IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2010, 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 COURSE – YEAR ONE

Wednesday 13th January 2010, 09:30-12:30

Answer ONE question from each attended course

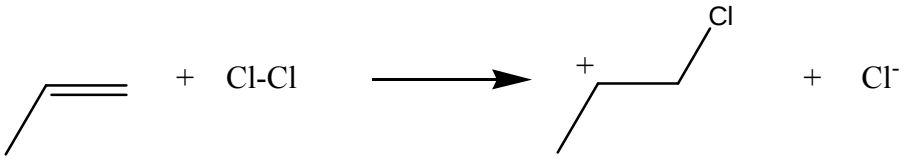
USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

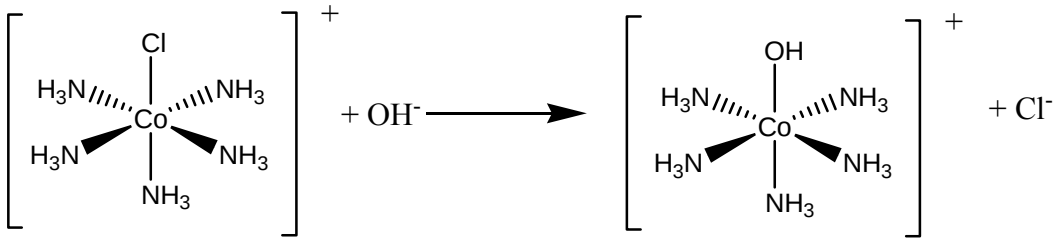
Question 1 – Reactivity and Characterisation

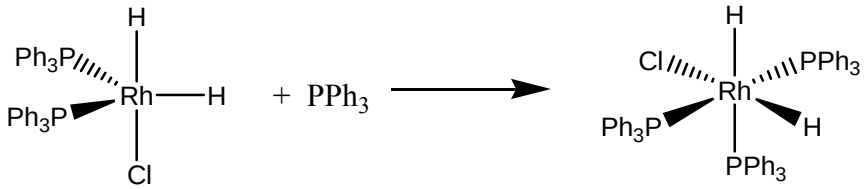
NB. 'Half a question' (out of 12.5 marks)

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

(a) $Me_3N + HO\text{-}OH \longrightarrow [Me_3N\text{-}OH]^+ + OH^-$

(b) 

(c) 

(d) 

(4 marks each plus 0.5 bonus mark)

Question 2 – Atomic structure

NB. This question is worth 25 marks

Answer part a) and **EITHER** part b) **OR** part c)

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

i) Give the electronic configuration for Ge and for the Ge^{2+} cation.

(2 marks)

ii) For the following three pairs of elements, explain with reasoning which of the pair of elements will have the highest first ionisation energy:

Be or B
Cl or Br
P or S

(6 marks)

iii) Explain how atomic radii and electronegativity vary across the second period of the Periodic Table.

(4 marks)

iv) Sketch the boundary surfaces of the orbitals associated with the quantum numbers n=3, l=2.

(3 marks)

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

i) Ca^{2+}, K^{+}, S^{2-} and Cl^{-} all have the same number of electrons. Calculate the effective nuclear charge for each of the four ions and hence place the four ions in order of increasing ionic radius.

(6 marks)

ii) Explain why the carbon atom possesses two unpaired electrons having identical spin quantum number values.

(4 marks)

QUESTION CONTINUED OVERLEAF

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

i) Following excitation, an electron in the Hydrogen 4p orbital decays to the 2s orbital. Calculate the energy involved in this transition, and explain whether the energy is positive or negative.

(6 marks)

ii) Calculate the frequency of the photon emitted for the process described above in part (i), [i.e. 4p $\rightarrow$ 2s]. Which part of the electromagnetic spectrum does this frequency correspond to?

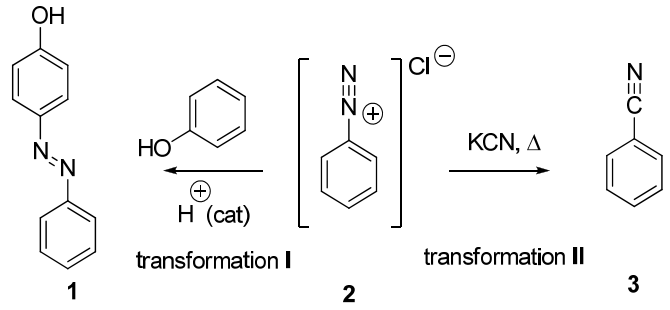
(4 marks)

Question 3 – Aromatic Chemistry

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

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

Consider the two transformations (**I** and **II**) drawn below:



(a) Answer **BOTH** parts of this question

(i) Use transformations **I** and **II** to explain the term 'ambident electrophile'.

(2 marks)

(i) How would you prepare reactant **2** from aniline (aminobenzene)? Give the reagents and draw a mechanism.

(5 marks)

(b) Draw a mechanism for transformation **I**.

(5.5 marks)

(c) Draw a mechanism for transformation **II**. What is the 'driving force' for this reaction?

(5.5 marks)

Question 4 – Chemical Equilibrium

NB. This question is worth 25 marks

Answer part a) and **EITHER** part b) **OR** part c).

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

i) Hydrogen burns in air according to the following equation:

$$\mathbf{H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightarrow H_2O\,(l)}$$

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

(3 marks)

ii) How many grams of glucose does a student need to consume per day assuming that they perform -2 MJ of work with maximum efficiency? Assume STP conditions.

$$\mathbf{C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O}$$

$\Delta_c H^{\ominus} = -2808$ kJ mol^{-1}. $\Delta_c S^{\ominus} = 182.4$ J mol^{-1} K^{-1}

(5 marks)

iii) In thermodynamics, what is meant by the terms Intensive and Extensive properties? Give **TWO** examples of each.

(2 marks)

iv) If $\mathbf{\Delta_r G^{\ominus}}$ for a reaction is -11.4 kJ mol^{-1}, what is the equilibrium constant for this reaction?

(3 marks)

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

The direct methanol fuel cell operates to produce electrical energy from the oxidation of methanol using two coupled electrochemical half cells (both written as reductions):

$$O_2 + 4H^+ + 4e^- \leftrightarrows 2\,H_2O$$

$$CO_2 + 6H^+ + 6e^- \leftrightarrows CH_3OH + H_2O$$

The $\Delta_r G^{\ominus}$ for the oxidation of methanol is -703 kJ mol^{-1}

i) Show how the two half cell reactions can be used to construct the complete reaction for oxidation of methanol.

(3 marks)

QUESTION CONTINUED OVERLEAF

ii) What is the theoretical standard cell potential for the direct methanol fuel cell?

(4 marks)

iii) What current would be produced by a direct methanol fuel cell which consumes one kilogram of methanol per hour?

(5 marks)

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

i) Calculate the entropy change for the transformation of ice to liquid water at 0^o C and comment on the sign. ($\Delta_{fus}H = 6.02$ kJ mol^{-1})

(5 marks)

ii) For the reaction

$$HA_{aq} + H_2O \rightarrow H_3O^+_{aq} + A^-_{aq}$$

The reaction Enthalpies and Entropies for the reaction are as follows:

A	ΔH^o /kJ mol^{-1}	ΔS^o /J K^{-1} mol^{-1}
F	-13.00	-83.89
Cl	-58.00	-57.05
Br	-63.00	-43.62
I	-59.00	-13.42

By calculating the pK_A for each of the acids HA, determine which is the strongest acid. Comment on your result.

(5 marks)

iii) Describe what an "activity coefficient" is, and explain why activity coefficients are required when dealing with liquid electrolytes.

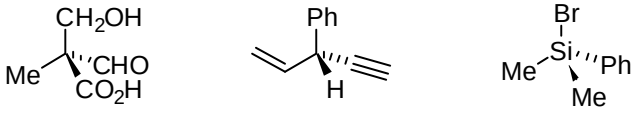
(2 marks)

Question 5 – Stereochemistry

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

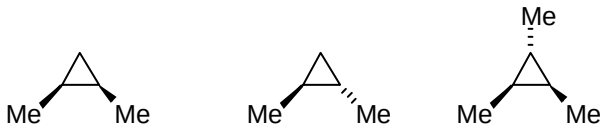
Answer part (a) and **EITHER** part (b) **OR** part (c) of this question.

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



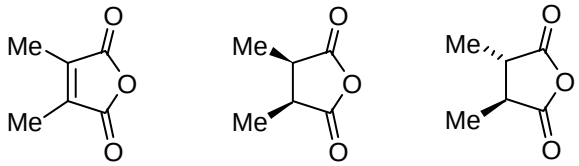
(6.5 marks)

(b) Only one of the following molecules has a dissymmetric enantiomeric form. Draw this enantiomer.



(6 marks)

(c) Only one of the following molecules is a *meso* compound. Which is it and why?



(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)

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

(i) When a silver surface is irradiated with light of wavelength 230 nm, the ejected electrons have a kinetic energy of 0.805 eV. Calculate the workfunction (in Joules) and the threshold frequency (in Hz) for electron emission from silver.

(4 marks)

(ii) The rotational spectrum of $^{9}Be^{16}O$ consists of a series of equally spaced lines with an average separation of 3.302 cm^{-1}. Calculate the moment of inertia of the molecule and the average BeO bond length.

(6 marks)

(iii) ICl_4^- is a square planar molecule. Give expressions for the moments of inertia of the molecule around its three principal axes and state what kind of "symmetric top" the molecule is. Assume that the ICl bond length is r, the mass of a Cl atom is m_{Cl} and the mass of an I atom is m_I.

(6 marks)

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

i) Explain why the anharmonic oscillator provides a better description of the vibrational behaviour of a diatomic molecule than the simple harmonic oscillator model. Why does the anharmonic oscillator model predict the existence of more than one line in the vibrational spectrum?

(4 marks)

ii) In the infrared spectrum of $^{24}Mg^{1}H$, the P(5) and R(2) lines are separated by 93.216 cm^{-1}. Determine the rotational constant B and the $^{24}Mg^{1}H$ bond length (in pm).

(5 marks)

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

The equilibrium oscillation wavenumber of a diatomic molecule is 590 cm^{-1} and the anharmonicity constant is 0.008. Determine the positions of both the fundamental peak and the first hot band peak in the IR spectrum and calculate the relative intensities of the two peaks at 600K. How would you confirm the existence of a hot band peak in a spectrum?

(9 marks)

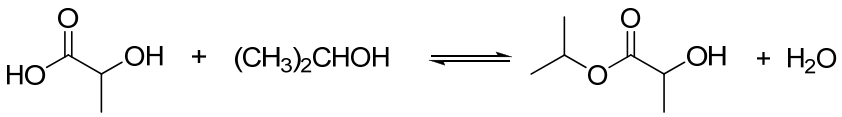
Question 7 – Introduction to Spectroscopy & Characterisation

NB. This question is worth 25 marks

Answer part (a) and **EITHER** part (b) **OR** part (c).

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

Lactic acid can be reacted with *iso*-propanol, with heating, to yield *iso*-propyl lactate.



i) Sketch the ^{1}H NMR spectra of lactic acid and *iso*-propyl lactate, pay attention to the chemical shifts, integrals and multiplicities of the resonances.

[You may assume coupling occurs only through 3 bonds or fewer and that ^{1}H, I=1/2, 100% abundant; all other nuclei are NMR inactive. You may also assume no coupling occurs between the hydroxyl H nuclei and any neighbouring H nuclei]

(10 marks)

The IR spectrum of lactic acid has carbon oxygen bond absorptions at 1280 cm^{-1} and 1720 cm^{-1}.

ii) Assign these absorptions and explain your reasoning.

(4 marks)

iii) Where in the IR spectrum would you expect the OH bonds to absorb?

(1 mark)

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

The UV-Vis spectrum of an aqueous solution of copper sulphate has an absorption maximum at 600 nm, which has a molar extinction coefficient of 20 $dm^{3}mol^{-1}cm^{-1}$.

i) What colour is the solution?

(1 mark)

QUESTION CONTINUED OVERLEAF

ii) Calculate the concentration of copper sulphate in a 0.6 cm cell which has 12.5% transmission at 600mm. State and define any equations used.

(3 marks)

iii) Explain why UV-Vis absorptions tend to be broad.

(2 marks)

iv) Describe the ionisation techniques used in electron ionisation (EI) and matrix assisted laser desorption ionisation (MALDI) mass spectrometry.

(4 marks)

c) Predict the number of vibrational modes and the number of IR absorptions you would expect to observe for [NO2]+ (g) and [NO2]- (g). Your answer should include diagrams showing the vibrational modes of the two molecules and a detailed rationalisation of the IR absorptions.

(10 marks)