IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2011, 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 14th January 2011, 09:30-12:30

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) OH^- + H_2O + Br^-

b) + H-Cl + Cl^-

c) + $CH_3CO_2^-$ + Cl^-

d) Ph_3P—Pd—PPh_3 +

(4 marks each plus 0.5 bonus mark)

Question 2 – Atomic and Molecular Structure

NB. This question is worth 25 marks.

Answer any **TWO** of the three parts a), b) and c) of this question.

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

i) Calculate the total energies in eV of the first three electron shells of the hydrogen atom (ionisation energy of hydrogen, $E_{i,H}$ = 1312.8 kJ mol^{-1}).

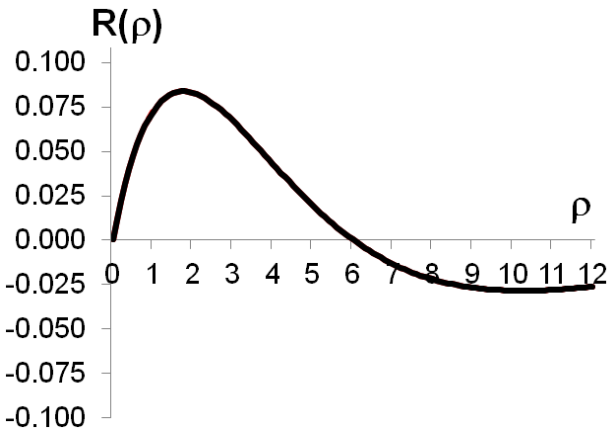
(5.5 marks)

ii) Give the wavelength in nm of the highest energy emission of the lithium dication (Li^{2+}).

(7 marks)

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

The plot of the radial component R(ρ) of a hydrogen wavefunction against the reduced radius is shown below (ρ = r/r_0; r_0 = first Bohr radius).



ρ	R(ρ)	ρ	R(ρ)
0	0.000	10	-0.029
1	0.072	11	-0.028
2	0.083	12	-0.027
3	0.067	13	-0.024
4	0.043	14	-0.021
5	0.019	15	-0.018
6	0.000	16	-0.016
7	-0.014	17	-0.013
8	-0.022	18	-0.011
9	-0.027	19	-0.009

i) Plot the radial distribution function (RDF) of the electron density based on the given R(ρ).

(7 marks)

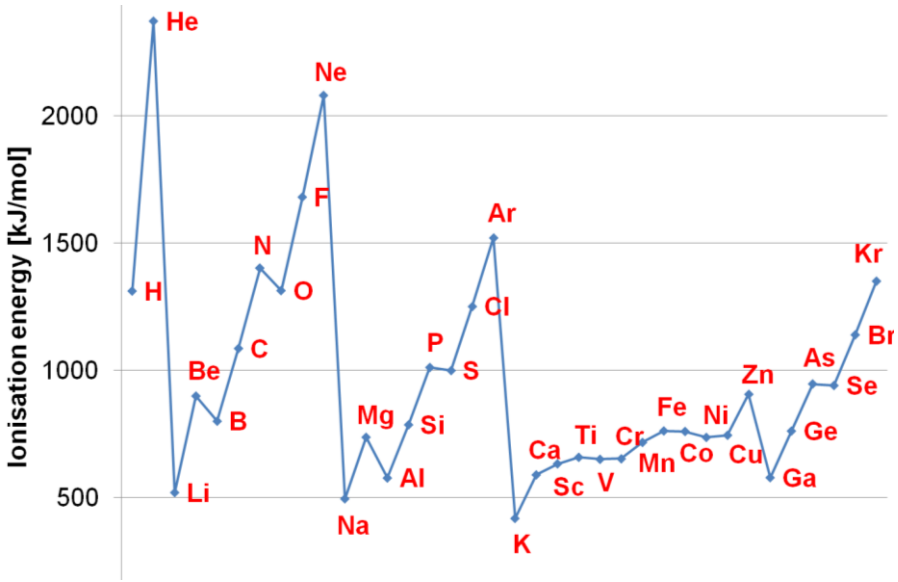
ii) Give the quantum numbers *n* and *l* corresponding to the plotted RDF. Explain your reasoning and indicate which orbital or orbital set it describes.

(5.5 marks)

QUESTION CONTINUED OVERLEAF

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

The following plot shows the evolution of the first ionisation energies of the elements with atomic number from 1 to 36.



i) Explain the variation of the first ionisation energy in the periodic table, including all apparent anomalies.

(7.5 marks)

ii) Calculate the electron affinity of oxygen in kJ mol^{-1} from its first ionisation energy and the absolute electronegativity according to Mulliken.
(χ_M = 7.54 eV; $E_{i,O}$ = 1313.9 kJ mol^{-1}).

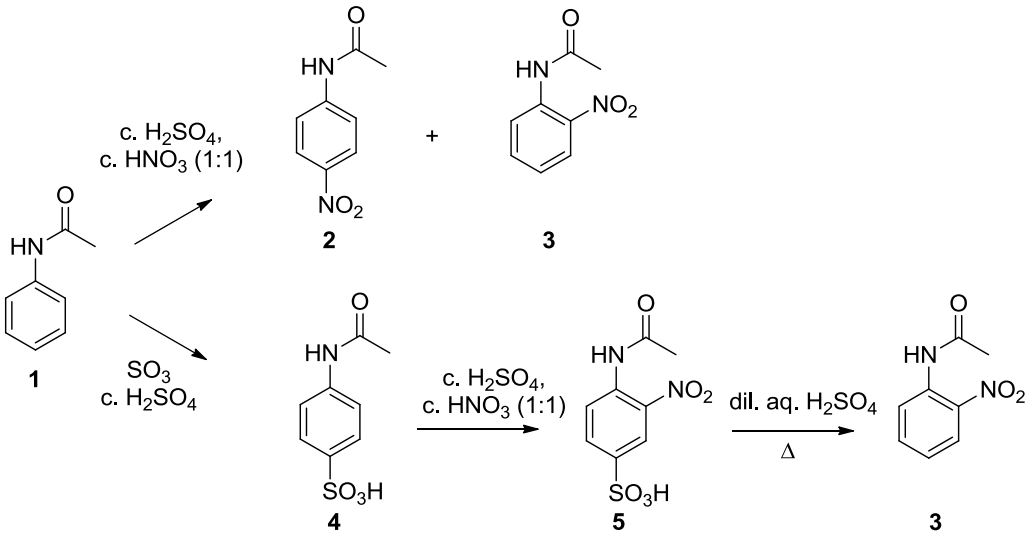
(5 marks)

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.

The scheme below shows two alternative syntheses of *ortho*-nitroacetanilide (**3**) from acetanilide (**1**). The three-step transformation gives *ortho*-nitroacetaniline (**3**) exclusively, whereas the one-step transformation also gives the *para* isomer (**2**).



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

For the transformation **1** → **2** + **3**:

i) Draw a mechanism.

(5 marks)

ii) Is this reaction under kinetic or thermodynamic control? Explain these two terms, including in your answer the definition of a 'rate determining step' (RDS).

(4 marks)

b) Explain why the sulfonylation reaction **1** → **4** is totally *para*-selective whereas the nitration reaction (**1** → **2** + **3**) is not.

(3.5 marks)

c) Explain why the nitration reaction **4** → **5** gives just isomer **5** as product.

(3.5 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) If the equilibrium constant for a reaction under standard conditions is 100, what is the free energy for this reaction?

(2 marks)

ii) What are meant by the terms Path function and State function? Give one example of each.

(2 marks)

iii) Distinguish between open, closed and isolated systems.

(2 marks)

iv) When sodium hydroxide dissolves in water, the solution warms. When sodium nitrate dissolves in water, the solution cools. Explain these results in terms of the enthalpies and entropies of dissolution for the corresponding reactions.

(2 marks)

v) What is the pH of vinegar? (vinegar is composed of a 1 mol dm^{-3} acetic acid solution)

pK_a(acetic acid) = 4.76

(2 marks)

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

A student in a hall of residence takes a 0.5 kg pack of doughnuts and microwaves it (P=800 W) for six minutes. C_p(pack of doughnuts) = 800 J K^{-1} kg^{-1}

i) Assuming the doughnuts do not lose any heat to their surroundings, estimate their increase in temperature. Comment on whether they are liable to set off the smoke detectors in the hall.

(3 marks)

ii) If the water content of the doughnuts is 20% by weight, recalculate the temperature increase, taking into account that the water will boil at 100^{o}C. Does this alter your conclusion about whether the smoke detectors will be triggered?

Note: assume the heat capacity remains constant and neglect the change of weight of the doughnuts as water evaporates.

$\Delta_{vap}H(H_2O)$ = 40.65 kJ mol^{-1}

(4 marks)

QUESTION CONTINUED OVERLEAF

Carbon dioxide sequestration is based on the reversible absorption of CO_2 by an amine

$$\text{Amine} + CO_2 \leftrightarrows \text{Amine-}CO_2$$

$\Delta_r H^{\ominus} = -41 \text{ kJ mol}^{-1}$
$\Delta_r S^{\ominus} = -105 \text{ J K}^{-1} \text{ mol}^{-1}$

iii) What is the Gibbs free energy of the above reaction under standard conditions?
(2 marks)

iv) What is the equilibrium constant for the above reaction under standard conditions?
(3 marks)

v) At what temperature does the reverse reaction become favoured? You may assume the enthalpy and entropy of reaction are temperature independent.
(3 marks)

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

A student decides to try "cluster ballooning" by attaching a large number of helium filled balloons onto her chair.

i) Calculate the minimum number of balloons (diameter = 30 cm, empty weight + weight of string = 5 g) required for the student and chair to lift off the ground. Assume standard conditions and that air and helium act as ideal (perfect) gases. The average molecular weight of air is 29 g mol^{-1}. The combined weight of the student and chair is 90 kg.
(4 marks)

ii) The human body can tolerate low oxygen levels for only short periods before unconsciousness and ultimately death ensues. At an oxygen partial pressure of 8.7 kPa, a person will lose consciousness in 5-10 minutes. What limit does this place on the maximum height our student should fly to?

Assume that the temperature remains the same during the ascent, and that pressure (in Pa) varies with altitude (in km) according to the equation

$$\text{Pressure} = 101 \times 10^3 \exp[-0.136 \times \text{altitude}]$$

The oxygen fraction in air is 0.21 and is independent of altitude.
(4 marks)

QUESTION CONTINUED OVERLEAF

The student uses an altimeter to record her height and to determine when she gets too close to the maximum permissible height. The altimeter is powered by a zinc-air battery requiring oxygen for its operation.

This battery operates with the following cell reaction

$$Zn + \tfrac{1}{2}O_2 + H_2O \leftrightarrows Zn(OH)_2 \qquad E^{\ominus} = 1.65\ V$$

iii) What is the Nernst equation for this battery?

(2 marks)

iv) If the altimeter requires a minimum of 1.5V to operate, will the student still be able to use the altimeter at the maximum permissible height determined above? What is the maximum height at which the altimeter will operate before the battery provides insufficient voltage?

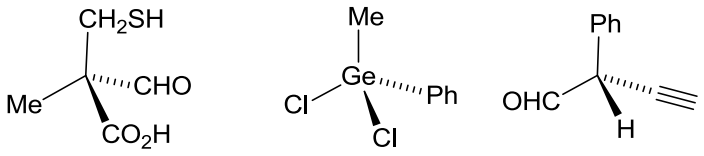
(5 marks)

Question 5 – Stereochemistry

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

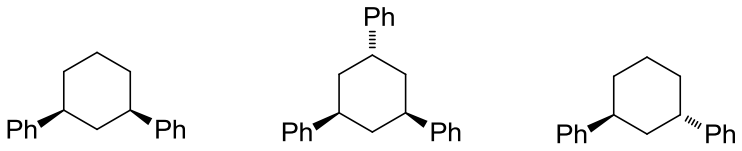
Answer part a) and **EITHER** part b) **OR** part c) of this question.

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



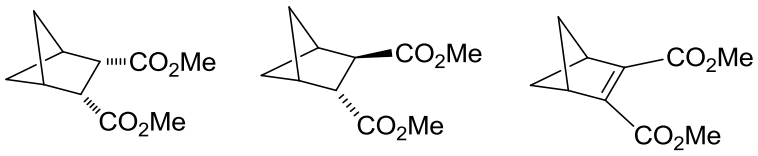
(6.5 marks)

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) of this question.

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

i) Beta Pictoris is the second brightest star in the constellation Pictor. The peak wavelength emission from Beta Pictoris is 360 nm. Estimate the star's surface temperature.

(4 marks)

ii) Assuming that the energy of the υ^{th} vibrational energy level is given by:

$$\varepsilon_\upsilon = \left(\upsilon + \frac{1}{2}\right)\overline{\omega}_e - \left(\upsilon + \frac{1}{2}\right)^2 \overline{\omega}_e x_e$$

generate an expression for the maximum value of υ for a diatomic molecule. Use your expression to estimate the dissociation energy of HCl. You may assume that $\omega_e = 2990\ cm^{-1}$ and $x_e = 0.0174$.

(7 marks)

iii) When the energy difference ($\Delta\varepsilon$) between vibrational levels is 2×10^{-20} J and the population ratio of adjacent levels (N_i+1/ N_i) is 0.3, what is the temperature?

(4 marks)

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

The IR spectrum of $^1H^{127}I$ exhibits absorption peaks at the following wavenumbers: 2257.1, 2270.2, 2283.3, 2296.4, 2322.6, 2335.7 and 2348.8 cm^{-1}.

i) Calculate the position of the band origin (in cm^{-1}) and the force constant.

(4 marks)

ii) Calculate the moment of inertia of $^1H^{127}I$.

(3 marks)

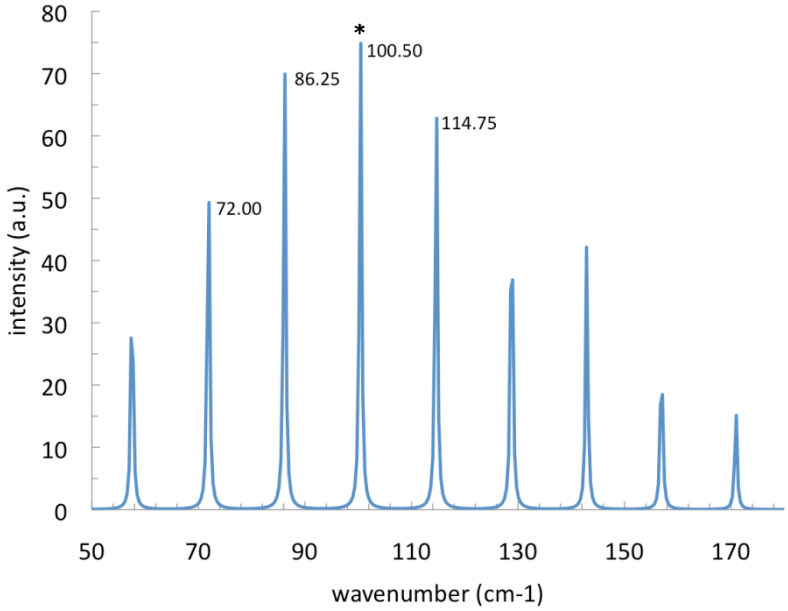
iii) Calculate the equilibrium H-I bond distance.

(3 marks)

QUESTION CONTINUED OVERLEAF

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

The pure microwave spectrum of $^{197}Au^{1}H$ is shown below. From the data presented:



i) Calculate the moment of inertia of the molecule.

(3 marks)

ii) Calculate the AuH bond length.

(2 marks)

iii) State the specific transition that gives rise to the peak marked with the asterisk.

(2 marks)

iv) Explain in detail why the peaks in the spectrum are not of constant intensity.

(3 marks)

Question 7 – 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.

2,2-Dichloropropane and 1,3-dichloropropane are isomers with the molecular formula $C_3H_6Cl_2$.

i) Sketch the ^{1}H NMR spectra of both of these isomers.

[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.]

(10 marks)

ii) Sketch the molecular ions for these isomers, observed by mass spectrometry.

[You may assume the following isotope abundancies: ^{1}H, 100%; ^{12}C, 100%, ^{35}Cl, 74.5% ,; ^{37}Cl, 24.5% abundant.]

(5 marks)

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

i) Explain why C_6D_6 can be used as a ^{1}H NMR solvent.

(3 marks)

ii) The C-H bonds in C_6H_6 show strong IR absorptions at 3000-3100 cm^{-1}. Predict the wavenumber of the stretching absorption for the C-D bonds in C_6D_6 and explain any assumptions.

(7 marks)

c) Compound A shows strong absorptions in the IR in the regions 3300-2800, 1711 and 1239 cm^{-1}. The ^{1}H NMR spectrum shows a septet at 2.59 ppm, with a relative integral of 1, and a doublet at 1.20 ppm, with a relative integral of 6. The mass spectrum shows a molecular ion at *m/z* 88 and fragmentation peaks at *m/z* 73, 71 and 43.

Identify the unknown compound A. Your answer should include a full assignment of all the spectral data and a sketch of the structure of molecule A.

[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.

(10 marks)