Centre No.						Paper Reference							Surname	Initial(s)
Candidate No.						6	2	4	6	/	0	2	Signature	

Paper Reference(s)

6246/02

Edexcel GCE

Chemistry

Advanced

Unit Test 6B (Synoptic)

Thursday 19 June 2008 – Morning

Time: 1 hour 30 minutes

Examiner's use only

Team Leader's use only

Question Number	Leave Blank
1	
2	
3	
4	
Total	

Materials required for examination
Nil

Items included with question papers
Nil

Candidates may use a calculator.

Instructions to Candidates

In the boxes above, write your centre number, candidate number, your surname, initial(s) and signature.
Check that you have the correct question paper. The paper reference is shown above.
Answer Section A in the spaces provided in this question paper.
Answer **TWO** questions in Section B in the spaces provided in this question paper. Indicate which question you are answering by marking the box (☒). If you change your mind about a question, put a line through the box (☒) and then mark your new question with a cross (☒).
Do not use pencil. Use blue or black ink.
Show all the steps in any calculations and state the units.

Information for Candidates

The total mark for this paper is 50. The marks for individual questions and parts of questions are shown in round brackets: e.g. **(2)**. There are 20 pages in this question paper. All blank pages are indicated.
A Periodic Table is printed on the back cover of this question paper.

Advice to Candidates

You are reminded of the importance of clear English and careful presentation in your answers. You will be assessed on your Quality of Written Communication in this paper.

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SECTION A

Answer ALL parts of this question in the spaces provided.

1. The enthalpy change for some reactions cannot be determined directly.

One such reaction is the thermal decomposition of potassium hydrogencarbonate, which in a closed system at 200 °C is an equilibrium reaction.

$$2KHCO_3 \rightleftharpoons K_2CO_3 + H_2O + CO_2$$

However, by determining the enthalpy change for the neutralisation of the two potassium salts with hydrochloric acid, ΔH for the reaction above can be found. The equations for the neutralisation reactions are:

$$K_2CO_3 + 2HCl \rightarrow 2KCl + H_2O + CO_2 \qquad \Delta H_1$$

$$KHCO_3 + HCl \rightarrow KCl + H_2O + CO_2 \qquad \Delta H_2$$

ΔH_1 and ΔH_2 for the neutralisation reactions were determined as follows:

- 30 cm^3 of 2 mol dm^{-3} hydrochloric acid (an excess) was placed in a polystyrene cup, and its temperature measured to the nearest 0.1 °C.
- A weighed quantity of the potassium salt (either the carbonate or the hydrogencarbonate) was added to the acid with rapid stirring, and the temperature measured again when the reaction was complete.

For the neutralisation using potassium carbonate, the results were as follows:

Amount of potassium carbonate used = 0.0187 mol

Initial temperature = 23.7 °C

Final temperature = 30.1 °C

(a) State Hess's Law.

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(1)

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(b) Use the data for the neutralisation of potassium carbonate to calculate the value of ΔH_1 to **two** significant figures. Remember to include a sign and units in your answer.

[Assume that the heat capacity of the solution is 4.18 J g^{-1} °C^{-1}, and that it has a mass of 30 g.]

(3)

(c) (i) Show how the two equations for the neutralisation reactions and their ΔH values can be combined to find a value of ΔH for the thermal decomposition of potassium hydrogencarbonate.

Calculate this enthalpy change using your value for ΔH_1 from part (b), given that $\Delta H_2 = +29.3$ kJ mol^{-1}.

(3)

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(ii) Explain why you would need to include the enthalpy of vaporisation of $H_2O(l)$, in order to obtain an accurate value of the enthalpy of decomposition of potassium hydrogencarbonate.

$$2KHCO_3(s) \rightleftharpoons K_2CO_3(s) + H_2O(g) + CO_2(g)$$

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(1)

(d) State and explain the effect of a decrease in temperature on the value of the equilibrium constant for the decomposition reaction and **hence** on the composition of the equilibrium mixture.

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(2)

(Total 10 marks)

Q1

TOTAL FOR SECTION A: 10 MARKS

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SECTION B

Answer any TWO questions from this section in the spaces provided.

If you answer Question 2 put a cross in this box ☒.

2. (a) (i) Propanoic acid, CH_3CH_2COOH, can be made from ethene via a Grignard reagent.

Draw the reaction scheme. For each step give the reagents and include the formula of the Grignard reagent.

(5)

(ii) What **type** of reagent is a Grignard reagent? Justify your answer by reference to the reaction used in part (i).

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(2)

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(b) Esters can be made either from carboxylic acids or from acid chlorides.

(i) Give in each case the equation for the reaction between:

ethanol and propanoyl chloride

(1)

ethanol and propanoic acid.

(1)

(ii) Explain which method gives the better yield of ester.

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(1)

(c) A mixture of aqueous propanoic acid and sodium propanoate forms a buffer solution.

(i) What is a buffer solution?

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(2)

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(ii) Calculate the mass of sodium propanoate that needs to be added to 125 cm^3 of a 0.10 mol dm^{-3} solution of propanoic acid at 25 °C, to give a buffer solution of pH 5.06.

[The value of K_a for propanoic acid at 25 °C is 1.30×10^{-5} mol dm^{-3}; molar mass of sodium propanoate is 96 g mol^{-1}]

(4)

(iii) Calculate the concentration of hydroxide ions in the buffer solution in part (ii).

[The value of K_w at 25 °C is 1.0×10^{-14} mol^2 dm^{-6}]

(2)

QUESTION 2 CONTINUES ON THE NEXT PAGE

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(iv) Why is a solution of propanoic acid alone **not** a buffer?

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(2)

Q2

(Total 20 marks)

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If you answer Question 3 put a cross in this box ☒.

3. (a) (i) Draw the shape of a water molecule. Justify your answer.

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(2)

(ii) Water has intermolecular hydrogen bonds, but hydrogen sulphide, H_2S, does not.

Explain how these arise in water and why they do **not** occur in hydrogen sulphide.

Give ONE resulting difference in physical properties of water and hydrogen sulphide.

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(3)

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(b) Copper(II) sulphate pentahydrate crystals, $CuSO_4.5H_2O$, contain hydrated copper(II) ions and are blue.

If heated strongly they turn white and steam is evolved.

If the white solid is cooled to room temperature and water is added the solid turns blue again and it gets very hot.

(i) Explain why the product is white.

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(3)

(ii) Explain, in terms of bonding, why the anhydrous solid gets hot when water is added to it.

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(c) Explain why the solubility in water of the hydroxides of Group 2 (Be to Ba) increases down the group.

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(3)

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(d) (i) Explain why water reacts rapidly at room temperature with silicon(IV) chloride, $SiCl_4$, but is without effect on tetrachloromethane, CCl_4.

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(4)

(ii) Suggest why the addition of sodium chloride to water gives a neutral solution, but addition of sodium propanoate to water gives an alkaline solution.

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(3)

Q3

(Total 20 marks)

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If you answer Question 4 put a cross in this box ☒.

4. (a) The conversion of butan-2-ol to 2-bromobutane can be performed as outlined below:

- Butan-2-ol is heated with a mixture of 50 % aqueous sulphuric acid and sodium bromide for 45 minutes.
- The crude 2-bromobutane is distilled off.
- The crude 2-bromobutane is shaken with pure water, which removes the sulphuric acid and some of the butan-2-ol that contaminates the product.
- The organic layer is separated and then shaken with concentrated hydrochloric acid to remove residual butan-2-ol.
- The organic layer is then shaken with dilute sodium carbonate solution.
- Anhydrous calcium chloride is added to the organic layer and allowed to stand for some hours.
- The organic layer is then redistilled in a dry apparatus.

(i) Explain, in terms of kinetic factors, why the mixture is heated for a significant amount of time.

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(1)

(ii) Why is sulphuric acid necessary in the reaction mixture?

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(2)

(iii) Suggest why butan-2-ol, which is only partially miscible with water, is much more soluble in concentrated hydrochloric acid.

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(2)

Leave blank

(iv) Why is the organic layer shaken with dilute sodium carbonate solution?

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(1)

(v) What is the purpose of the anhydrous calcium chloride?

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(1)

(vi) How would you heat the mixture safely? Explain your choice of method.

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(2)

QUESTION 4 CONTINUES ON THE NEXT PAGE

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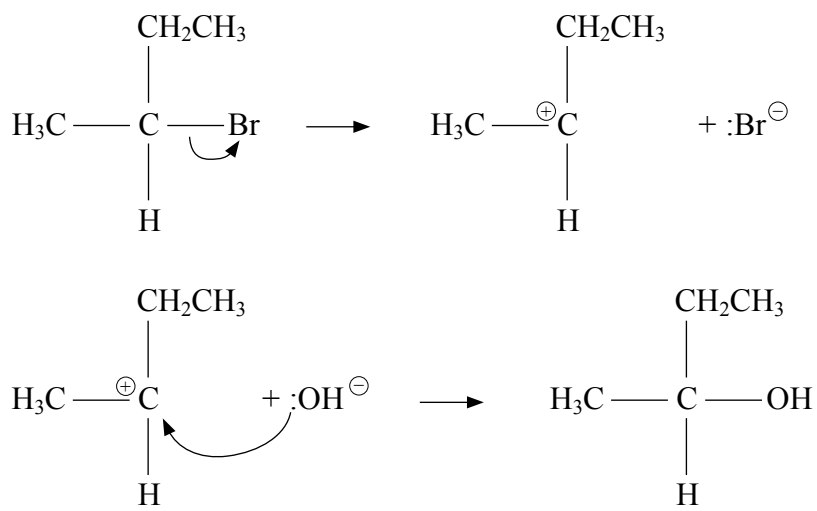
(b) Both 2-bromobutane and butan-2-ol are chiral molecules.

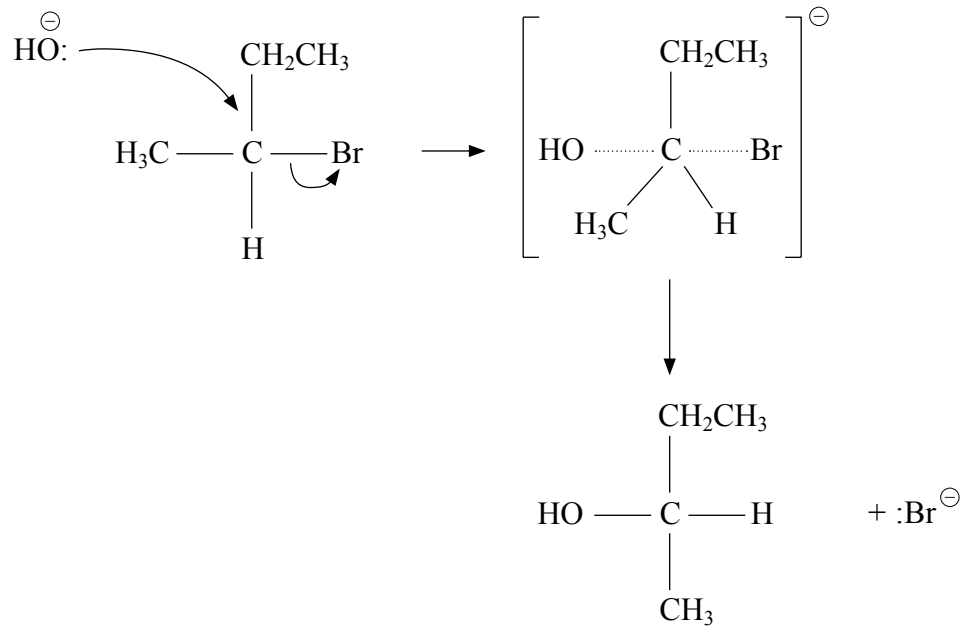
If one optical isomer of 2-bromobutane is used to make butan-2-ol by reaction with aqueous hydroxide ions, the product mixture is **not** optically active.

The mechanism for the reaction is either S_N1 or S_N2; these are given below

S_N1



S_N2



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Explain which one of these mechanisms is consistent with the lack of optical activity in the product mixture.

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(3)

(c) The oxidation of butan-2-ol with hot potassium dichromate(VI) in acidic solution produces butanone, $CH_3COCH_2CH_3$.

(i) What would you **see** as the reaction proceeds?

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(1)

(ii) The dichromate(VI) ion is reduced under these conditions to chromium(III) ions.

The half-equation for the oxidation of butan-2-ol to butanone is

$$CH_3CH(OH)CH_2CH_3 \rightarrow CH_3COCH_2CH_3 + 2H^+ + 2e^-$$

Write the ionic half-equation for the reduction of dichromate(VI) ions, and hence derive the overall equation for the oxidation of butan-2-ol.

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(2)

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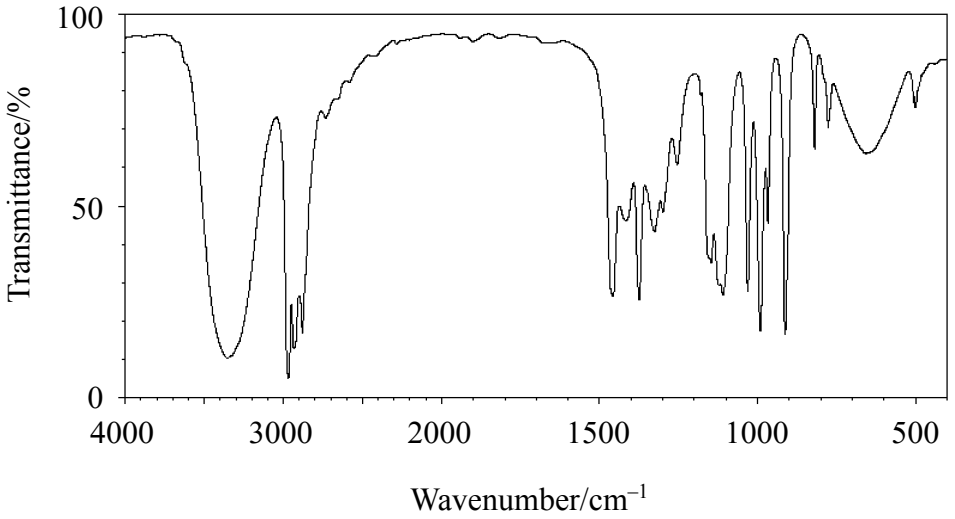
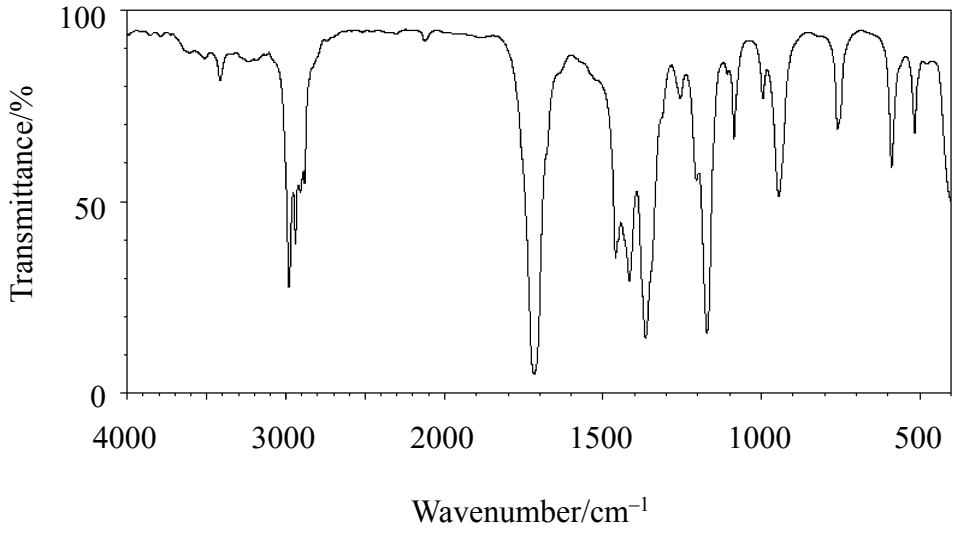
(iii) The IR spectra of butan-2-ol and of the organic product from its oxidation with dichromate(VI) ions are given below.

Spectrum of butan-2-ol



Spectrum of the organic product from the oxidation of butan-2-ol



Bond	Wavenumber/cm^{-1}	Bond	Wavenumber/cm^{-1}
C—H (alkanes)	2850–3000	C—O (alcohols, esters)	1000–1300
C—H (alkenes)	3000–3100	O—H (hydrogen-bonded alcohols)	3230–3550
C═O (aldehydes, ketones, carboxylic acids)	1680–1750	O—H (hydrogen-bonded carboxylic acids)	2500–3300

N 3 1 8 3 1 A 0 1 6 2 0

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What evidence is there from the spectra that the reaction in part (ii) has occurred?

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(2)

(d) When potassium dichromate(VI) is dissolved in water, the following equilibrium is set up

$$Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^+(aq)$$

(i) If a solution of barium ions is then added to **this solution**, solid barium chromate, $BaCrO_4$, is precipitated; it is sparingly soluble in water, so the equilibrium given below also exists in the solution

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightleftharpoons BaCrO_4(s)$$

Explain what happens to the pH when the barium ions are added.

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(2)

QUESTION 4 CONTINUES ON THE NEXT PAGE

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(ii) If a solution of lead(II) ions is added instead of barium ions, solid $PbCrO_4$ is precipitated. This is almost completely insoluble in water so all chromate(VI) ions are removed from solution

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$$

State how the pH of this solution differs from your answer in part (i).

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(1)

Q4

(Total 20 marks)

TOTAL FOR SECTION B: 40 MARKS

TOTAL FOR PAPER: 50 MARKS

END

N 3 1 8 3 1 A 0 1 8 2 0

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THE PERIODIC TABLE

Key

Molar mass g mol^{-1}
Symbol
Name
Atomic number

Period	1	2	Group										3	4	5	6	7	0
1	1 H Hydrogen 1																	4 He Helium 2
2	7 Li Lithium 3	9 Be Beryllium 4											11 B Boron 5	12 C Carbon 6	14 N Nitrogen 7	16 O Oxygen 8	19 F Fluorine 9	20 Ne Neon 10
3	23 Na Sodium 11	24 Mg Magnesium 12											27 Al Aluminium 13	28 Si Silicon 14	31 P Phosphorus 15	32 S Sulphur 16	35.5 Cl Chlorine 17	40 Ar Argon 18
4	39 K Potassium 19	40 Ca Calcium 20	45 Sc Scandium 21	48 Ti Titanium 22	51 V Vanadium 23	52 Cr Chromium 24	55 Mn Manganese 25	56 Fe Iron 26	59 Co Cobalt 27	59 Ni Nickel 28	63.5 Cu Copper 29	65.4 Zn Zinc 30	70 Ga Gallium 31	73 Ge Germanium 32	75 As Arsenic 33	79 Se Selenium 34	80 Br Bromine 35	84 Kr Krypton 36
5	85 Rb Rubidium 37	88 Sr Strontium 38	89 Y Yttrium 39	91 Zr Zirconium 40	93 Nb Niobium 41	96 Mo Molybdenum 42	99 Tc Technetium 43	101 Ru Ruthenium 44	103 Rh Rhodium 45	106 Pd Palladium 46	108 Ag Silver 47	112 Cd Cadmium 48	115 In Indium 49	119 Sn Tin 50	122 Sb Antimony 51	128 Te Tellurium 52	127 I Iodine 53	131 Xe Xenon 54
6	133 Cs Caesium 55	137 Ba Barium 56	139 La Lanthanum 57	178 Hf Hafnium 72	181 Ta Tantalum 73	184 W Tungsten 74	186 Re Rhenium 75	190 Os Osmium 76	192 Ir Iridium 77	195 Pt Platinum 78	197 Au Gold 79	201 Hg Mercury 80	204 Tl Thallium 81	207 Pb Lead 82	209 Bi Bismuth 83	210 Po Polonium 84	210 At Astatine 85	222 Rn Radon 86
7	223 Fr Francium 87	226 Ra Radium 88	227 Ac Actinium 89															

140 Ce Cerium 58	141 Pr Praseodymium 59	144 Nd Neodymium 60	(147) Pm Promethium 61	150 Sm Samarium 62	152 Eu Europium 63	157 Gd Gadolinium 64	159 Tb Terbium 65	163 Dy Dysprosium 66	165 Ho Holmium 67	167 Er Erbium 68	169 Tm Thulium 69	173 Yb Ytterbium 70	175 Lu Lutetium 71
232 Th Thorium 90	(231) Pa Protactinium 91	238 U Uranium 92	(237) Np Neptunium 93	(242) Pu Plutonium 94	(243) Am Americium 95	(247) Cm Curium 96	(245) Bk Berkelium 97	(251) Cf Californium 98	(254) Es Einsteinium 99	(253) Fm Fermium 100	(256) Md Mendelevium 101	(254) No Nobelium 102	(257) Lr Lawrencium 103

N 3 1 8 3 3 1 A 0 2 0 2 0