IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 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

ADVANCED CHEMISTRY THEORY IB

Physical Chemistry and Maths Test

Monday 14th June 2016, 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 1/0616 **Turn Over**

1P2 – Molecular Driving Forces

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

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

i) The ideal gas equation PV= nRT is only valid for certain conditions. State what assumptions you have to make for the ideal gas equation to be valid.

(2 marks)

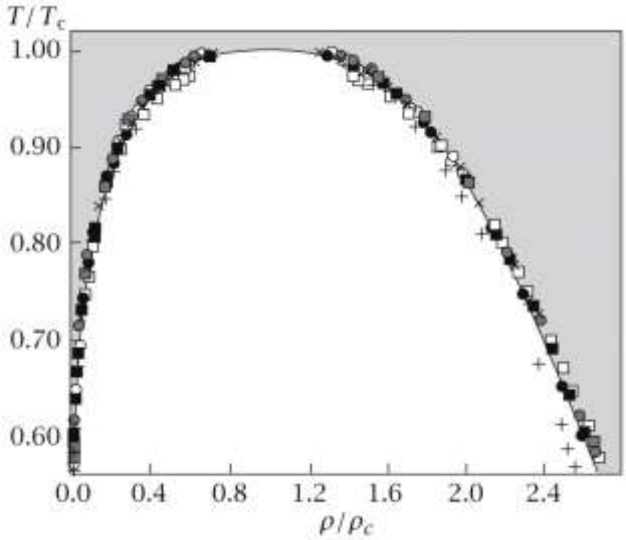
ii) The van der Waals gas equation is given below. Define all of the terms in the equation. Explain the physical meaning of the a and b constants

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

(3 marks)

iii) The diagram below is a plot of reduced density ρ/ρ_C against reduced temperature T/T_C, for 8 different gases. Which law is this illustrating? and how is it important with respect to the van der Waals gas equation?

(3 marks)



QUESTION CONTINUED OVERLEAF

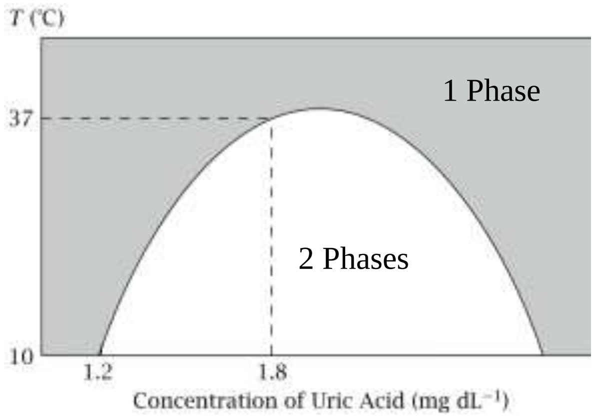
iv) For the equilibria between, for a single component system, the liquid and gas phase show how the chemical potentials are related. The chemical potential for an ideal gas is given by μ_v and for the condensed phase μ_c. Using these two equations obtain an expression for the vapour pressure of the molecules A. Explain, with reference to the Helmholtz free energy A, why there is only one term for μ_c. Also explain what the z and the w_{AA} represent.

$$\mu_v = kT\ln\left(\frac{p}{p^{\varnothing}}\right)$$

$$\mu_c = \left(\frac{\partial A}{\partial N}\right)_{T,V} = \left(\frac{zw_{AA}}{2}\right)$$

(5 marks)

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 of 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. In the cold your extremities (hands, feet) will be lower than this.*



(2 marks)

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

Suppose you want to add a perfuming agent to a liquid aerosol spray. You want its vapour pressure to treble if the temperature increases from 25^{0}C to 37^{0}C. Calculate the pair interaction energy that this agent should have in the pure liquid state. Assume that the number of nearest-neighbour molecules in the liquid is z = 4. Comment on the sign and magnitude of the pair interaction energy.

(10 marks)

QUESTION CONTINUED OVERLEAF

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

Sketch, as accurately as possible on graph paper, the phase diagram of CO_2 clearly labelling the axes, phases, triple point, freezing point, boiling and critical points. Think carefully about your axes, also plot the temperature in Kelvin. The 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). 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.

(10 marks)

1.P3 – Quantum Chemistry

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

a) Answer **ANY TWO** parts of this question.

i) What is the relevance of the fact that the measurable properties of the model systems described in the course do not change with time?

(4 marks)

ii) For a free particle moving in one direction a solution to the Schrodinger equation is:

$$\psi = A\exp(ikx)$$

Explain how the allowed value(s) for k is (are) found and find that (or those) values.

(4 marks)

iii) Sketch a clearly labelled diagram showing the wavefunctions for the first three energy levels of the particle in a box. Comment on key features and how they change with quantum number.

(4 marks)

iv) For the particle in a box explain why the quantum number cannot be equal to zero. The wavefunction is given below.

$$\psi = C\left\{\sin\left(\frac{\mathrm{n\pi x}}{L}\right)\right\}$$

(4 marks)

v) Consider the functions exp ($-ax^2$) and exp (ax^2). For each function identify if it is an acceptable wavefunction or not. Explain your answer.

(4 marks)

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

For the harmonic oscillator, one wavefunction when tried as a solution to the Schrödinger equation produces the following result (after the normalisation constant is cancelled from each term).

$$-\frac{\hbar^2}{2\mu}(4a^2x^3 - 6ax)\exp(-ax^2) + \frac{1}{2}kx^3\exp(-ax^2) = E.x(\exp(-ax^2))$$

The wavefunction chosen <u>does</u> satisfy the Schrodinger equation

i) What is the wavefunction in this case? Explain your answer.

(4 marks)

QUESTION CONTINUED OVERLEAF

ii) What condition must apply in order for it to be a solution? Explain your answer.

(4 marks)

iii) The fundamental vibrational frequency (ω_0) is as given below.
To which energy level does this eigenfunction correspond?

$$\omega_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

(5 marks)

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

An oxygen molecule is able to move over a distance of 10cm in one dimension at room temperature (25^{o}C). If the translational energy available to the molecule is ½ (k_BT), what is the quantum number of the level that it occupies? Comment on the value that you obtain.

(4 marks)

1.P4 – Spectroscopy

Answer part a) **AND** either part b) **OR** part c) of this question.

The following information may be useful:
Charge on an electron is 1.602×10^{-19}C
Mass of an electron is 9.1×10^{-31} kg
Planck's constant has a numerical value of 6.626×10^{-34} J s
Speed of light has a numerical value of 2.998×10^{8} m s^{-1}
The Boltzmann Constant has a value of 1.38 x 10^{-23} J K^{-1}

Remember to define any symbols or terms that you use.

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

i) Light is a form of propagating electromagnetic radiation. Write down an expression which describes a monochromatic planar light wave and explain how all of the terms relate to properties of the wave.

(4 marks)

ii) Assuming that all of the following spectral features are homogeneously broadened, calculate the limiting lifetime for:

a. A 1500cm^{-1} vibrational absorption band with a 20cm^{-1} bandwidth
b. A 500MHz spin transition with a 5 Hz linewidth
c. Absorption by a coloured molecule at 2eV with a 200meV linewidth

(6 marks)

iii) The molecule described in question ii) c) above is found to have a fluorescence lifetime of 1ns. Explain the discrepancy between this observation and the lifetime calculated from the linewidth measurement.

(2 marks)

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

An aromatic linear polyene has length of 8Å

i) Calculate the energy gap between the ground and first excited states, assuming that the outer shell electrons behave like a particle in a one-dimensional box.

(6 marks)

ii) Calculate the peak absorbance wavelength for this molecule and comment on the colour it will appear to the human eye explaining the reasons for your answer.

(4 marks)

QUESTION CONTINUED OVERLEAF

iii) Sketch the approximate relationship between the electronic absorption and emission spectra for this molecule highlighting any key features that one might expect to observe.

(3 marks)

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

A volatile pure liquid comprising a single polyatomic molecule is placed in a sealed sample cell in an FTIR spectrometer

i) Explain the principle of operation of the FTIR spectrometer.

(2 marks)

ii) Describe an alternative method for measuring an IR absorbance spectrum

(2 marks)

iii) Describe an alternative method for measuring vibrational spectra other than IR absorbance and sketch how such a spectrometer works.

(2 marks)

iv) Explain why the infrared spectrum of a liquid will only show one strong vibrational peak per normal mode for most vibrations, even though the quantum mechanical harmonic oscillator has multiple levels. Weaker peaks ~1% of the strength of the normal mode absorbances are observed. How do they relate to the normal modes and at what frequencies are they found?

(2 marks)

v) The sample is warmed so that the liquid is now vapourised. A low frequency vibration at 200cm^{-1} is measured at a temperature of 300K and 400K. Explain why the intensity of the 200cm^{-1} band changes intensity between the two temperatures and calculate the ratio of absorbances between the two temperatures.

(5 marks)