IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 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

PHYSICAL CHEMISTRY I

Tuesday 21st June 2011, 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 **EITHER** part a) **OR** part b). Then answer **BOTH** part c) **AND** part d).

a) A reaction is observed to have a near zero activation energy. Comment on what you expect to see when you measure the temperature dependence of the rate for this reaction.

(5 marks)

b) With the use of a diagram explain why a catalyst does not affect the equilibrium of a reaction.

(5 marks)

c) Consider a reaction which has an overall stoichiometry of:

A + B + C-> Products

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 M/s

What is the initial rate of the reaction when all the reactants are at 0.100 M concentrations?

(9 marks)

d) The hydrogenation of ethylene in the presence of mercury vapour is represented by the overall reaction shown below:

$C_2H_4 + H_2 \rightarrow C_2H_6$

The reaction is thought to proceed through the following steps.

$Hg + H_2 \rightarrow Hg + 2H$ Rate constant: k_1 (1)

$H + C_2H_4 \rightarrow C_2H_5$ Rate constant: k_2 (2)

$C_2H_5 + H_2 \rightarrow C_2H_6 + H$ Rate constant: k_3 (3)

$H + H \rightarrow H_2$ Rate constant: k_4 (4)

Assuming that H and C_2H_5 attain equilibrium determine the rate of formation of C_2H_6 in terms of the rate constants and concentrations [Hg], $[H_2]$ and $[C_2H_4]$.

(11 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) The diagrams below represent the dipole interactions of two HF molecules. Consider carefully the orientation of the second HF, q2,–q2 and L2, in the first diagram below. State the potential energy due to the dipole interaction between them. Identify all of the terms in the equation. Indicate how, mathematically, you would modify this equation to represent the orientation of the HF molecules in the second diagram.

(3 marks)

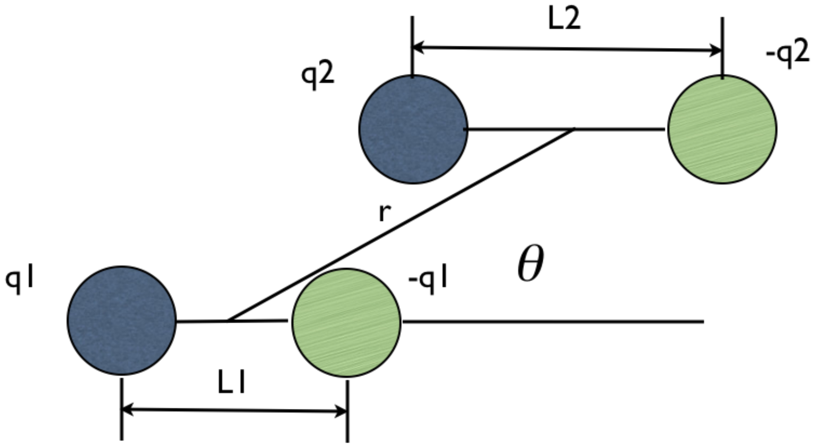

Diagram 1

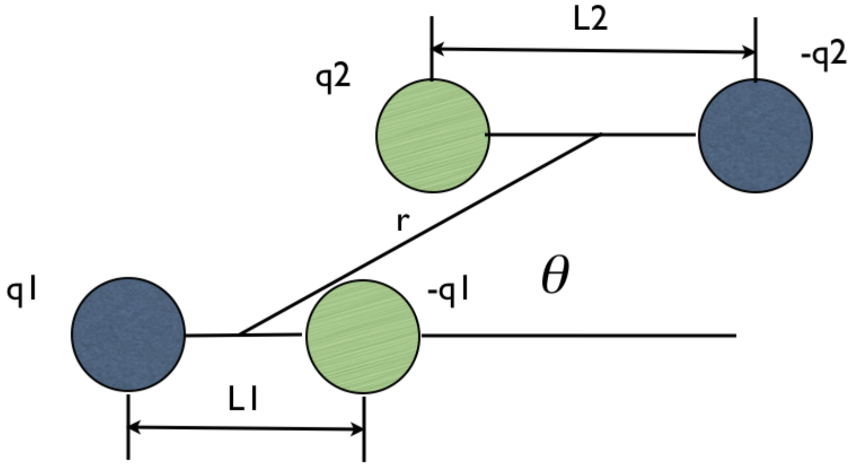

Diagram 2

QUESTION CONTINUED OVERLEAF

ii) Calculate the atmospheric pressure on Mars in Pascals given that a column of Mercury on the surface of Mars has a height of 0.06 cm. The density of Mercury is 13.596 g cm^{-3} and gravity on Mars has a value 370.67 cm s^{-2}.

(2 marks)

iii) Identify the equation below and all of its terms. For the expression to the right of the second equal sign, identify the most important term and comment on how the expression simplifies when V_m becomes large.

$$Z = \frac{PV_m}{RT} = 1 + \frac{B_{2v}(T)}{V_m} + \frac{B_{3v}(T)}{V_m^2} + ...$$

(4 marks)

iv) Calculate the spacing, d, between the (1,1,1) planes in an orthorhombic crystal of dimensions a = 0.56 nm, b = 0.63 nm and c = 0.76 nm.

(3 marks)

v) How does the molar Gibbs energy vary as a function of pressure and temperature? Explain in terms of the molar Gibbs energy how materials melt and vaporise.

(3 marks)

b) For molecular collisions we have the concept of a mean free path λ, the average distance a molecule travels between collisions, and the collision frequency Z, the average number of collisions made by a molecule per unit time. State the mathematical expressions for λ and Z, defining all terms used. Calculate λ and Z for Ar at 20˚C and 1 bar given that σ = 0.36 nm^2, 1 bar = 10^5 Pa and the mass of Ar is 39.95 g mol^{-1}.

(10 marks)

c) Using the following information draw the phase diagram for H_2O. The triple point occurs at 273.16 K and 611 Pa, the critical point occurs at 647.3K and 218.3 atm, freezing point is 273.15 K and the boiling point is 373.15 K. Clearly label the axes and identify the phases on the diagram. Explain the significance of the Triple point and the Critical point. Explain with reference to the slope of the solid-liquid interface why the application of pressure turns ice into water.

(10 marks)

1.P3 – Quantum Chemistry

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

a) A particle restricted to move along the x axis between $x = 0$ and $x = L$ obeys the Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = E_n\psi_n$$

i) Show that solutions are wavefunctions of the form

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

with associated energies given by $E_n = \frac{n^2h^2}{8mL^2}$

(4 marks)

ii) Explain why the allowed energies E_n of this particle are not continuous.

(2 marks)

iii) An electron confined to a region of the x-axis of length 2.0 Å can be promoted to an excited state by a photon of wavelength 8.79×10^{-9} m. Calculate the quantum number n of the resulting excited state.

(3 marks)

iv) For a particle confined to a three-dimensional cubic box of side L, the wavefunctions and corresponding energy levels are given by:

$$\psi_{n_x,n_y,n_z} = N\sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right)$$

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

Determine the values of n_x, n_y, n_z for the state with energy $E_{n_x,n_y,n_z} = \frac{3h^2}{2mL^2}$

How many states have a lower energy than this, and what energies do they have?

(3.5 marks)

QUESTION CONTINUED OVERLEAF

b) For a particle described by a wavefunction ψ, the probability of finding it at a point in space is proportional to the probability density $\psi^*\psi$.

i) How does a probabilistic interpretation restrict the values that ψ can take?

(2 marks)

ii) For a particle in a one-dimensional box described by $\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$,

is the maximum probability density always in the centre of the box?

Explain your answer.

(1.5 marks)

iii) For the $n = 2$ state of a particle in a one-dimensional box, is the probability of finding the particle between $x = 0$ and $x = L/4$ the same as that of finding it between $x = 3L/4$ and $x = L$? Explain your answer.

(1.5 marks)

iv) Determine whether the particle-in-a-box wavefunctions are eigenfunctions of the linear momentum operator

$$\hat{p} = -i\hbar\frac{d}{dx}$$

and comment on the physical significance of this result.

(2 marks)

v) For a particle on a ring described by $\psi = A\exp(im_l\phi)$, how does the probability density vary around the ring for $m_l = 0$ and $m_l = \pm 1$? Explain your answer.

(2 marks)

vi) Determine whether the particle-on-a-ring wavefunctions are eigenfunctions of the angular momentum operator

$$\hat{p} = -i\hbar\frac{d}{d\phi}$$

and comment on the physical significance of this result.

(2 marks)

vii) Why is the $m_l = 0$ solution allowed for the particle on a ring, while there is no allowed $n = 0$ solution for a particle in a box?

(1.5 marks)

QUESTION CONTINUED OVERLEAF

c) The ground state wavefunction ψ for the hydrogen atom can be written in spherical polar coordinates as

$\psi = Ne^{-kr}$ where $k = \dfrac{m_e e^2}{4\pi\varepsilon_0\hbar^2}$ and the corresponding energy $E = -\dfrac{m_e e^4}{32\pi^2\varepsilon_0^{\,2}\hbar^2 n^2}$ when $n = 1$.

i) For what value of r is the ground state ψ a maximum?

(1 mark)

ii) Are there any radial nodes in the ground state ψ?

(1 mark)

iii) Hydrogen atom wavefunctions have the general form

$\psi(r,\theta,\phi) = R_{n,l}(r)\Theta_{l,m_l}(\theta)\exp(im_l\phi)$

Does an electron in the hydrogen atom ground state described by $\psi = Ne^{-kr}$ have a definite value of angular momentum? If so, what is its value?

(2 marks)

iv) Explain why the bound hydrogen atom energy levels converge to a well-defined limiting value, while the particle-in-a-box energy levels diverge.

(2 marks)

v) Determine the energy required to remove an electron from the hydrogen atom with zero kinetic energy (i.e. its first ionisation energy). Give your final answer in electron volts (eV).

(3 marks)

vi) The absorption and emission lines of the hydrogen atom spectrum are given by the Balmer/Rydberg empirical formula:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Use this and the energy expression given above to derive an expression for the Rydberg constant R in terms of fundamental constants. Explain any assumptions you make.

(3.5 marks)