IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 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

PHYSICAL CHEMISTRY I

Thursday 21st June 2012, 09:30-11:30

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.

1.P1 – Chemical Kinetics

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

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

i) Define what is meant by a *rate law* and *the order of a reaction*

(2 marks)

ii) Explain the physical significance of both parameters in the Arrhenius equation.

(3 marks)

iii) For the reaction:

A+A ------> Products

the rate law is shown to be second order such that:

$$\frac{d[A]}{dt} = -k[A]^2$$

By deriving an expression for the integrated rate law show that the half-life for this system is given by:

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

where $[A]_0$ is the initial concentration.

The second order rate constant for the decomposition of A is measured to be 2.42×10^{-2} $dm^3\ mol^{-1}s^{-1}$. If the concentration of A after 300s is 0.068 mol dm^{-3} what will the concentration of A be after 700s?

(10 marks)

b) The concentration of MEGABenzene was found to vary with time as follows:

Time/s	0	300	600	900	1200
[MEGABenzene]/(mol dm^{-3})	0.482	0.323	0.216	0.144	0.097

Using graphical methods, determine whether the order of the reaction is first or second order. In addition, determine the rate constant for the reaction.

(10 marks)

c) With the use of the Lindeman-Hinshelwood mechanism, explain how the isomerisation of cyclopropane into propene can exhibit first or second order kinetics.

(10 marks)

1.P2 – States of Matter

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

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

i) Show that for r = $2^{1/6}$ σ the Lennard – Jones potential is at a minimum.

(3 marks)

ii) State which of the following molecules possesses a permanent dipole moment: N_2, O_3 and CO_2. Indicate the molecular reasoning for your answer.

(2 marks)

iii) State the van der Waals equation for a molar volume of gas where V may be expressed as V_m. Express the compressibility, Z, of the gas in terms of this expression. What happens to this expression when the gas is at high volume?

(4 marks)

iv) Copper, which crystallises as a face-centred cubic lattice, has a density of 8.930 g cm^{-3} at 20^{0} C. Calculate the radius of a copper atom, assuming that the atoms touch along a face diagonal. Molecular weight of Copper is 63.55gmol^{-1}.

(6 marks)

b) Calculate the dipole moment for the peptide linkage given in the table. Use your result to calculate the dipole – dipole interaction energy for two peptide linkages interacting at a distance of 3 nm, and angle of

i) 30 degrees (an alpha helix)
ii) 90 degrees (a beta sheet)

Which structure, alpha helix or beta sheet, is more stable?

1D = 3.356 x 10^{-30} Cm ε_0 = 8.85 x 10^{-12} J^{-1} C^2 m^{-1} and e = 1.602 x 10^{-19} C

ATOM	X in pm	Y in pm	Z in pm	Charge
H	128	87	0	0.18
N	132	0	0	-0.36
C	0	0	0	0.45
O	-62	-107	0	-0.38

(10 marks)

QUESTION CONTINUED OVERLEAF

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

i) Sketch the phase diagram of CO_2 clearly labelling the axes, phases, triple point, freezing point, boiling and critical points. Critical point of CO_2 occurs at (31^0C, 72.9 atm), Triple point of CO_2 occurs at (-56.35^0C, 5.11 atm) and the sublimation temperature is (-78.6^0C).

(6 marks)

ii) CO_2 does not have a permanent electric dipole moment and has a net charge of zero, however, it is possible to liquefy and solidify it, what molecular interactions make this possible? Describe the distance dependence of these interactions.

(4 marks)

1.P3 – Quantum Chemistry

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

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

i) For a particle of mass m moving in a small two-dimensional box with equal sides of length L, the energy levels are given by

$$E_{n_x,n_y} = \left(n_x^2 + n_y^2\right)\frac{h^2}{8mL^2}$$

Determine the number of states of this system that have energy equal to

$$E = \frac{50h^2}{8mL^2}$$

In each case, give the corresponding values of n_x and n_y.

Briefly explain how a square box can have degenerate states, by sketching the two wavefunctions that have $E = \dfrac{5h^2}{8mL^2}$

(5 marks)

ii) How many nodes are there in the angular part of the wavefunction ψ_{1s} for the hydrogen atom ground state?

$$\psi_{1s} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

What is the angular momentum associated with an electron in this state?

(2 marks)

iii) Calculate the wavelength of a photon emitted if the electron in a hydrogen atom makes a transition from the n = 3 to n = 2 energy levels.

(3 marks)

iv) The Hamiltonian operator $\hat{H}$ for the H_2^+ cation can be written as:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{R_{AB}}\right)$$

Which terms in $\hat{H}$ correspond to kinetic energy, and which to potential energy? What assumption has been made here about the kinetic energy of the two hydrogen nuclei?

(2.5 marks)

QUESTION CONTINUED OVERLEAF

b) For the quantum mechanical model of a *particle in a one-dimensional box*, the allowed energy levels are given by

$$E_n = \frac{n^2 h^2}{8ma^2}$$

where m is the mass of the particle and a is the length of the box.

i) Show that the change in energy required to go from level $n \rightarrow n+1$ is

$$\Delta E = \frac{(2n+1)h^2}{8ma^2}$$

(3 marks)

ii) By calculating ΔE between the ground and first excited states, explain why the difference between adjacent energy levels is significant for an electron confined to a one-dimensional box of length 1.0 Å, but not for a particle of mass 1 g confined to a box of length 1 m.

(3.5 marks)

iii) The wavefunctions for a particle in a one-dimensional box are

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

For what value of x is the ground state wavefunction a maximum?

Find the values of x for which the first excited state wavefunction goes to zero.

(3 marks)

iv) The probability of finding a particle in the region of the box $0 \le x \le b$, where $0 \le b \le a$, is given by

$$\int_0^b |\psi|^2 dx = \frac{b}{a} - \left(\frac{1}{2n\pi}\right) \sin\left(\frac{2n\pi b}{a}\right)$$

For a box of length 1.0 Å, what is the probability of locating a particle in the n = 1 level between x = 0 and x = 0.2 Å.

What does the probability of finding a particle in the same region become as $n \rightarrow \infty$?

Briefly explain the significance of these results.

(3 marks)

QUESTION CONTINUED OVERLEAF

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

The quantum mechanical particle on a ring is described by wavefunctions ψ that solve a Schrödinger equation:

$$-\frac{\hbar^2}{2mr^2}\frac{d^2\psi}{d\phi^2} = E\psi$$

where *m* is the mass of the particle, *r* is the radius of the ring and ϕ the angle coordinate.

i) What is the boundary condition for ψ?
Which condition for allowed wavefunctions does this follow from?

(2 marks)

ii) Show that wavefunctions of the form $\psi = A\exp(im_l\phi)$ are solutions of the Schrödinger equation, and hence find an expression for the allowed energy levels.

(4 marks)

iii) How would the energy of the first excited state change if the radius of the ring were doubled?

(1 mark)

iv) What is the energy for the $m_l = 0$ solution?
What is the 'wavelength' associated with this wavefunction?

(1.5 marks)

v) How does the probability of locating the particle around the ring vary with ϕ? Justify your answer.

(2 marks)

vi) By referring to the Heisenberg uncertainty principle, briefly explain why a particle on a ring can have a well-defined quantised angular momentum.

(2 marks)