IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2016, for Internal Students of the Imperial College of Science, Technology and Medicine

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

1A PAPER ONE

Monday 11th January 2016, 14:00-16:15

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

1.I4 – Atomic Structure

Answer parts a), b) and c) and **EITHER** part d) **OR** part e) of this question.

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

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

(2 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	I_2	E_a
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 shown?

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

(2 marks)

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

i) In the emission spectrum of hydrogen, which electronic transition of the three shown below would produce a line in the visible region of the electromagnetic spectrum?

$n = 2 \rightarrow n = 1$
$n = 3 \rightarrow n = 2$
$n = 2 \rightarrow n = 3$ (1 mark)

ii) What are the values of the $\boldsymbol{n}$, $\boldsymbol{l}$ and $\boldsymbol{m_l}$ quantum numbers that describe the 5f orbitals?

(1.5 marks)

QUESTION CONTINUED OVERLEAF

iii) For n = 5 and l = 2, draw and label all the orbitals associated with the different values of m_l.

(2.5 marks)

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

i) Give the ground state electron configurations of:

Rh^{3+} and Eu^{2+} (3 marks)

ii) Identify the elements that have the following ground-state electron configurations:

$[Kr]5s^2 4d^{10} 5p^1$ and $[Xe]6s^2 4f^6$

(3 marks)

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

i) Following excitation, an electron in the hydrogen 5f orbital decays to the 3p orbital. Using the Rydberg equation, calculate the energy (in kJ mol^{-1}) involved in this process.

(3 marks)

ii) Using Slater's Rules, confirm that the experimentally observed electronic configuration of Rb, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$ is energetically more stable than $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^1$.

(3 marks)

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

i) Calculate the effective nuclear charge on one of the 6s electrons in a tungsten atom.

(3 marks)

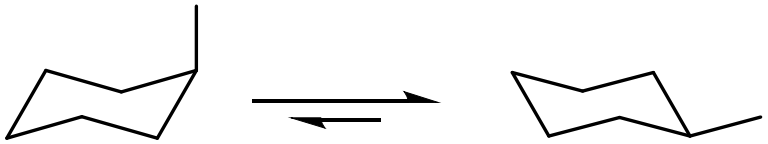
ii) Using the Rydberg equation, calculate the initial energy level when an electron in a hydrogen atom transitions to n = 2 and emits a photon of wavelength of 4.28×10^{-7} m.

(3 marks)

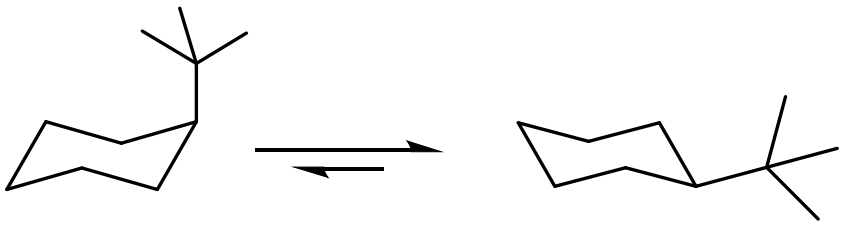
1.O2 – Alkanes, Alkenes & Alkynes

Answer **ALL** parts of this question.

a) Explain fully why the conformational distribution of the two cyclohexane derivatives below is as shown. Your answer should make use of appropriately labelled diagrams where necessary.



0.10 0.90



0.01 0.99

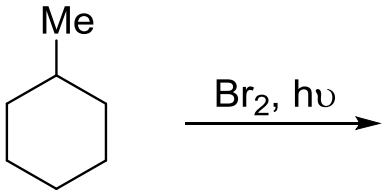
(8 marks)

b) For cyclopentane, cyclobutane and cyclopropane provide a simple drawing and brief discussion to account for the lowest energy conformation that each molecule adopts.

(3 marks)

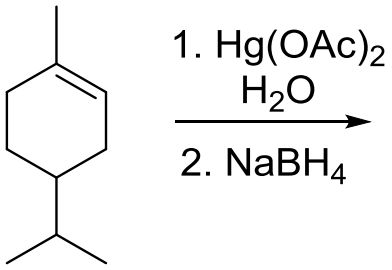
c) Identify the major product(s) formed in **TWO** of the following transformations. Provide full mechanisms and give detailed explanations for any selectivity observed.

i)

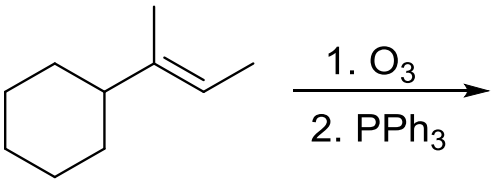


QUESTION CONTINUED OVERLEAF

ii)

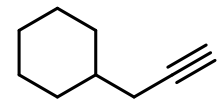


iii)

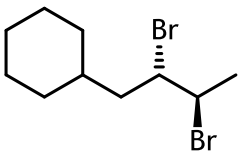


(8 marks)

d) Using the alkyne below, suggest a route to the target compound. This is a multistep process and you should identify the reagents required for each step and account for the stereochemical outcome of your sequence.



Starting material



Target compound

(6 marks)

1.P1 – Chemical Kinetics

Answer **ALL** parts of this question.

a) The rate law for the reaction A+B+2C→4D was found to be $v=k[A][B][C]^3$. What are the units of k?

(1 mark)

b) Tungsten silicide (WSi_2) is used both in the semiconductor industry and as a high temperature coating. Its fluorine chemistry has recently been investigated where the reaction rate for the reaction

$$WSi_2\ (s) + 8HF\ (g) \rightarrow W\ (s) + 2SiF_4\ (g) + 4H_2\ (g)$$

was measured at five different temperatures, with data given in Table 1.

By graphical means, determine the Arrhenius parameters for this reaction. Show your working.

T (°C)	450	500	550	600	650
***k* (mol L^{-1} s^{-1})**	0.038	0.044	0.050	0.056	0.062

Table 1. A table showing the variation in the reaction rate for the reaction of tungsten silicide with hydrogen fluoride with respect to temperature.

(10 marks)

c) Consider a reaction A + B + C-> Products (a reaction which is not elementary). Several initial conditions of this reaction are investigated and the following data are obtained:

Run #	$[A]_0$	$[B]_0$	$[C]_0$	v_0
1	0.151 M	0.213 M	0.398 M	0.480 M/s
2	0.251 M	0.105 M	0.325 M	0.356 M/s
3	0.151 M	0.213 M	0.525 M	1.102 M/s
4	0.151 M	0.250 M	0.480 M	0.988 s

What is the initial rate of the reaction when all the reactants are at 0.100 M concentrations assuming a rate law with the form: rate = $k\,[A]^a\,[B]^b\,[C]^c$?

(8 marks)

QUESTION CONTINUED OVERLEAF

d) The mechanism for the formation of oxygen from ozone after intensive ultraviolet radiation in the stratosphere is given by:

$$Cl + O_3 \xrightarrow{k_1} O_2 + ClO$$

$$O_3 \xrightarrow{k_2} O + O_2$$

$$ClO + O \xrightarrow{k_3} Cl + O_2$$

Identify the intermediate(s) and using the steady state approximation, derive an expression for the rate law, in terms of the concentration of O_3.

(6 marks)