IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2014, 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 17th June 2014, 09:30-11:45

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** then either part b) **OR** part c) of this question.

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

i) Using the concept of a collision tube it can be shown that the volume of a collision tube swept out by a molecule in a time Δt is given by $c\,\Delta t\sigma$ where c is the average speed of the molecules and σ is the cross sectional area. Using this expression show that the expression for the collision density Z_{AB} of a gas consisting of molecules of A and B is given by:

$$Z_{AB}=\sigma c[B][A]N_A^2$$

(9 marks)

ii) What is the physical significance of the Arrhenius parameters?

(4 marks)

iii) A reaction is shown to have a very low activation energy. How and why would you expect its rate of reaction to vary with temperature?

(2 marks)

b) Given the mechanism below show that the rate law for the reaction of hydrogen and bromine is given by:

$$\frac{d[HBr]}{dt}=\frac{k[H_2][Br_2]^{3/2}}{[Br_2]+k'[HBr]}$$

(10 marks)

Mechanism:

Initiation	$Br_2 + M \rightarrow Br\cdot + Br\cdot + M$
Propagation	$Br\cdot + H_2 \rightarrow HBr + H\cdot$
Propagation	$H\cdot + Br_2 \rightarrow HBr + Br\cdot$
Retardation	$H\cdot + HBr \rightarrow H_2 + Br\cdot$
Termination	$Br\cdot + Br\cdot + M \rightarrow Br_2 + M^*$

Third body M, a molecule of an inert gas removes the energy of recombination.

QUESTION CONTINUED OVERLEAF

c) The enzyme carbonic anhydrase catalyses the hydration of CO_2 in red blood cells to give hydrogencarbonate ion:

$$CO_2 + H_2O \longrightarrow HCO_3^- + H^+$$

The following data were obtained for the reaction at pH=7.1, 272.5 K and an enzyme concentration of 2.3 nmol dm^{-3}. Determine the maximum velocity and Michaelis Menten constant for the reaction.

[CO_2]/mmol dm^{-3}	1.25	2.5	5	20
v/mmol dm^{-3} s^{-1}	2.78×10^{-2}	5.00×10^{-2}	8.33×10^{-2}	1.67×10^{-1}

(10 marks)

1.P2 – States of Matter

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

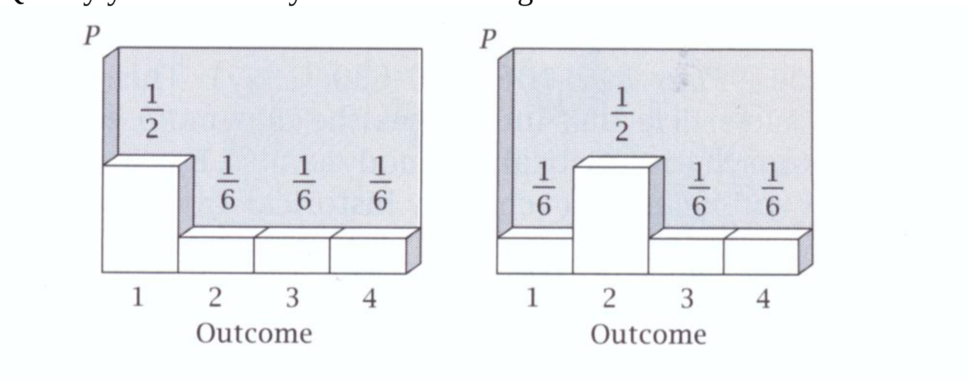
a) Answer **ALL** parts of this question.

i) For a lattice gas how many arrangements are there for 15 indistinguishable lattice gas particles distributed on:

A. V = 20 sites
B. V = 16 sites
C. V = 15 sites

(3 marks)

ii) Which of the two distributions shown below has the greater entropy? Qualify your answer by mathematical argument.

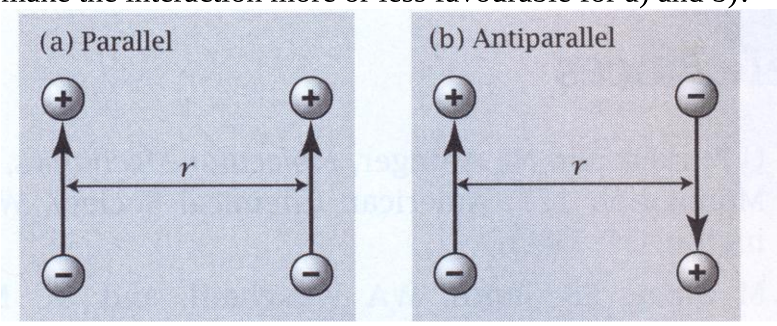


(3 marks)

iii) The vapour pressure of water is 23 mm Hg at T= 300 K and 760 mm Hg at T = 373 K. Calculate the enthalpy of vapourization ΔH_{vap}. Assuming that each water has z = 4 nearest neighbours, calculate the interaction energy w_{AA}.

(3 marks)

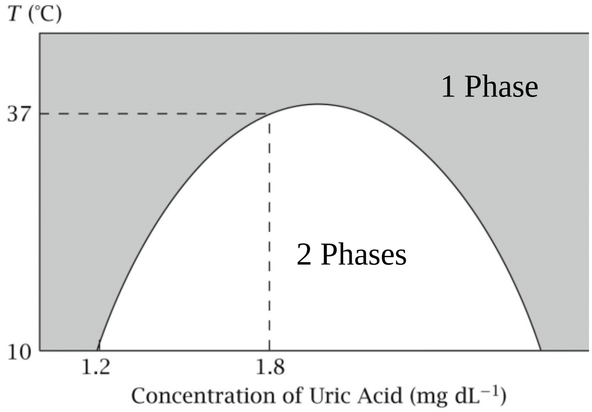
iv) Which dipole pair in the figure below has the lower energy: the parallel pair (a) or the anti-parallel pair (b)? If you double the distance between the dipole centres, by what factor does each pair interaction change? Does it make the interaction more or less favourable for a) and b)?



(4 marks)

QUESTION CONTINUED OVERLEAF

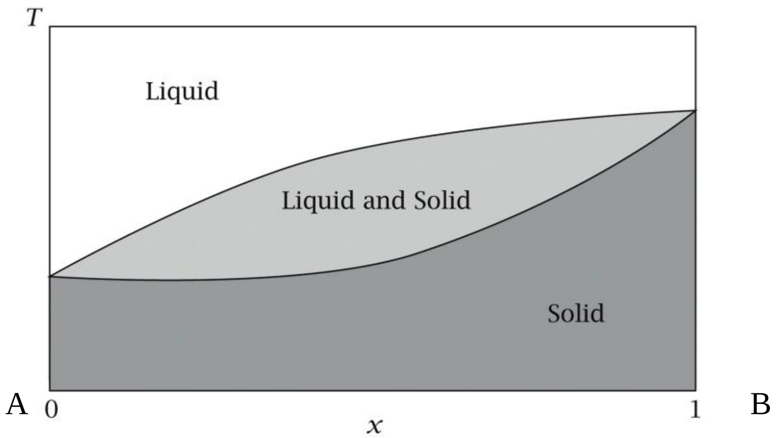
v) Ian has gout. Gout is a disease of crystallisation of uric acid in the blood. The diagram below is the phase diagram for the crystallisation uric acid, the grey region represents one phase whilst the white region represents two phases.



Ian claims he can always tell when winter is here. With reference to the above diagram, how does he do it? *Hint: A human's normal body temperature is 37 ^{0}C and in the cold your extremities (hands, feet) will be lower than this.*

(2 marks)

b) Below is a general phase diagram of a two-component freezing process.

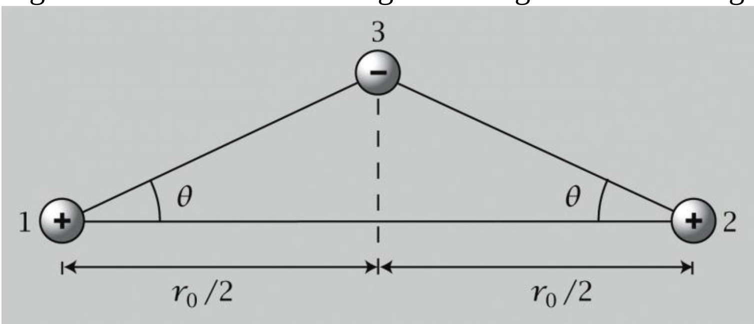


Draw clearly labelled diagrams of Gibbs free energy versus composition for the following conditions

i) Temperatures at which the system is a solid (1 mark)
ii) Temperature at which pure B melts (2 marks)
iii) Two-Phase Region (4 marks)
iv) Temperature at which pure A melts (2 marks)
v) Temperatures at which the system is a liquid (1 mark)

QUESTION CONTINUED OVERLEAF

c) Consider two fixed unit positive charges separated by a distance r_0, and a unit negative charge that is free to move along a dividing line as in the figure below



i) For fixed r_0, how does the Coulombic energy depend on r_0 and θ?

(3 marks)

ii) For what angle θ is the Coulombic energy at a minimum?

(3 marks)

iii) What is the energy at its minimum value?

(2 marks)

iv) At what angle θ is the energy equal to zero?

(2 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) Name model quantum mechanical systems for which the spacing between energy levels

a. increases

b. decreases

c. is constant

as the total energy increases.

(1.5 marks)

ii) True or False?

a. For a one-dimensional quantum harmonic oscillator, the total energy is a function of position along the *x*-axis.

b. The quantum particle in a box has a well-defined momentum.

c. Electrons described by wavefunctions can have continuous energies.

d. A probability density can never be negative.

e. A wavefunction must be real everywhere.

f. The ground state wavefunction for a quantum particle on a ring has infinite wavelength.

g. As temperature increases, the wavelength at which black body radiation is most intense gets longer.

h. When UV light of increasing frequency shines on an alkali metal in vacuum, a plot of the maximum kinetic energy of electrons emitted versus the frequency of light used gives a straight line, with a slope of Planck's constant.

(4 marks)

iii) The work function of Na is 2.28 eV, where 1 eV is 1.602 x 10^{-19} J. Calculate the maximum kinetic energy of photoelectrons emitted from Na exposed to 200 nm UV radiation. What is the longest wavelength that will cause the photoelectric effect in Na?

(3.5 marks)

QUESTION CONTINUED OVERLEAF

iv) The energy of the ground state of the hydrogen atom is given by $E = -\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2}$. Use this expression to calculate the energy required to remove the electron with zero kinetic energy (i.e. the ionisation energy) in eV.

(3.5 marks)

b) For a particle confined to a three-dimensional rectangular box of side lengths L_x, L_y and L_z, the wavefunctions and corresponding energy levels are

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

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

i) What values can the quantum numbers n_x, n_y and n_z take?
Explain your answer.
Can these quantum numbers vary independently?

(2.5 marks)

ii) An electron in a three-dimensional rectangular box with side lengths 3.00 Å, 5.00 Å and 6.00 Å makes a transition from the first excited state to the ground state. Calculate the frequency of the photon of light emitted.

(3.5 marks)

iii) Where in the box is the electron in part (ii) most likely to be found in the ground state? Briefly explain your answer (you do not need to carry out any integration to do this).

(2 marks)

iv) In a cubic box of side length L and for $E < \frac{15h^2}{8mL^2}$, how many different states (allowed values of n_x, n_y, n_z) are there, and how many different energy levels? Briefly explain why these two numbers differ.

(3 marks)

v) Explain how degeneracy can occur for a particle in a rectangular box with sides of different lengths L_x, L_y and L_z.

(1.5 marks)

QUESTION CONTINUED OVERLEAF

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

A quantum mechanical particle constrained to move on a circle is described by wavefunctions $\psi = A\exp(im_l\phi)$ that solve the 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 circle and ϕ is the angle coordinate.

i) Describe and explain the boundary condition that ψ obeys.

(2 marks)

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

(4 marks)

iii) Does ψ contain any information about the position of the particle as a function of ϕ? Explain your answer.

(2 marks)

iv) The angular momentum operator for a particle moving on a circle is

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

Calculate the resulting momentum values for $m_l = +1$ and $m_l = -1$ and explain their physical significance.

(2.5 marks)

v) By referring to the Heisenberg Uncertainty Principle, briefly explain the connection between your answers to parts (iii) and (iv) above.

(2 marks)