IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2015, for Internal Students of the Imperial College of Science, Technology and Medicine

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

ADVANCED CHEMISTRY THEORY IB

Physical Chemistry

Thursday 18th June 2015, 09:30-12:30

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.

Year 1/0615 **Turn Over**

1.P2 – Molecular Driving Forces

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

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

i) Which of the following statements is false and why:

a. Systems always seek to minimise the free energy.
b. Systems always seek to maximise their entropy.
c. Each microstate is equally probable.
d. Probability of observing a particular macrostate is independent of the number of microstates it possesses.
e. The entropy of an isolated system must always increase.

(2 marks)

ii) The heat of sublimation of graphite is ΔH_{sub} = 716.7 kJ mol^{-1}. Use this number to estimate the strength of a carbon–carbon bond. Assume that each carbon has 4 neighbours.

(2 marks)

iii) For water illustrate the first-order transition free energy as a function of density, you need three diagrams one at low T, midpoint T and high T. From the diagrams how do you know that it is a first order phase transition?

(5 marks)

iv) For a solution containing a mole fraction of 20% methanol in water, calculate the entropy of solution. Also evaluate the free energy of solution at 300K, assuming that there is no interaction energy.

(3 marks)

v) From the fundamental equation of energy U (S,V,N) derive the differential form of the equation of the fundamental energy equation with respect to measurable physical quantities. Use this to obtain a useful differential form of the fundamental entropy equation.

(3 marks)

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

You have a one-dimensional lattice that contains N_A particles of type A and N_B particles of type B. They completely fill the lattice, so the number of sites is $N_A + N_B$.

i) Express the entropy $S(N_A,N_B)$ as a function of N_A and N_B.
ii) Give the relationship between the chemical potential μ_A and the quantity $(\partial S/\partial N_A)_{N_B}$.
iii) Express $\mu_A(N_A,N_B)$ as a function of N_A and N_B.

(10 marks)

QUESTION CONTINUED OVERLEAF

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

Using the following information show the phase diagram for H_2O. The triple point is (273.16K and 611 Pa), critical point (647.3K and 218.3 atm), freezing point is (273.15K) and the boiling point is (373.15K). 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 part a) and then **EITHER** part b) **OR** part c) of this question.

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

i) True or False?

a. For a one-dimensional quantum harmonic oscillator, the ground-state wavefunction has its maximum value in the centre of the potential, but for highly excited states the maxima are close to the edge.

b. The quantum particle on a ring has a well-defined momentum.

c. Different wavefunctions can have the same energies.

d. The Heisenberg Uncertainty Principle states that exact values of position and energy cannot both be known for a particle.

e. Wavefunctions for a quantum harmonic oscillator must be real.

f. For the hydrogen atom, the spacing between energy levels increases as the value of the principal quantum number increases.

g. There is a finite probability that the quantum particle in a box defined by an infinitely steep potential will be found outside the box.

h. The linear momentum operator in one dimension is $\widehat{p_x} = -\hbar \frac{d}{dx}$

i. A wavefunction must be single-valued.

j. For the hydrogen atom, the Hamiltonian operator includes both kinetic and potential energy terms.

(5 marks)

ii) The wavefunction describing a quantum free particle travelling in the –*x* direction is:

$$y = A\exp(-ikx)$$

Briefly explain why this particle's position is undetermined.

(3 marks)

iii) For the particle in a cubic box, with energies given by

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

how many degenerate energy levels are there when $\frac{h^2}{8mL^2}$ takes the values of 12, 14 and 27? Briefly explain your answer.

(4.5 marks)

QUESTION CONTINUED OVERLEAF

b) For a quantum harmonic oscillator, the energy levels are given by

$E = \left(\nu + \frac{1}{2}\right)\hbar\omega_0$, where ω_0 is the classical vibration frequency $\omega_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$.

i) What is ν and what values can it take?

(2 marks)

ii) Define k and μ.

(3 marks)

iii) A hydrogen atom is adsorbed onto the surface of a gold nanoparticle by a bond of force constant 855 N m^{-1}. Calculate the wavelength of a photon needed to excite a transition between the ground and first excited state energy levels of this system. What assumption concerning the masses do you have to make in this case? How different is the excitation energy from the first to the second excited states?

(5 marks)

iv) Explain why the quantum harmonic oscillator has zero-point energy that cannot be removed.

(2.5 marks)

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

A quantum 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) What are the boundary conditions for this particle's wavefunctions?

(2 marks)

ii) Show that solutions of the above Schrödinger equation that obey the boundary conditions have 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)

QUESTION CONTINUED OVERLEAF

iii) What is n, and what are the allowed values it can take? Explain why these values and not others are allowed.

(2 marks)

iv) For n = 1, where is the quantum particle in a one-dimensional box most likely to be found? Explain your answer.

(2 marks)

v) When a particle of mass 9.1×10^{-31} kg in a one-dimensional box goes from the n = 5 to the n = 2 level, it emits a photon of frequency $6.0 \times 10^{14}\,s^{-1}$. What is the length of the box?

(2.5 marks)

1.P5 – Thermodynamics 1: Chemical Equilibria

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

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

i) Explain the significant differences between H^+ ions and other cations. Why do H^+ ions have a very high mobility through water?

(3 marks)

ii) Air is 21% oxygen. What is the partial pressure of oxygen in a 10 dm^3 gas cylinder containing 5 moles of air at 20 °C? Clearly state all assumptions made.

(4 marks)

iii) Ethanol (C_2H_5OH) can be used in a direct ethanol fuel cell to provide electrical energy according to the following overall reaction:

$$\mathbf{C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O}$$

Using the data given below, calculate the maximum work that could be extracted from 1 dm^3 of ethanol in a direct ethanol fuel cell.

$\Delta_f G^{\ominus}$ [C_2H_5OH] = -175 kJ mol^{-1}
$\Delta_f G^{\ominus}$ [CO_2] = -394 kJ mol^{-1}
$\Delta_f G^{\ominus}$ [H_2O] = -237 kJ mol^{-1}
Density of $C_{12}H_{26}$ = 0.79 kg dm^{-3}

(5 marks)

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

Butyric acid (C_3H_7COOH) is a weak organic acid found in many foods. It has a pK_a of 4.8.

i) Show that the pH of a weak acid can be given by the equation below (where c is the total acid concentration):

$$pH = \frac{pK_a}{2} - \frac{log_{10}(c)}{2}$$

(3 marks)

ii) What is the pH of a 0.5 $mol.dm^{-3}$ solution of butyric acid in water?

(2 marks)

iii) 5g of sodium butyrate (C_3H_7COONa) was dissolved in 100 cm^3 of the solution described in (ii) above. Calculate the pH of the resulting solution?

(3 marks)

QUESTION CONTINUED OVERLEAF

iv) How would adding a small amount of HCl affect the pH of each of the solutions described in (ii) and (iii) above?

(2 marks)

v) Methyl orange is an indicator with a pK_a of 3.47, it is red in its protonated form and yellow in its deprotonated form. What colour would methyl orange be in each of the solutions described in (ii) and (iii) above?

(3 marks)

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

PLA is a biodegradable polymer that can be synthesised by direct condensation of lactic acid ($CH_3CH(OH)COOH$).

i) Explain why polymerisation reactions may need to be carried out below a critical temperature.

(3 marks)

ii) A polymerisation of 60 cm^3 of lactic acid is carried out in a sealed flask immersed in a small bath containing 100 cm^3 of water initially at 80 °C. Assuming that all heat evolved by the reaction is transferred to the water in the bath, what will the temperature of the water bath be after the polymerisation has occurred? What mass of liquid water will remain in the bath?

Clearly state all assumptions.

(10 marks)

$\Delta H^{\ominus}$ of polymerisation [$CH_3CH(OH)COOH$] = -27.0 kJ mol^{-1}

$\Delta_{vap}H^{\ominus}$ [H_2O] = 40.7 kJ mol^{-1}

Density [$CH_3CH(OH)COOH$] at 80 °C = 1.21 g cm^{-3}

Density [H_2O] at 80 °C = 0.971 g cm^{-3}

$C_{P.m}$ [H_2O] = 75.3 J.mol^{-1} K^{-1}

Note: $\Delta H^{\ominus}$ of polymerisation is per mole of monomer.