THE COLLEGE OF THE BAHAMAS

EXAMINATION

SEMESTER 04-2008

ANSWER KEY

FACULTY OF PURE AND APPLIED SCIENCES

SCHOOL OF SCIENCES AND TECHNOLOGY

X NASSAU
FREEPORT
EXUMA
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DATE AND TIME OF EXAMINATION: 9 am, Tuesday 2nd December 2008
DURATION: 3 HOURS

COURSE NUMBER: CHEM 235

COURSE TITLE: Inorganic Chemistry

STUDENT NAME:

STUDENT NUMBER:

LECTURER'S NAME Dr. F. Banks

INSTRUCTIONS TO CANDIDATES: This paper has 9 pages and 2 sections. Please follow the instructions given with each section.

SECTION I: Multiple Choice Questions

Mark the letter corresponding to the best or most appropriate alternative on the separate answer sheet provided. Shade over the answer letter using a number 2 pencil. Each question is worth 1 mark, for a total of 40 marks.

1) The Pauli exclusion principle, in effect, states that:
   - A No two electrons can occupy the same atomic orbital.
   - B Two electrons in different atoms cannot have the same four quantum numbers.
   - C When electrons are in the same orbital their spins must be parallel.
   - D No orbital can hold more than two electrons.
   - E Electrons in degenerate orbitals have their spins paired.

2) One reason why it is incorrect to say of the formation of the ionic bond "the metal ‘wants’ to lose an electron whilst the non-metal ‘wants’ to gain an electron" is because:
   - A The first ionization energy of a metal is endothermic.
   - B The first ionization energy of a metal is exothermic.
   - C The first electron affinity of most non-metals is endothermic.
   - D Ionic bonds are formed by the loss or gain of more than one electron.
   - E Small, highly charged cations have high polarizing power.

Questions 3 to 7 involve the following classification of elements:

- A metals
- B extended structures with covalent bonds
- C diatomic molecules
- D monatomic molecules
- E elements with appreciable characteristics of both metals and non-metals

Into which classification would you place the elements with characteristics described below?

3) An outer electronic configuration of s^2p^6.D
4) The lowest electronegativity.A
5) The highest melting point for lighter (Z<20) main-group elements.B
6) Group VII elements.C
7) The group IV element between silicon and tin.E

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QUESTIONS 8 to 12

These questions concern the following types of substance.

- A hydride of an alkali metal or alkaline earth metal
- B chloride of a non-metallic element
- C halogen
- D d-block element
- E compound of a d-block element

Select from A to E the heading under which you could best classify the substance described in each question below.

8) An orange solid which forms an orange solution in water. Addition of dilute sulphuric acid to this solution followed by aqueous potassium iodide liberates iodine.E
9) A colourless liquid which is insoluble in water.B
10) A substance which is a good conductor of electricity in the solid state. The substance is insoluble in water and reacts with dilute hydrochloric acid to liberate a colourless gas.D
11) A liquid at room temperature which reacts vigorously with water to form a solution of low pH. This solution liberates a colourless, flammable gas when granulated zinc is added to it.B
12) A coloured liquid at room temperature which disproportionates when heated with concentrated aqueous sodium hydroxide.C

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QUESTIONS 13 to 18

These questions concern the following elements of period III of the periodic table.

- A sodium
- B magnesium
- C aluminium
- D chlorine
- E argon

Select from A to E the element which:

13) has the highest first ionization energy.E
14) has an outer electron shell configuration of $3s^2$B
15) forms a hydroxide which is amphoteric.C
16) forms no compounds.E
17) shows a +7 oxidation state.D
18) is a powerful oxidizing agent.D

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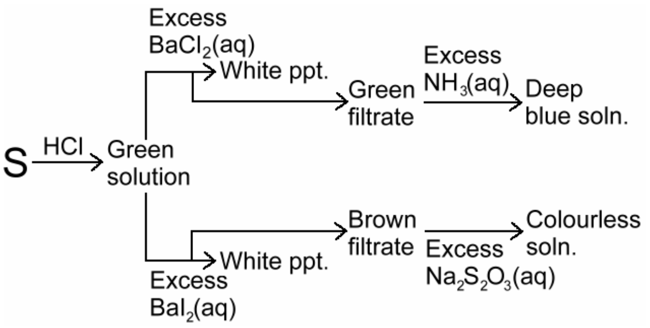
19) Below is a reaction scheme for a salt S:



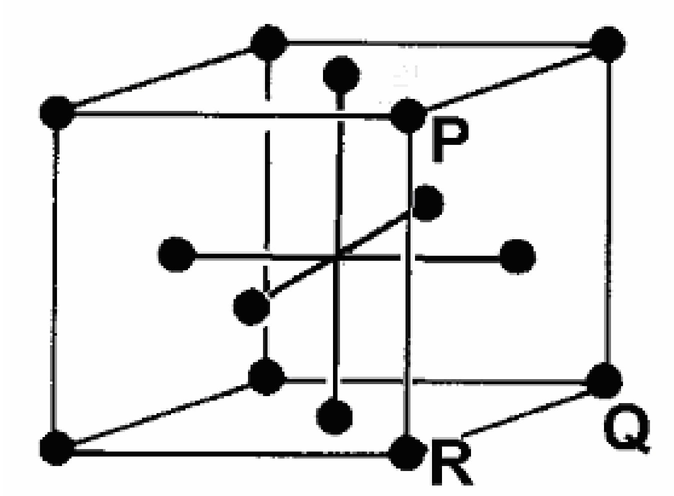
What is S?

A Chromium(III) chloride
B Chromium(III) sulphate
C Copper(II) chloride
D Copper(II) sulphate
E Iron(II) chloride

20) Which one of the following statements about sulfur and oxygen is true?

A Both are solid at room temperature.
B Both form hydrides which have acidic properties.
C Both form ionic chlorides.
D Neither forms ionic compounds.
E Neither can easily be reduced.

Questions 21 to 23 concern the following diagram of the unit cell of a metallic lattice.



21) The occupancy of the unit cell is:

A 1 atom
B 2 atoms
C 3 atoms
D 4 atoms
E 5 atoms

22) The lattice is described as:

A simple cubic
B body-centred cubic
C face-centred cubic
D hexagonal close packed
E rhombic.

23) The diagonal distance PQ in terms of the radius of an atom, r, is given by:

A PQ = r
B PQ = 2r
C PQ = 3r
D PQ = 4r
E PQ = 5r

24) A metal reacts on heating with both dry chlorine and also dry hydrogen chloride to give a different ***solid*** product in each case. Which of the following metals behaves in this way?

A Iron
B Magnesium
C Zinc
D Sodium
E Aluminium

25) In which one of the following respects is hydrogen ***different*** in its properties from a halogen?

A It reacts with alkali metals to form ionic compounds.
B It reacts with non-metals to form covalent compounds.
C It forms a range of compounds with carbon.
D It consists of diatomic molecules.
E It burns in air.

26) Which one of the following substances normally consists of discrete small molecules when in the solid state?

A Carbon
B Magnesium oxide
C Aluminium
D Carbon dioxide
E Silicon dioxide

27) The electronic configuration of the element radium can be represented as [noble gas]$7s^2$. Which one of the following statements is least ***LIKELY*** to be true?

A Radium has an oxidation number of +2 in its compounds.
B Radium decomposes water at room temperature, liberating hydrogen.
C Radium carbonate is not readily decomposed on heating.
D Radium hydroxide is amphoteric.
E Radium sulfate is insoluble in water.

28) Which one of the following techniques is used to elucidate crystal structure?

A titration
B mass spectrometry
C weighing
D volume measurement
E x-ray diffraction

29) In which one of the following compounds does nitrogen have the lowest oxidation number?

A N_2O_5

B NO_2

C N_2O

D N_2O_4

E Mg_3N_2

30) Fluorine reacts with water at room temperature to liberate mainly oxygen according to the equation

$2F_2(g) + 2H_2O(l) \rightarrow 4HF(g) + O_2(g)$

In which one of the following ways is the water acting in this reaction?

A an acid

B a base

C an oxidizing agent

D a reducing agent

E a solvent

31) sp^3 hybridised atoms give rise to molecules which show the following geometry:

A linear

B trigonal planar

C tetrahedral

D square pyramidal

E square planar

32) For atomic orbitals to overlap effectively to form σ-molecular orbitals, they must:

A have the right symmetry

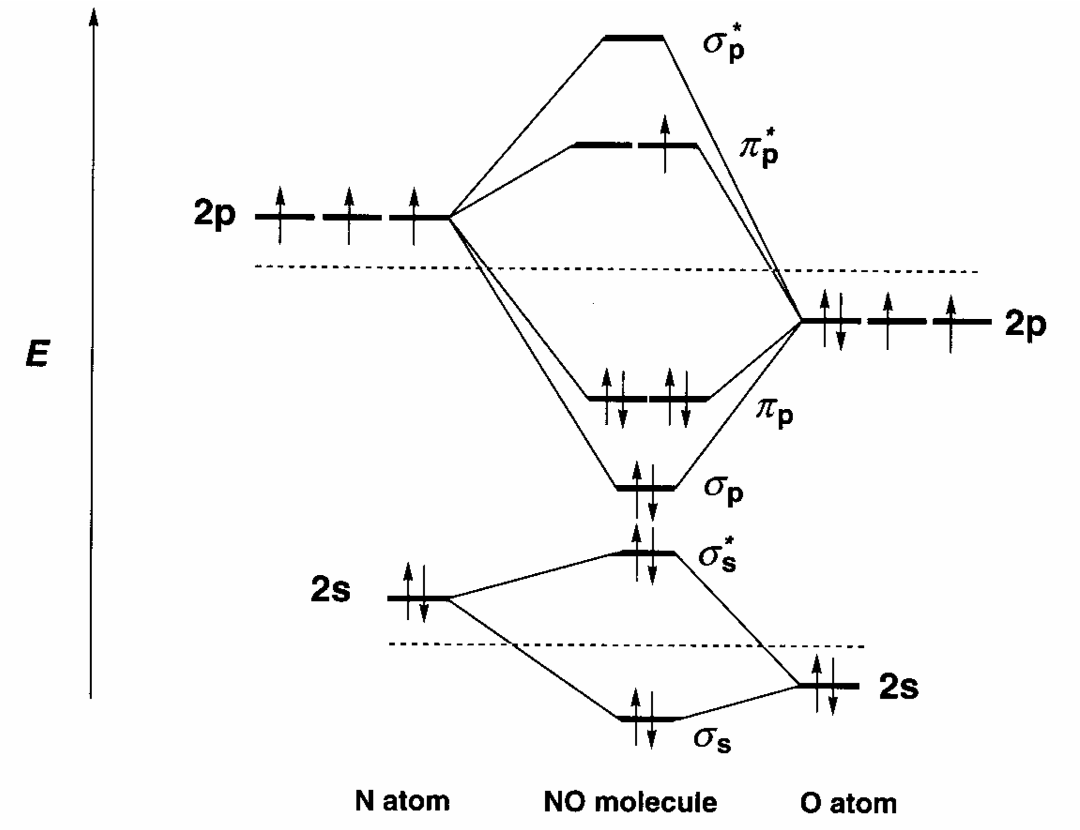
B have similar energies

C be s-orbitals

D be symmetrical about the internuclear axis.

E have all of the properties described in A, B & D above.

Questions 33 to 35 refer to the above diagram, which represents the energy levels in a molecule of nitrogen oxide.



33) The nitrogen oxide molecule is expected to be

A paramagnetic

B diamagnetic

C ferromagnetic

D non-magnetic

E A, B & C above.

34) The bond order in the NO molecule is

A 1.5

B 2

C 2.5

D 3

E 3.5

35) In the NO^+ ion, the bond between the atoms, as compared with that in NO, would be expected to be:

A longer and stronger.

B shorter and stronger.

C longer and weaker.

D shorter and weaker.

E the same length and strength.

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36) Which one of the following is ***NOT*** a characteristic property of a d-block element or its compounds?

A catalytic activity.
B formation of coloured ions.
C ready formation of simple negative ions.
D paramagnetism.
E formation of complex ions.

37) When an excess of aqueous ammonia is added to a solution of a zinc salt the white precipitate formed initially dissolves to give a colourless solution. Which one of the following formulae correctly represents the complex ion formed in this reaction?

A $[Zn(NH_3)_4]^{2+}$
B $[Zn(OH)_4]^{2-}$
C $[Zn(H_2O)_4]^{2+}$
D $[Zn(H_2O)_4]^{2-}$
E $[Zn(OH)_4(H_2O)_2]^{2-}$

38) Only one third of the total chlorine in a compound with the empirical formula $CrCl_3.6H_2O$ can be precipitated by silver nitrate solution at room temperature. Which one of the following is the best representation of the formula?

A $[Cr(H_2O)_6]^{3+}(Cl^-)_3$
B $[Cr(H_2O)_5Cl]^{2+}(Cl^-)_2.H_2O$
C $[Cr(H_2O)_4Cl_2]^+Cl^-.2H_2O$
D $[Cr(H_2O)_3Cl_3].3H_2O$
E $Cr^{3+}(Cl^-)_3.6H_2O$

39) Which one of the following chlorides ***cannot*** be prepared by the action of chlorine on the element?

A sodium chloride
B magnesium chloride
C phosphorus trichloride
D carbon tetrachloride
E aluminium chloride

40) Which one of the following molecules shows sp^3d hybridisation?

A $BeCl_2$
B BCl_3
C $SnCl_4$
D PCl_5
E SCl_6

SECTION II: Short answer questions

Answer **ANY FOUR** of the following questions in the spaces provided on your question paper unless otherwise instructed. If you attempt more than four questions, only your first four answers will be marked! Illustrate your answers with chemical equations wherever appropriate.

There is a total of 60 marks for this section.

1) This question concerns the 1st transition series of elements.

a) What is meant by term “transition element” in the context of this first series? (2)

An element which as the free element or in its compounds has partially filled 3d-orbitals.

b) Why is zinc not strictly included as a transition metal? (1)

Zinc, whether free or combined, has a full 3d subshell.

c) Give the electronic configurations of Zn^{2+}, Fe^{2+}, and Fe^{3+}. You may use the abbreviation [Ar] if you wish (2)

Zn^{2+}: $[Ar]4s^0 3d^{10}$

Fe^{2+}: $[Ar]4s^0 3d^6$

Fe^{3+}: $[Ar]4s^0 3d^5$

d) How do you account for the fact that

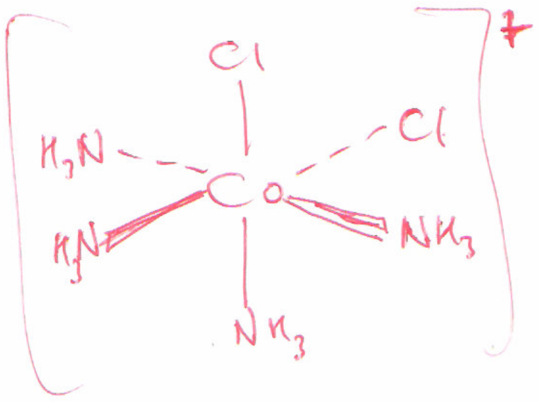
i) the octahedral complex, $[Fe(CN)_6]^{4-}$, is diamagnetic? (4)

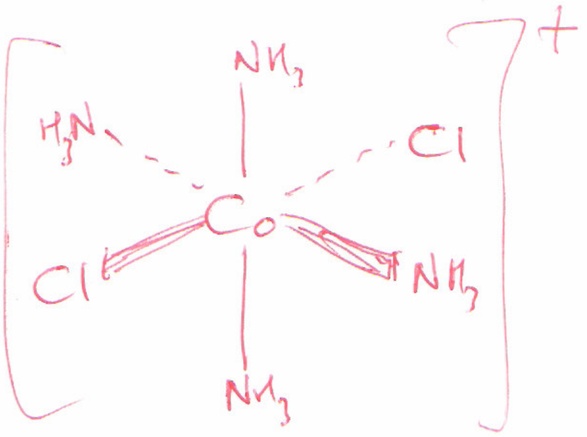
In octahedral complexes, the 3d subshell is split into two sets of orbitals (1), 3 at low energy and 2 at higher energy (1). In the above complex the energy gap between the two sets is large enough (1) to force all 6 of the 3d-electrons into the lower set, spins paired.(1) Hence there are no unpaired electrons and the compound is diamagnetic.

ii) in solution Zn^{2+} ions are colourless but Fe^{3+} ions are coloured? (4)

Zn^{2+} is has all 3d-orbitals filled (1) so there can be no d-d transitions.(1/2) In Fe^{3+} there are empty d-orbitals(1) so d-d transitions are possible(1/2). It is these that make such compounds coloured, since the energy difference corresponds to the visible part of the spectrum.(1)

e) Cobalt forms the complex ion $[Co(NH_3)_4Cl_2]^+$ which exists as a violet and a green form. Draw diagrams to show how the two forms arise. (2)





2) This question concerns the hydrides of a range of elements.

f) In each of the following cases give the name of a hydride and, if required, write an equation for the reaction described or implied. (The same hydride may be used more than once if necessary.)

i) A hydride which is not hydrolysed by cold water. (2)

Name: methane

ii) A hydride which reacts violently with water to give a basic solution. (2)

Name: sodium hydride

Equation: $NaH(s) + H_2O(l) \rightarrow NaOH(aq) + H_2(g)$

iii) A hydride which, on electrolysis in the molten state, gives hydrogen at the anode. (2)

Name: LiH

Equation at anode: $2H^- \rightarrow H_2(g) + 2e^-$

iv) A hydride which in water is a dibasic acid. (2)

Name: H_2S

Equation: $H_2S(aq) + H_2O(l) \rightarrow\rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq)$

v) A hydride which is soluble in water and hydrolysed slightly to give a basic solution. (2)

Name: ammonia

Equation: $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

vi) A hydride which can act as a ligand with d-block metal ions. (2)

Name: water

Equation: $CuSO_4(s) + 4H_2O(l) \rightarrow [Cu(H_2O)_4]^{2+}(aq)$

vii) A solid hydride which reacts violently with water and has a polymeric structure. (2)

Name: AlH_3

Equation: $AlH_3(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3H_2(g)$

g) Give the names of TWO hydrides which can combine with each other by addition and write an equation for the reaction. (2)

Names of hydrides: ammonia and hydrogen chloride

Equation: $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

3) This question concerns the halides of various elements.

a) Suggest how you could synthesise anhydrous iron(II) chloride in the laboratory. Include a balanced equation. (3)

Heat (1) the iron in a stream of dry hydrogen chloride gas(1).

$Fe(s) + 2HCl(g) \rightarrow FeCl_2(s) + H_2$ (1)

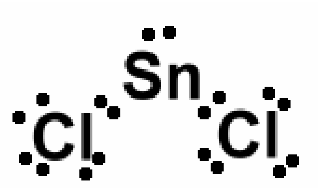
b) Draw a diagram showing the shape of a molecule of $BeCl_2$ and name this shape. (2)

Cl-Be-Cl (1) linear (1)

c) What type of hybridisation of atomic orbitals is used to explain this shape? (1)

sp

d) Draw a Lewis diagram for $SnCl_2$ and predict its shape. (2)



e) Lead forms a chloro-complex, $[PbCl_4]^{2-}$ as well as a simple chloride.

i) What is the probable shape of this complex? (1)

tetrahedral

ii) The complex is *labile*. What does this mean? (1)

It readily exchanges ligands with its environment

iii) When concentrated hydrochloric acid is added to a solution of lead(II) nitrate, a white precipitate is first obtained. On further addition of acid, the precipitate redissolves. Dilution with water again produces a white precipitate. Explain these observations in terms of the chemistry involved. Include chemical equations. (5)

Initially the insoluble chloride is formed (1) giving the white ppt.(1)

$Pb^{2+}(aq) + 2Cl^{-}(aq) \rightarrow PbCl_2(s)$(1)

As the concentration of Cl^- rises the soluble complex is formed and the ppt. redissolves(1)

$PbCl_2(s) + 2Cl^{-}(aq) \rightleftharpoons [PbCl_4]^{2-}(aq)$(1)

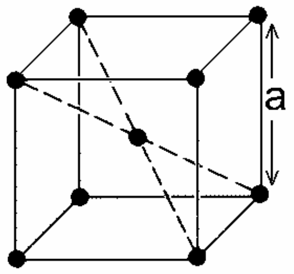
On dilution this latter equilibrium is displaced to the left again and the ppt. reappears.(1)

4) The following question concerns metallic lattices. There are two main types of metallic lattice apart from the face-centred cubic close-packed lattice (fcc). One of these is the body-centred cubic lattice.

a) What is meant by the term *unit cell*? (2)

A unit cell is the smallest part of the lattice which shows all the symmetry of the lattice.

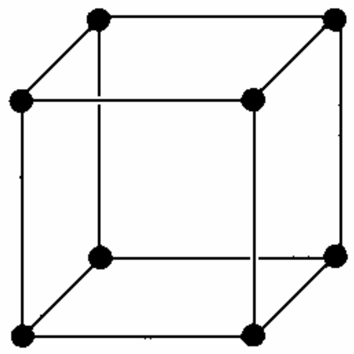
b) Sketch the unit cell of the body-centred cubic lattice below. (2)



c) Is the body-centred cubic lattice "close packed"? Give a reason for your answer. (2)

It is not close-packed because it does not pack as many atoms as possible in a give volume.

d) The element polonium (group VI) crystallises with a simple cubic lattice. The unit cell is as shown below:



i) Show that the occupancy of the cell is 1. (2)

Each atom is shared between 8 units cells.(1) Hence the occupancy is $8 \times (1/8) = 1$ (1)

ii) What is the coordination number of a polonium atom? (1)

6

iii) What is meant by the term "packing fraction" for a metallic lattice? (1)

The packing fraction is the percentage or fraction of space in a lattice actually occupied by atoms (assuming they are hard speres)

iv) Calculate the packing fraction for the simple cubic unit cell. (5)

Volume, V, of 1 atom is $\frac{4}{3}\pi r^3$ (1) where r = radius of atom.

Volume of unit cell = a^3 = length of any edge of unit cell.(1)

But $a = 2r$ (1) and so $V = (2r)^3 = 8r^3$ (1)

therefore packing fraction $= \dfrac{\frac{4}{3}\pi r^3}{8r^3} = \dfrac{\pi}{6} = 0.523... = \underline{\underline{52.3\%}}$ (1)

5) This question concerns the metallic elements of group I of the periodic table.

a) What common feature of electronic structure do these elements share? (1)

1 electron in the valence shell

b) The element lithium is, in many ways, different from the other elements of group I. State one way that the chemistry of lithium or its compounds differs from that of the group members.. Write a chemical equation to illustrate your answer. (2)

The carbonate decomposes to the oxide on heating. Other group I carbonates are stable to heat. (1)

$Li_2CO_3(s) \rightarrow Li_2O(s) + CO_2(g)$ (1)

c) In what way is the standard electrode potential for lithium ($E^{\ominus}$ for $Li^+(aq) + e^- \rightarrow Li(s) + e^-$) anomalous in the context of group I and its trends? Give a brief explanation of this anomalous behaviour. (4)

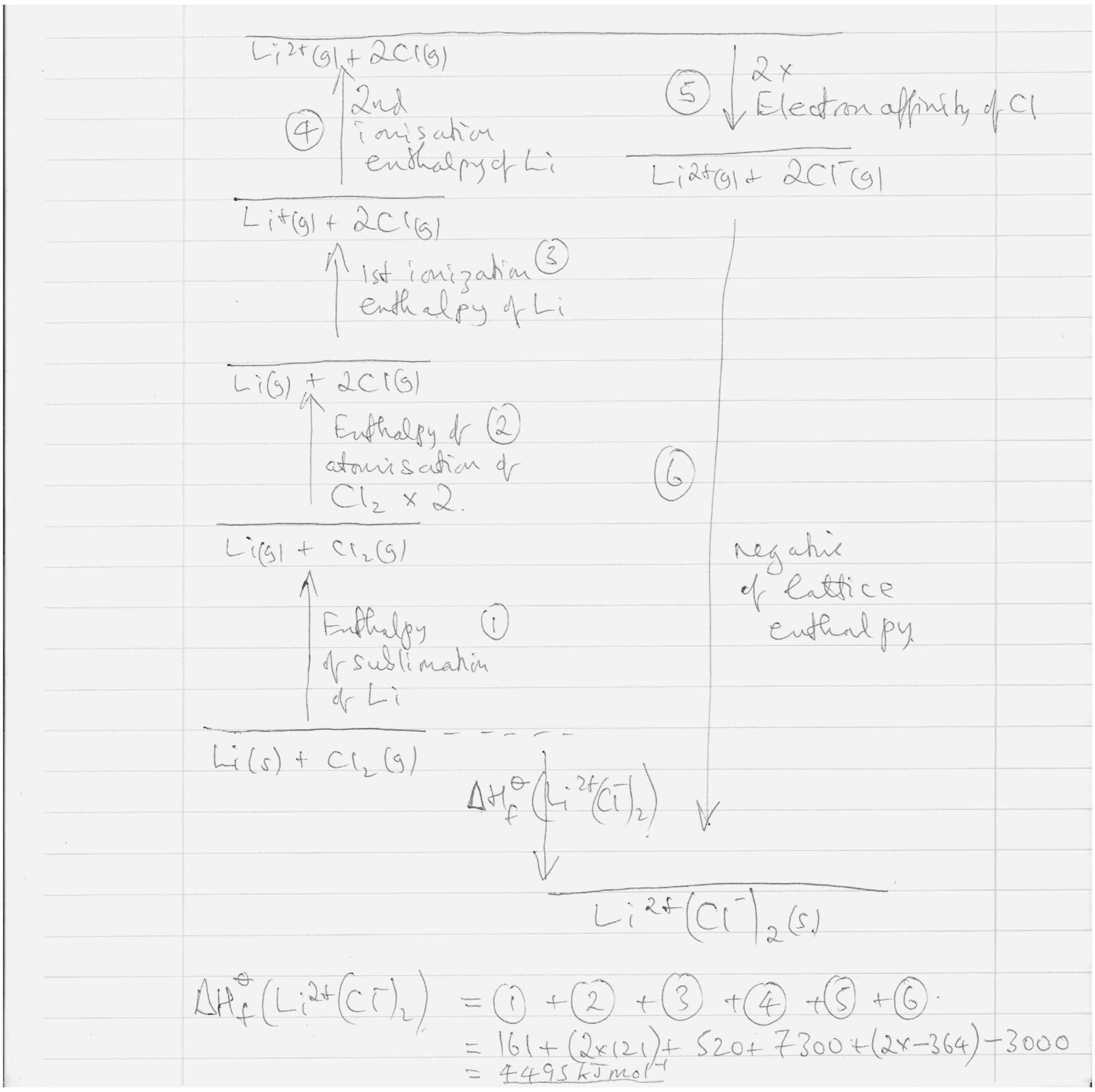
The $E^{\ominus}$ value is the most negative for any element in the group, (1) though the trend for the remaining elements is to become more negative(1). This is due to the small size of Li^+,(1) which is highly polarising and hence has a very high heat of hydration. (1)

It gives the students less stress to have the reference information on the same page as the question.

d) Given the following standard enthalpy changes:

Sublimation enthalpy of lithium metal	161 kJ mol^{-1}
First ionization enthalpy of lithium	520 kJ mol^{-1}
Second ionization enthalpy of lithium	7300 kJ mol^{-1}
Enthalpy of atomisation of chlorine (per mole of chlorine atoms)	121 kJ mol^{-1}
Electron affinity of chlorine	-364 kJ mol^{-1}
Lattice enthalpy of $Li^{2+}(Cl^-)_2$ (an estimate)	3000 kJ mol^{-1}
Standard enthalpy of formation of lithium chloride, Li^+Cl^-	-409 kJ mol^{-1}

i) Using the lined sheets provided, draw a Born-Haber cycle for the formation of $Li^{2+}(Cl^-)_2$, labelling all enthalpy changes, and hence calculate the standard enthalpy of formation of $Li^{2+}(Cl^-)_2$. (5)



$\Delta H_f^{\ominus}(Li^{2+}(Cl^-)_2) = ① + ② + ③ + ④ + ⑤ + ⑥$

$= 161 + (2 \times 121) + 520 + 7300 + (2 \times -364) - 3000$

$= 4495\ kJ\ mol^{-1}$

Half-mark for each step, one and a half for the calculation.

ii) Use your result from part (i) and the standard enthalpy of formation of Li^+Cl^- to calculate ΔH for the decomposition of $Li^{2+}(Cl^-)_2(s)$ to $Li^+Cl^-(s)$ and $Cl_2(g)$ and suggest why $Li^{2+}(Cl^-)_2$ is not formed.(3)

The decomposition of $Li^{2+}(Cl^-)_2(s)$ to $Li^+Cl^-(s)$ and $Cl_2(g)$:

$Li^{2+}(Cl^-)_2(s) \rightarrow Li^+Cl^-(s) + \frac{1}{2}Cl_2(g)$

is highly exothermic, ΔH is given by $\Delta H_f(Li^+Cl^-) - \Delta H_f(Li^{2+}(Cl^-)_2)$ (1) = -409 – 4495 = 4904 kJ mol^{-1} (1) It would be expected to decompose instantly to LiCl and chlorine. (1)

6) The following question involves valence bond theory and hybridisation of atomic orbitals.

a) Given the electronic structures of B: $1s^22s^22p_x^1$ and C: $1s^22s^22p_x^2$, how many bonds might you expect each of these atoms to form without promotion of electrons? (2)

B would form 1 bond (1) and C would form 2 (1)

b) In fact, B forms 3 bonds and C forms 4. How can you explain this in terms of a *valence state* of the molecules? (4)

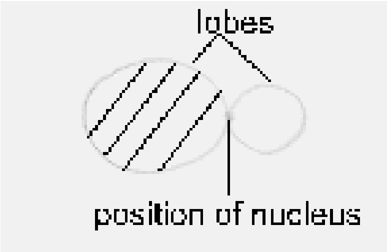
In B an electron is promoted from the 2s orbital to an empty 2p orbital (1). This gives 3 half-full valence shell orbitals (1). This is known as the valence state (1). These orbitals can overlap with half-full orbitals on other atoms to form 3 bonds. A similar promotion in C give 4 half-full orbitals and hence 4 bonds. (1)

c) What shapes are the molecules of BCl_3 and CCl_4? (2)

These are trigonal planar (1) and tetrahedral (1) respectively.

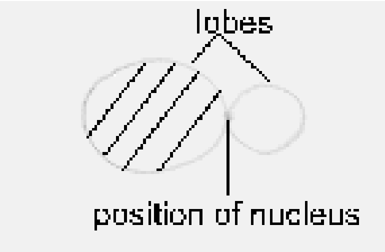
d) What hybridisation states explain these shapes? Draw a diagram of each type of hybrid orbital and label the following features: lobe, position of nucleus. Indicate the relative phases of the lobes. (6)

sp^2 hybridisation (1) gives a trigonal planar shape, and sp^3 (1) gives a tetrahedral shape.



(2)

sp^2



(2)

sp^3

e) Why are the bonds formed by the overlap of these hybrid orbitals with other orbitals particularly strong?(1)

The large lobe of the orbital gives good overlap with other orbitals.

END OF EXAMINATION