

CCHE 4271

FIRST PUBLIC EXAMINATION
Preliminary Examination in Chemistry

SUBJECT 1: INORGANIC CHEMISTRY

TRINITY TERM 2010

Monday 7th June 2010, 9.30 *a.m.* to 12.00 *noon*

Time allowed: 2½ hours

Candidates should answer **ALL** questions in **SECTION A** and **ANY TWO** questions from **SECTION B**

Please use **separate booklets** for answers to questions from Section A and Section B

The numbers in square brackets indicate the marks the Examiners expect to assign to each part of the question.

Each question in Section A is assigned a maximum mark of 10, and each question in Section B is assigned a maximum mark of 25.

Please do not turn over this page until you are told you may do so by an invigilator.

SECTION A.

Answer *ALL* five questions in this section

1. Answer *ALL* parts (a) – (c).

- (a) Explain the concept of *effective nuclear charge*. [2]
- (b) Sketch the radial distribution functions for the $3d$ and $4s$ orbitals of calcium. How can they be used to rationalise the electron configuration of calcium? [3]
- (c) List the following elements in order of decreasing first ionisation energy, giving reasons for your ordering: [5]

Mg P Al Ba S O

2. Answer *BOTH* part (a) and part (b).

- (a) Predict the structure of each of the following four molecules and identify any that contain a centre of inversion: [6]
- SO₂F₂ ICl₄[−] BO₃^{3−} XeOF₄
- (b) Explain the features of an improper rotation symmetry operation. Identify which of the molecules considered in part (a) contain an improper rotation axis (S_n). For each improper rotation axis identified, show its position on a sketch of the molecule and give its order (value of n). [4]

3. Answer *BOTH* part (a) and part (b).

(a) Comment on the melting points (in °C) of elements in Group 1: [4]

Li	Na	K	Rb	Cs
181	98	64	39	29

(b) Explain briefly why sodium almost invariably forms Na^+ ions in its compounds. Then explain the circumstances under which Na^- can be prepared. [6]

4. Answer *BOTH* part (a) and part (b).

(a) Account for the variation in hydration enthalpies (in kJ mol^{-1}) for the following species: [6]

Ca^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
-1653	-1900	-1981	-2113	-2174	-2161	-2105

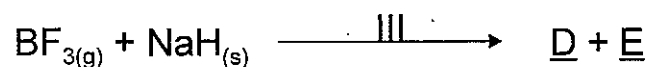
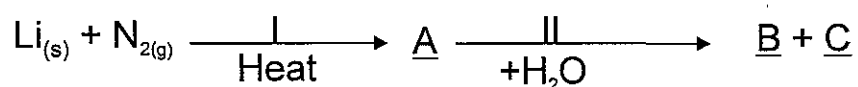
(b) Predict the number of unpaired electrons associated with the metal ion in each of the following species: [4]



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5. Answer *BOTH* part (a) and part (b).

- (a) Identify, showing your reasoning, the compounds **A–E** in the schemes below, making use of the information given. The schemes do not necessarily specify the stoichiometry of each reaction; for the transformations labelled I–III write balanced equations for the reactions. [8]



A – Red moisture-sensitive solid.

B – Pungent, toxic, colourless gas.

C – White solid which dissolves in water to give a basic solution.

D – Highly flammable gas with a density of $1.23 \times 10^{-3} \text{ kg dm}^{-3}$ at standard temperature and pressure.

E – White solid which dissolves in water to give a neutral solution.

- (b) Explain why BF_3 is a weaker Lewis Acid than BX_3 ($X = \text{Cl} - \text{I}$) [2]

[1 mole of gas has a volume of 22.4 dm^3 at standard temperature and pressure. Atomic masses: H: 1.0, B: 10.8, F: 19.0, Na: 23.0.]

SECTION B.

Answer *ANY TWO* questions from this section.

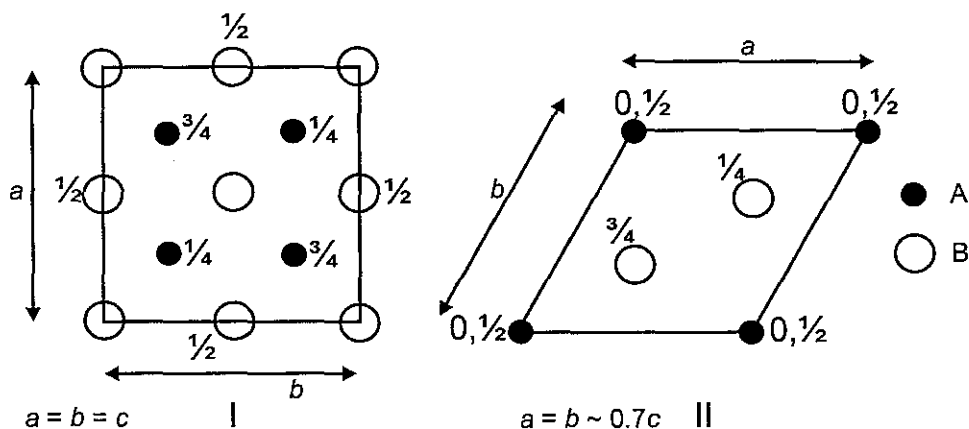
6. Answer *ALL* parts (a) – (d).

(a) Two crystal structures (labelled I and II) commonly adopted by binary solids are shown in projection below. For each determine the following:

(i) the stoichiometry, [2]

(ii) the coordination number and environment of each atom type. [4]

Give an example of a compound which adopts each structure. [2]



The fractional coordinates along the axis perpendicular to the plane of the paper, are given as fractions of the lattice parameter c and are 0 unless stated.

(b) Sketch and describe the common structures adopted by metals and calculate the packing efficiency of the atoms in one of these structures. [5]

(c) The structures of many ionic compounds are often described as resulting from the filling, with cations of radius r_+ , of some or all of the interstices in an array of anions of radius r_- . Calculate the minimum value of r_+/r_- that you would expect for compounds adopting:

(i) the halite (NaCl) structure,

(ii) the CsCl structure. [4]

(d) Suggest with reasons the crystal structures which might be adopted by the following compounds. [8]

FeSe

NH₄F

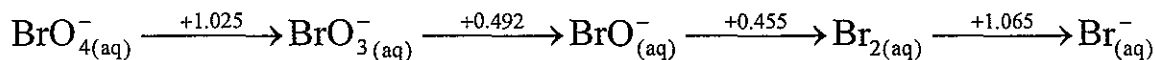
ZnO

MgCl₂

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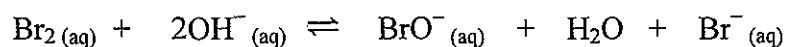
7. Answer ALL parts (a) – (e).

The following Latimer diagram shows the standard reduction potentials (in V) for some bromine-containing species in basic aqueous solution:



(a) Construct a Frost oxidation state diagram for bromine in basic aqueous solution and interpret your diagram with respect to the redox chemistry of the species involved. [6]

(b) Bromine will react in basic aqueous solution at 0 °C to give the following equilibrium:



Calculate the equilibrium constant for this reaction at 0 °C. [7]

(c) The hypobromite ion product BrO^- formed at 0 °C is unstable and will undergo a further reaction at room temperature or above. Using your Frost diagram identify this further reaction that BrO^- will undergo and give a balanced equation for it. [4]

(d) Discuss the trend in standard reduction potentials under acidic conditions: [3]

$$E^\ominus (\text{ClO}_4^-/\text{ClO}_3^-) \quad 1.20 \text{ V}$$

$$E^\ominus (\text{BrO}_4^-/\text{BrO}_3^-) \quad 1.85 \text{ V}$$

$$E^\ominus (\text{IO}_4^-/\text{IO}_3^-) \quad 1.63 \text{ V}$$

(e) Discuss the trend in single bond energies (in kJ mol^{-1}): [5]

F–F	159		
Cl–Cl	242	F–Cl	255
Br–Br	193	F–Br	249
I–I	151	F–I	280

[Note that at $T = 273 \text{ K}$, $RT/F = 0.024 \text{ V}$ and $(RT/F)\ln 10 = 0.055 \text{ V}$]

8. Answer *ALL* parts (a) – (c).

(a) Draw and label a molecular orbital diagram for the homonuclear diatomic molecule N_2 . Label the molecular orbitals on your diagram and annotate the diagram with pictorial representations of these molecular orbitals. [7]

(b) Comment on the following bond lengths (in pm): [4]

N_2	110	NO	115	O_2	121
PN	149	PO	147	SO	148

(c) Draw a simple molecular orbital scheme to describe the σ bonding in XeF_2 . Use only one $5p$ orbital of Xe and one $2p$ orbital from each F atom in your scheme. Label the molecular orbitals on your diagram and annotate the diagram with pictorial representations of these molecular orbitals. [6]

(i) Comment on the charge distribution in the molecule. [2]

(ii) Explain qualitatively how the characteristics of the molecular orbitals would change if the Xe $5d_{z^2}$ orbital was included in your bonding scheme. [3]

(iii) Compare and contrast the bonding in XeF_2 with the bonding in bridging B–H–B groups in B_2H_6 . [3]

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9. Answer ALL parts (a) – (e).

(a) Define the lattice enthalpy of an inorganic solid. [2]

(b) Discuss the basis of the Kapustinskii equation for estimating the lattice enthalpy of an ionic solid and the approximations entailed in its use. [5]

$$\Delta H_L = \frac{W \nu z_+ z_-}{r_+ + r_-}$$

where: W is a constant: $1.08 \times 10^5 \text{ pm kJ mol}^{-1}$,
 ν is the number of distinct ions in the formula unit,
 z_+ and z_- are the charge numbers of the cation and anion,
 r_+ and r_- are the radii of the cation and anion in pm.

(c) Use the data below to assess the stabilities of $\text{CoF}_3(\text{s})$ and $\text{CoI}_3(\text{s})$ with respect to $\text{CoF}_2(\text{s})$ and $\text{CoI}_2(\text{s})$ respectively. Comment on the validity of using the Kapustinskii equation for determining the lattice enthalpies of these compounds in this case. [10]

Standard reaction enthalpies /kJ mol⁻¹ at 298 K

$\text{Co}^{2+}(\text{g})$	$\rightarrow$	$\text{Co}^{3+}(\text{g}) + \text{e}^{-}(\text{g})$	3230
$\text{F}_2(\text{g})$	$\rightarrow$	$2\text{F}(\text{g})$	158
$\text{F}(\text{g}) + \text{e}^{-}$	$\rightarrow$	$\text{F}^{-}(\text{g})$	-350
$\text{I}_2(\text{s})$	$\rightarrow$	$2\text{I}(\text{g})$	214
$\text{I}(\text{g}) + \text{e}^{-}$	$\rightarrow$	$\text{I}^{-}(\text{g})$	-303

Ionic radii /pm

Co^{2+} : 65	Co^{3+} : 55	F^{-} : 133	I^{-} : 218
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(d) It is sometimes stated that “fluorine tends to bring out the highest oxidation state of an element”. Give examples to support this assertion and, in the light of your calculation in (c), discuss why it is usually valid. [3]

(e) Comment on the information in the table below which lists the third ionisation energies (in kJ mol^{-1}) and the stable trihalides (MX_3) of some transition elements: [5]

V	2870	all VX_3 , $X = \text{F, Cl, Br, I}$
Mn	3248	MnF_3 only
Fe	2957	FeX_3 , $X = \text{F, Cl, Br}$
Ni	3933	no stable NiX_3

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