IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2012, for Internal Students of the Imperial College of Science, Technology and Medicine

This paper is also taken for the relevant examination for the Associateship

CHEMISTRY FOUNDATION YEAR ONE

Friday 13th January 2012, 09:30-12:30

PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING OF ANY PRIOR CORE COURSE.

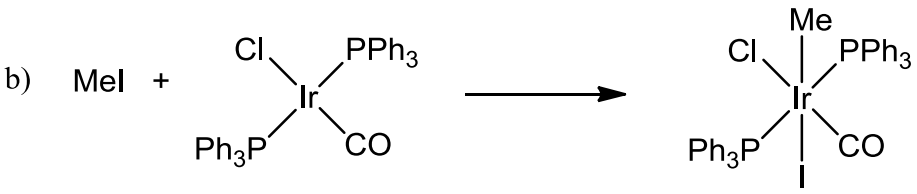
USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

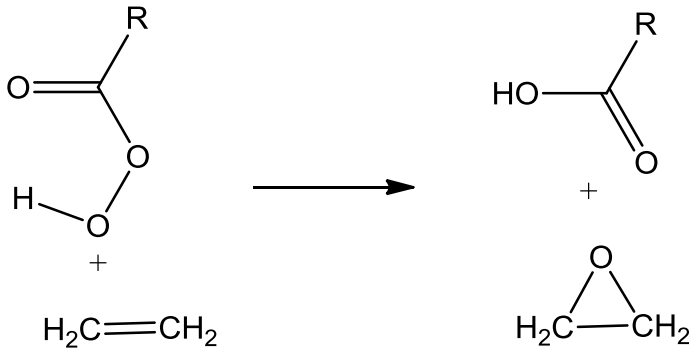
Question 1 – Reactivity and Characterisation

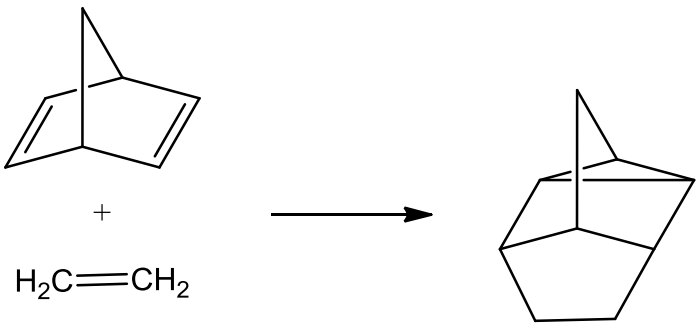
NB. 'Half a question' (out of 12.5 marks)

Give the reaction type for **THREE** of the following reactions. For the reactions of metal containing compounds give the oxidation state for **ALL** metal atoms. For other reactions draw appropriate arrows to indicate the direction of electron flow.

a) $RMgX + RHgCl \longrightarrow MgXCl + R_2Hg$

b) 

c) 

d) 

(4 marks each plus 0.5 bonus mark)

Question 2 – Atomic and Molecular Structure

NB. This question is worth 25 marks.

Answer part a) **AND** part b) and **EITHER** part c) **OR** part d) of this question.

a) Answer **ALL** parts of this question.

i) Define the terms *Ionisation Energy* and *Electron Affinity*.

(4 marks)

The first and second ionisation energies, I_1 and I_2, and the electron affinities, E_a, of the hypothetical elements X, Y and Z are given below (the values are given in kJ mol^{-1}):

	I_1/kJ mol^{-1}	I_2/kJmol^{-1}	E_a/kJ mol^{-1}
X	496	4562	71
Y	1681	3375	333
Z	589	1145	65

Using this information answer the following questions, giving your reasons in each case:

ii) Which of the three elements, X, Y or Z, is most likely to have a +2 oxidation state?

(2 marks)

iii) Which one of the three elements will be the easiest to reduce?

(2 marks)

iv) Will the following gas-phase reaction proceed in the way drawn or not?

$$X^+ + Y \rightarrow X + Y^+$$

(2 marks)

QUESTION CONTINUED OVERLEAF

b) Answer **ALL** parts of this question.

The ground state electronic configurations of Ti, Gd and Ag are:

i) Ti: $[Ar]4s^2 3d^2$

ii) Gd: $[Xe]4f^7 5d^1 6s^2$

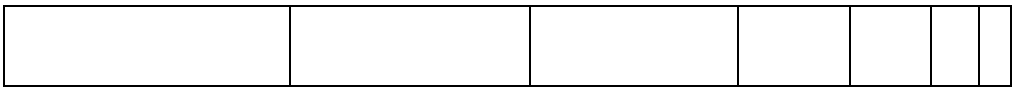
iii) Ag: $[Kr]4d^{10} 5s^1$

For each case, state whether or not they follow the Aufbau principle. If not, explain why and state what the configuration would be if the principle was followed.

(9 marks)

c) Answer **ALL** parts of this question.

The electronic line spectrum of hydrogen gas is shown schematically below:



A **B** **C** **D** **E** **F** **G**

i) State in which direction the energy increases, **A → G OR G → A**.

(1 mark)

ii) State in which direction the wavelength increases, **A → G OR G → A**.

(1 mark)

iii) Explain why the spectrum shows discrete lines.

(2 marks)

iv) What do transitions in the Lyman series all have in common? (use a sketch to illustrate your answer)

(2 marks)

d) Use Slater's Rules to predict which one of the two elements, K and Br, requires less energy to be ionised to K^+ and Br^+ respectively. Explain your answer.

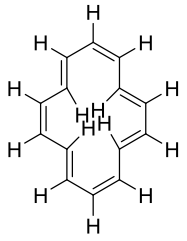
(6 marks)

Question 3 – Aromatic Chemistry

NB. 'Half a question' (out of 12.5 marks)

Answer part a) **AND** part b) and **EITHER** part c) **OR** part d) of this question.

a) Compound **1** is known to be highly distorted and does not display aromatic behaviour although it fulfills the Hückel [4n+2] 'condition'. Why might this be?



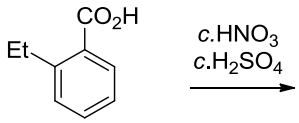
1

(2 marks)

b) If benzene is treated with the 'super-acid' system HF-SbF_5 in a suitable non-nucleophilic solvent and a ^1H NMR spectrum recorded, the following signals are obtained: δ 5.69 (2H), 8.22 (2H), 9.42 (1H) and 9.58 (2H) ppm. Propose a structure for this species and indicate which protons resonate at each chemical shift.

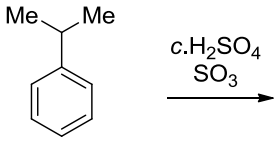
(4 marks)

c) Draw the expected major product of the following reaction, draw a mechanism and briefly justify the regiochemical outcome.



(6.5 marks)

d) Draw the expected major product of the following reaction, draw a mechanism and briefly justify the regiochemical outcome.



(6.5 marks)

Question 4 – Chemical Equilibria

NB. This question is worth 25 marks.

Answer part a) and **EITHER** part b) **OR** part c) of this question.

a) Answer **ALL** parts of this question.

i) Using the enthalpy of formation values given below, calculate the enthalpy of combustion of two moles of octane (C_8H_{18}) under standard conditions

$\Delta_f H^o [C_8H_{18(l)}] = -250$ kJ mol^{-1}
$\Delta_f H^o [CO_{2(g)}] = -394$ kJ mol^{-1}
$\Delta_f H^o [H_2O_{(l)}] = -286$ kJ mol^{-1}

(2 marks)

ii) If the equilibrium constant for a reaction at 300 K is 0.01, what is the reaction free energy?

(2 marks)

iii) If the standard redox potential for a two electron reaction is -0.2 V, what is the corresponding standard free energy change?

(2 marks)

iv) Assuming that air can be treated as an ideal gas, calculate the mass of 1 m^3 of air under standard conditions.

Assume that the average molecular mass of air is 28 g mol^{-1}

(2 marks)

v) Which one of the following (A-E) is always true for a spontaneous process at constant temperature? Briefly explain your reasoning.

A. $\Delta S_{system} > 0$
B. $\Delta S_{system} + \Delta S_{surroundings} = q/T$
C. $\Delta S_{system} + \Delta S_{surroundings} > 0$
D. $\Delta S = q/T$
E. $\Delta S < q/T$

(2 marks)

QUESTION CONTINUED OVERLEAF

vi) Hydrobromic acid, HBr, is a weaker acid than hydroiodic acid, HI. Which is the stronger base, Br^- or I^- and why?

(2 marks)

vii) Lithium metal is burned in air to produce lithium oxide according to the following equation:

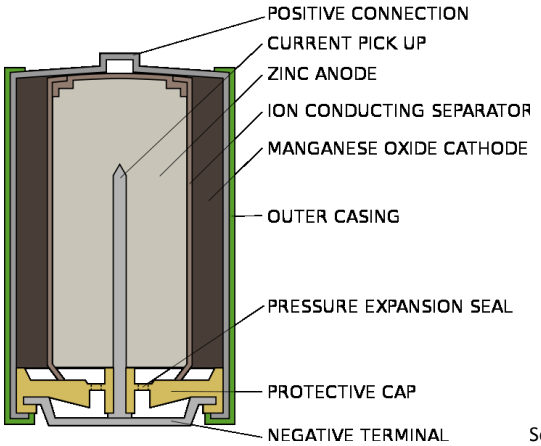
$$\mathbf{2Li\ (s) + \tfrac{1}{2}\ O_2\ (g) \rightarrow Li_2O\ (s)}$$

What would you expect the sign to be (+ve or -ve) for the corresponding reaction enthalpy, entropy and Gibbs free energy under standard conditions? Explain the reason for each of these choices.

(3 marks)

b) Answer **ALL** parts of this question.

An alkaline zinc battery, commonly used to power electronic equipment, is shown in cross section below:



Source: \\commons.wikimedia.org

$$ZnO_{(s)} + H_2O_{(l)} + 2e^- \leftrightarrows Zn_{(s)} + 2OH^-_{(aq)} \qquad E^o = -1.211\ V$$

$$2MnO_{2(s)} + H_2O_{(l)} + 2e^- \leftrightarrows Mn_2O_{3(s)} + 2OH^-_{(aq)} \qquad E^o = 0.390\ V$$

i) State the Nernst equation, defining all the terms used.

(3 marks)

ii) Using the electrochemical data given above, calculate the standard potential of this cell. State any assumptions you have used.

(2 marks)

QUESTION CONTINUED OVERLEAF

iii) Write down the Nernst equation for the above battery including all relevant chemical species.

(2 marks)

iv) Explain what happens to the cell voltage as described by the Nernst equation derived from the equations above when (a) the pH increases; (b) the battery changes from its fully charged to half-charged state?

(3 marks)

c) Answer **ALL** parts of this question.

Over the last several years, there have been several news stories about lithium batteries "exploding" due to self-discharge leading to thermal runaway.

A primary lithium battery, weighing 21.9 g has nominal voltage of 3.6 V and a charge capacity of 3.6 Ah (i.e. it can supply a current of 3.6 A for one hour). It has a heat capacity of 795 J kg^{-1} K^{-1}.

i) Assume all the energy in the battery was dissipated as heat (i.e. $\Delta w = 0$). How much heat would be generated if the battery underwent self-discharge?

(2 marks)

ii) Using the heat capacity above, and the generated heat calculated in (i), what might the ultimate battery temperature rise to? Assume the initial battery temperature is 25^{o}C.

(2 marks)

iii) In reality, the ultimate battery temperature is considerably less than that calculated in (ii). Provide two reasons why this might be so.

(2 marks)

Consider the detonation of TNT (trinitrotoluene or more correctly 2-methyl-1,3,5-trinitrobenzene, 227.13 g mol^{-1}) in pure oxygen for which the sole products are CO_2, H_2O and N_2.

iv) Calculate the heat liberated by the detonation of 21.9 g of TNT.

$\Delta_f H^o$ (TNT) = 3400 kJ mol^{-1};

$\Delta_f H^o$ (CO_2) = -394 kJ mol^{-1};

$\Delta_f H^o$ (H_2O) = -286 kJ mol^{-1}

(2 marks)

v) Compare the results of (iii) and (iv). Are the comparisons of thermal runaway of a lithium battery to a bomb justified? Are there any other factors that need to be taken into account?

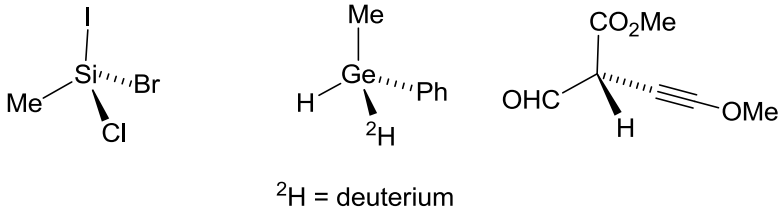
(2 marks)

Question 5 – Stereochemistry

NB. 'Half a question' (out of 12.5 marks)

Answer part a) and **EITHER** part b) **OR** part c) of this question.

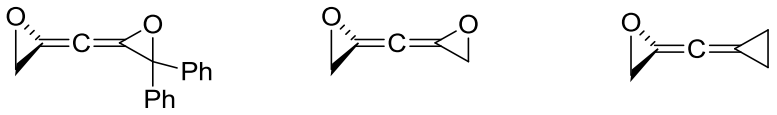
a) Assign (*R*) or (*S*) absolute stereochemical descriptors to all stereogenic centres in the following three molecules. Show your working.



^{2}H = deuterium

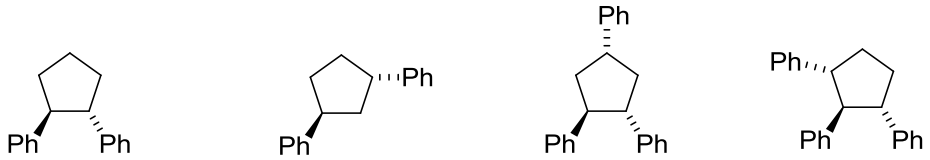
(6.5 marks)

b) Only one of the following molecules has an asymmetric enantiomeric form. Draw this enantiomer and justify your selection by reference to the other two molecules.



(6 marks)

c) Only one of the following molecules is a *meso* compound. Draw this molecule and explain the reason for your choice. Also indicate why the other molecules shown are not *meso* compounds.



(6 marks)

Question 6 – Introduction to Spectroscopy & Characterisation

NB. This question is worth 25 marks.

Answer part a) and **EITHER** part b) **OR** part c) of this question.

a) Answer **ALL** parts of this question.

i) What vibrational frequency in wavenumbers corresponds to a thermal energy of k_BT at 25^oC?

(3 marks)

ii) What is the wavelength of this radiation?

(2 marks)

iii) The vibrational frequency of a typical carbonyl group is 1700 cm^{-1}. What is the force constant of the C=O bond, assuming harmonic motion.

(4 marks)

iv) Explain briefly why the anharmonic oscillator description of a diatomic molecule is more realistic than the harmonic oscillator model.

(2 marks)

b) Answer **ALL** parts of this question.

i) Derive the separation between neighbouring rotational peaks in the spectrum of a molecule assuming the rigid rotor approximation.

(6 marks)

The far-infrared spectrum of $^1H^{127}I$ consists of a series of equally spaced lines with $\Delta\varpi = 12.8\ cm^{-1}$.

ii) Calculate the moment of inertia of HI.

(4 marks)

iii) Calculate the internuclear distance of HI.

(4 marks)

c) Answer **BOTH** parts of this question.

Consider the normal modes of vibration of a linear molecule AB_2.

i) Sketch all the normal modes of this molecule.

(4 marks)

ii) Which of these modes are IR active and which are Raman active. Justify your answer referring to the dipole moment and polarisability of the molecule for each of the modes.

(10 marks)

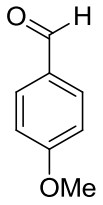
Question 7 – Introduction to Spectroscopy and Characterisation

NB. This question is worth 25 marks.

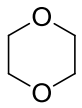
Answer part a) and **EITHER** part b) **OR** part c) of this question.

a) Sketch and assign the ^{1}H NMR spectra for compounds A-C.

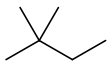
[You may assume coupling occurs only through 3 bonds or fewer and that ^{1}H, I=1/2 is 100% abundant; all other nuclei are NMR inactive.]



A



B


C

(15 marks)

b) Answer **ALL** parts of this question.

i) State the type of molecular transition excited using infra-red electromagnetic radiation. What is the selection rule for IR absorption?

(2 marks)

ii) Explain the number of observed absorptions and their wavenumbers, for the compounds shown below.

Compound	Infra-red absorption / cm^{-1}
NO^{+}	2273
NO^{-}	1365
HCl	2290
DCl	2145

[D=^{2}H]

(8 marks)

c) An unknown compound shows the following spectroscopic characteristics.

The IR spectrum shows strong absorptions at 1792, 694 cm^{-1} (there are other weaker absorptions).

The ^{1}H NMR spectrum shows a triplet at 1.25 ppm, with a relative integral of 3, and a quartet at 2.93 ppm, with a relative integral of 2.

The mass spectrum shows a molecular ion at *m/z* 94 (25%), 92 (75%) and fragmentation peaks at *m/z* 63 (25%), 61 (75%) and 57 atomic mass units (amu).

Interpret each of the pieces of spectroscopic data, and hence identify the unknown compound. Explain how the data supports your assignment.

(10 marks)