IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2013, 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**

Monday 17th June 2013, 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.
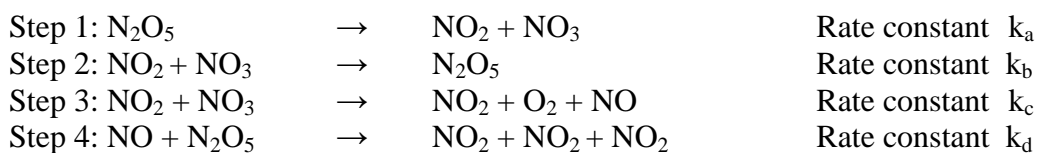
1.P1 – Chemical Kinetics

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

a) The decomposition of nitrogen pentoxide:

$$2N_2O_5 \, (g) \rightarrow 4NO_2 \, (g) + O_2 \, (g)$$
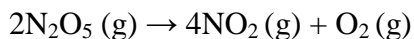
is measured to be first order with respect to N_2O_5. Account for this observation using the following mechanism:

|			
Step 1: N_2O_5	$\rightarrow$	$NO_2 + NO_3$	Rate constant k_a
Step 2: $NO_2 + NO_3$	$\rightarrow$	N_2O_5	Rate constant k_b
Step 3: $NO_2 + NO_3$	$\rightarrow$	$NO_2 + O_2 + NO$	Rate constant k_c
Step 4: $NO + N_2O_5$	$\rightarrow$	$NO_2 + NO_2 + NO_2$	Rate constant k_d

(14 marks)

b) Depending on the conditions of the reaction, the isomerization of cyclopropane is observed to follow first order or second order kinetics. With the use of an appropriate mechanism explain how pressure can be used to switch between these two regimes.

(11 marks)

c) Depending on the temperature and pressure of a reaction vessel the reaction between oxygen and hydrogen can prove to be either explosive or non-explosive.

$$2H_2 \, (g) + O_2 \, (g) \rightarrow 2H_2O \, (g)$$
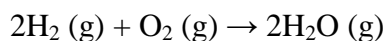
With the use of a diagram explain this observation.

(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 dipole moment for HCl is 3.44×10^{-30} Cm.
The overall average dipole-dipole interaction energy is given by

$$V = -\frac{2\mu_1^2\mu_2^2}{3(4\pi\varepsilon_0)^2 kTr^6}$$

Show that the units of the right side of the equation are energy. Calculate the value of the coefficient of r^{-6} in the above equation at 300 K for two HCl (g) molecules. Comment on the magnitude of your result.

(4 marks)

ii) Silver crystallizes in a face centred cubic structure with a unit cell length of 408.6 pm. Use the Bragg equation to calculate the first observed diffraction angle from the 111 planes using X-rays with a wavelength of 154.433 pm.
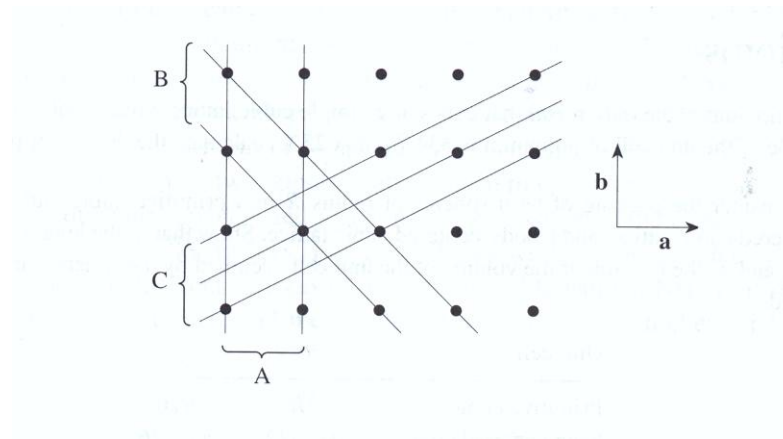
(3 marks)

iii) Use the figure below and the following information to estimate the molar volume of ammonia at 215 ^{0}C and 400 bar. Values for ammonia $T_c = 405.30$ K and $P_c = 111.30$ bar. The value of R the gas constant is 0.08314 L bar mol^{-1} K^{-1}
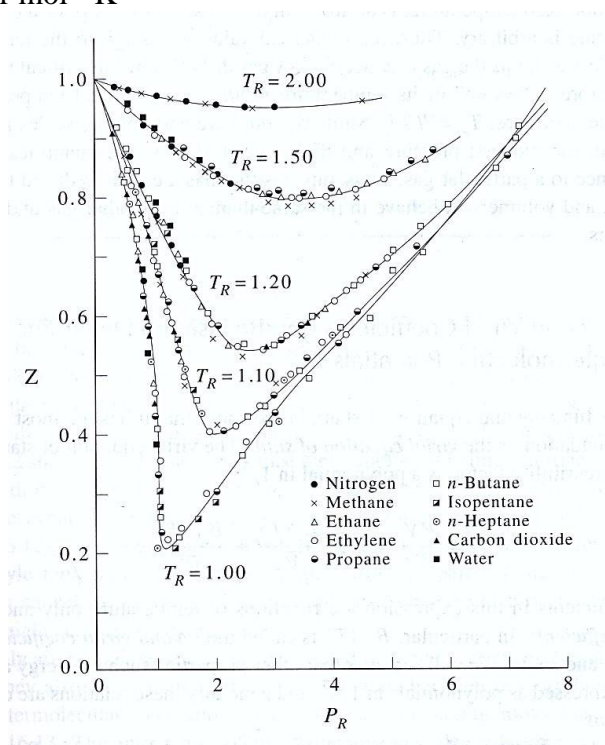
(4 marks)

iv) Determine the Miller indices of each set of lines shown in the figure below.
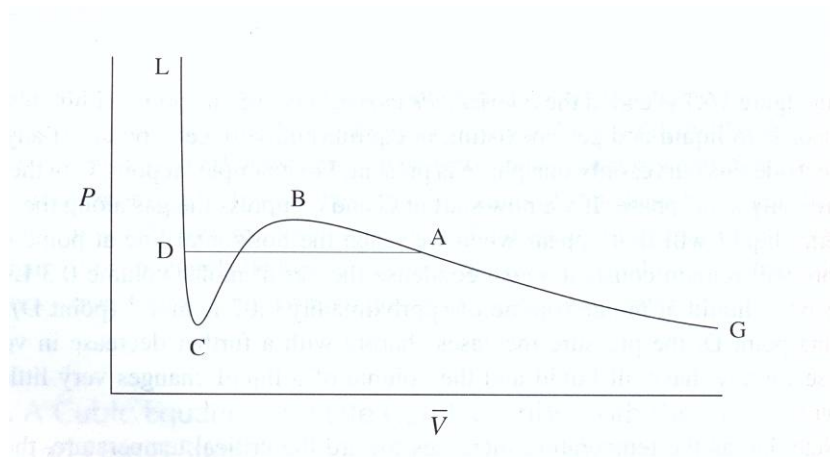

(4 marks)

b) Explain what is meant by the critical temperature of a gas. The diagram below shows a single van der Waals isotherm for $T < T_c$. On a simple reproduction of the diagram indicate which regions represent the gaseous and liquid phases.

For the diagram below: -

   i)   What process does the line G to A represent?
   ii)   For the line A to D what do the points represent?
   iii) What process is occurring from point D to L?
   iv)   What does the steepness of the curve from D to L indicate?
   v)   What does the segment A to B represent?
   vi)   What does the segment C to D correspond to?
   vii) Identify, with respect to volume, the intercepts of the line D to A with the curve.

(10 marks)

c)   Sketch the phase diagram for oxygen using the following data: triple point, 54.3K and 1.14 torr; critical point, 154.6 K and 37 828 torr; normal melting point, -218.4 °C; and normal boiling point, -182.9 °C. Clearly label the axes and identify the phases on the diagram. Explain the significance of the triple point and the critical point. Does oxygen melt under an applied pressure as water does? *Hint: - you may wish to compress one of the axes*.

(10 marks)

4

1.P3 – Quantum Chemistry

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

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

   i) Which three of the following are requirements for well-behaved/allowed wavefunctions?

   - They go to zero for at least two values of a spatial coordinate
   - They are continuous
   - They cannot become infinite over a finite region of space
   - Their values are always real
   - They are single-valued
   - They are exponential functions

   (3 marks)

   ii) Give the boundary conditions for the wavefunctions of a quantum particle on a ring / circle radius r,

   $$y = A \exp(im_l f)$$

   and a quantum particle in a one-dimensional box of length L,

   $$y = \sqrt{2/L} \sin(n\rho x / L)$$

   In each case, which requirement for well-behaved wavefunctions does the boundary condition follow from?

   (4 marks)

   iii) The position of a quantum particle in a one-dimensional box is partly defined along the x-axis. Why is its momentum partly undefined, yet its energy well defined for a particular value of quantum number n? Can this particle have zero momentum?

   (3 marks)

   iv) The quantum particle on a ring is an eigenfunction of the momentum operator $\hat{p}_x = -i\hbar \dfrac{d}{dx}$.

   Physically, why can such a particle have a well-defined momentum? Can its momentum be zero?

   (2.5 marks)

b) Between $x = 0$ and $x = L$ along the x-axis the potential $V = 0$, while outside this region $V = \infty$. A particle moving between $x = 0$ and $x = L$ is described by the Schrödinger equation:

$$-\frac{h^2}{8\rho^2 m}\frac{d^2 y_n}{dx^2} = E_n y_n$$

i) Why is there no potential energy term $V(x)$ in this Schrödinger equation?

(1 mark)

ii) Show by substitution that wavefunctions

$$y_n = \sqrt{\frac{2}{L}}\sin\!\left(\frac{n\rho x}{L}\right)$$

are solutions of the above Schrödinger equation, and hence determine the energies E_n

(4 marks)

iii) Wavefunctions of the form

$$y_n = \sqrt{\frac{2}{L}}\cos\!\left(\frac{n\rho x}{L}\right)$$

could also be solutions of the same Schrödinger equation. Briefly explain why the sin functions are chosen for the potential described above.

(1.5 marks)

iv) Sketch the allowed ground state wavefunction. Explain how you would calculate the probability of finding a particle between $x = L/3$ and $x = 2L/3$, without calculating a value explicitly.

(2 marks)

v) The wavefunctions given in part (ii) can be used to model ρ electrons in conjugated hydrocarbons, by allowing a maximum of two electrons per energy level E_n.

For butadiene, which energy levels contain ρ electrons in the ground state? Calculate the wavelength of light that will promote butadiene from its ground to first electronic excited states, taking L to be 5.78×10^{-10} m.

(4 marks)

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

i) The energy levels of a quantum harmonic oscillator are $E = \left(v + \frac{1}{2}\right)\hbar\omega_0$; the allowed energies of an electron in a hydrogen atom are

$$E = -\frac{m_e e^4}{32\rho^2 \epsilon_0^2 \hbar^2 n^2}.$$

Sketch both sets of energy levels. In each case, do they converge, diverge, or are they equally spaced?

(3 marks)

ii) For a particle travelling along the +x direction where there is no change in potential energy at all, the wavefunction is $y = A\exp(ikx)$.
Explain what A and k are. Do they affect the energy of the particle?

(3 marks)

iii) What is the de Broglie relationship?
Explain why this relationship is significant for both light and electrons.

(4 marks)

iv) For a particle in a two-dimensional square box with sides of length L, the wavefunctions and associated energies are:

$$y = \frac{2}{L}\sin\left(\frac{n_x \rho x}{L}\right)\sin\left(\frac{n_y \rho y}{L}\right)$$

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

Explain why the ground state is not degenerate, but the first excited state is doubly degenerate.

(2.5 marks)