) added = 0.0500 L x 0.1010 mol L^{-1} = 0.00505 mol ***1 mark***

n(NaOH) needed to neutralise xs acid = 0.02345 L x 0.1500 mol L^{-1} = 0.003518 mol ***1 mark***

n(NH_3) = 0.00505 mol – 0.003518 mol = 0.001532 mol = n(N) in original sample ***2 marks***

mass (N) in original sample = 0.001532 mol x 14.01 g mol^{-1} = 0.02146 g ***1 mark***

% N in original sample = (0.02416 g/0.0986 g) x100 = 21.77% ***2 marks***

QUESTION EIGHT (6 marks)

For each of the following compounds, state with brief explanation whether its solubility in water will increase, decrease or be unaffected by a decrease in pH:

(a) $PbSO_4$

Increase as SO_4^{2-} is a weak base and reacts with added H^+/H_3O^+ (HSO_4^- is a weak acid). This removes the SO_4^{2-} from the solution and equilibrium shifts to oppose the change so $PbSO_4$ dissolves.

1 mark for "increase", 1 mark for linking to weak base and reaction with acid

(b) AgCl

No effect. Cl^- is neutral so will not react with added acid (HCl is a strong acid).

1 mark "no effect" 1 mark for linking to neutral Cl^- or HCl strong acid

(c) CuS

Increase as S^{2-} is a weak base and reacts with added acid (HS^- is a weak acid).

1 mark for "increase", 1 mark for linking to weak base and reaction with acid

Note that to get full marks need to link one answer to equilibrium shift to oppose the change.

QUESTION NINE (5 marks)

A compound consists of 14.29% carbon, 57.14% oxygen, 1.19% hydrogen and an element X having the same number of moles as there are moles of carbon.

(a) Identify X.

14.29 g C/12 = 1.19 mol C

1.19 mol H

57.14 g O/16 = 3.57 mol O ***2 marks all 3 correct moles, 1 mark any 1 correct***

1.19 mol X = 27.38 = Na ***1 mark***

(b) Determine the empirical formula of the compound.

$HCNaO_3$ ***1 mark***

(c) Suggest the likely identity of the compound.

Sodium bicarbonate or sodium hydrogen carbonate ***1 mark***

QUESTION TEN (12 marks)

Write net equations for each of the following reactions, using appropriate ionic and molecular formulae for the reactants and products. Omit all ions of molecules that do not take part in the reaction. The equations must be balanced. All reactions occur in aqueous solution unless otherwise indicated.

(a) Solid calcium carbonate is heated to a very high temperature.

$CaCO_3 \longrightarrow CaO + CO_2$ *1 mark*

(b) Lithium nitride is added to water to produce a solution that turns pink litmus blue.

$Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$ *1 mark correct products*
1 mark for correct balancing

(c) Concentrated hydrochloric acid is added to a solution of sodium hypochlorite.

$H^+ + ClO^- \longrightarrow HClO$ *2 marks*

(d) Solutions of barium hydroxide and sulfuric acid are mixed

$Ba(OH)_2 + H_2SO_4 \longrightarrow BaSO_4(s) + 2H_2O$ *1 products, 1 balancing*

(e) Excess concentrated ammonia is added to a solution of zinc chloride.

$4NH_3 + Zn^{2+} \longrightarrow [Zn(NH_3)_4]^{2+}$ *1 mark correct products*
1 balancing

(f) A mixture of acidified potassium dichromate and ethanol is heated.

$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow$ **$2Cr^{3+} + 7\,H_2O$**

$H_2O + C_2H_5OH \longrightarrow$ **$CH_3COOH + 4H^= + 4e^-$**

$2Cr_2O_7^{2-} + 3C_2H_5OH + 16H^+ \longrightarrow 4Cr^{3+} + 3CH_3COOH + 11H_2O$

1 mark correct products, 2 marks correct balancing but if final eqn not balanced can get 1 mark for each correctly balanced half equation

QUESTION ELEVEN (13 marks) ***Change to 11 marks***

When aqueous ammonia is added drop-wise to a copper sulfate solution, a blue solid of copper hydroxide forms. As further ammonia is added, the solid redissolves and a dark blue solution forms.

The following equilibria explain these observations:

A: $Cu(OH)_{2(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2OH^-_{(aq)}$

B: $Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)}$

(a) Give the equilibrium expression for each of these processes.

$K_A = [OH^-]^2[Cu^{2+}]$ *1 mark*

$K_B = [Cu(NH_3)_4{}^{2+}]/[Cu^{2+}][NH_3]^4$ *1 mark*

(b) Explain why copper hydroxide can form when ammonia is added.

Ammonia is a weak base and, in aqueous solutions, reacts with water to form a low concentration of OH^- (and NH_4^+). The OH^- reacts with Cu^{2+} ions to form the $Cu(OH)_2$ ppt

2 marks – 1 mark for weak base, 1 mark for linking to formation of OH^-

(c) The equilibrium constant for process A is 2.20×10^{-20} while the equilibrium constant for process B is 1.2×10^{13}. Use these values to explain why initially a precipitate forms with limited ammonia but, when excess ammonia is added, the solid redissolves to form the dark blue ammonia complex.

Possible answer: On addition of a small amount of ammonia the presence of OH^- results in formation of $Cu(OH)_2$ as the equilibrium constant is very small and favours the precipitate on the left. *1 mark*

On addition of excess ammonia the concentration of NH_3 increases so that the second equilibrium shifts to favour the formation of the complex ion product – especially as the large K means the prodcuts are favoured. *2 marks*

The removal of Cu^{2+} ions (by formation of complex ion) means that the first equilbrium shifts to right to oppose the change and this means the $Cu(OH)_2$ solid dissolves *1 mark*

Note – overall 4 marks for a good discussion or 1 mark for sensible statement up to 4 mark maximum

(d) What happens to the concentration of each of the following species, once equilibrium is re-established, upon addition of $Cu^{2+}_{(aq)}$ to the dark blue solution?

(i) $[Cu(NH_3)_4]^{2+}_{(aq)}$

Increases *1 mark*

(ii) NH_3

Decreases *1 mark*

(iii) $Cu^{2+}_{(aq)}$

Increases *1 mark*

QUESTION TWELVE (6 marks) ***Change to 7 marks***

The average chemical formula for common diesel fuel is $C_{12}H_{26}$. Dodecane ($C_{12}H_{26}$) has an enthalpy of combustion of –8072 kJ mol^{-1} and a density of 0.745 g mL^{-1}. 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 CO_2(g) and H_2O(*l*). $M(C_{12}H_{26})$ = 170 g mol^{-1}.

(a) (2 marks) Write down a balanced equation for the combustion of dodecane.

$$2C_{12}H_{26} + 37O_2 \longrightarrow 24CO_2 + 26H_2O$$

1 mark correct products, 1 for correct balancing (can be done with ½ number of moles compared to above)

(b) (2 marks) Calculate the energy density, expressed as kJ of heat given off in combustion per litre of fuel (kJ/L) for dodecane.

1 litre weighs 745 g = 4.38235 mol dodecane ***1 mark***

4.38235 mol × -8072 kJ mol^{-1} = 35734 kJ L^{-1} ***1 mark***

(c) (3 marks) What mass of CO_2 is produced in order to generate 15,000 kJ of energy? *(Changed to 3 marks instead of 2 marks)*

(15,000 kJ/8072 kJ mol^{-1}) x 12 x 44 g mol^{-1} = 981 g

1 mark *1 mark* *1 mark*

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 Lanthanide Series	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 Actinide Series	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