IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JUNE 2010, 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 14th June 2010, 09:30-11:30

USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

1P1 – Chemical Kinetics

Answer part (a) **AND** either part (b) **OR** part (c):

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

The recombination of iodine atoms in the gas phase in the presence of Argon was investigated and the order of the reaction determined by the method of initial rates. The results are given in table I below, where the concentrations of Argon are:

(a) 1.0×10^{-3} M, (b) 5.0×10^{-3} M and (c) 10.0×10^{-3} M.

Table I - Initial rates, v, for the reaction: $2I(g) + Ar(g) \rightarrow I_2(g) + Ar(g)$

$[I]_0 / (10^{-5}$ M)		1.0	2.0	4.0	6.0
$v / (M\ s^{-1})$	(a)	8.7×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b)	4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c)	8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

i)   Using these data find the orders of the reaction with respect to the concentrations of $I(g)$ and $Ar(g)$ atoms, the overall order of reaction and the rate constant.

(13 marks)

ii)   What effect would removing all the Argon have on the overall rate of reaction?

(2 marks)

b) Depending on the pressure of the system, gas phase reactions such as the isomerisation of cyclopropane can follow first or second order kinetics. Using mathematical arguments explain this observation.

(10 marks)

c) The table below shows the pre-exponential factors for four different reactions. In the first three cases the experimentally determined values are lower than that predicted from theory but in the case of K+Br$_2$ -> KBr + Br the experimentally determined value is *larger* than the theoretical values.

Using mathematical arguments explain this latter observation.

	A/(Lmol^{-1}s^{-1})	A/(Lmol^{-1}s^{-1})
	Experiment	Theory
2NOCl→2NO+2Cl	9.4×10^9	5.9×10^{10}
2ClO→Cl$_2$+O$_2$	6.3×10^7	2.5×10^{10}
H$_2$+C$_2$H$_4$ →C$_2$H$_6$	1.24×10^6	7.4×10^{11}
K+Br$_2$→KBr+Br	1.0×10^{12}	2.1×10^{11}

(10 marks)

1P2 – States of Matter

Answer part (a) **AND** either part (b) **OR** part (c)

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

   i) Sketch how temperature influences the Maxwell distribution of molecular speeds, clearly identifying the axes used.

   (3 marks)

   ii) State the van der Waals equation, identifying each of the terms used. Explain the origin of the two modifications relative to the perfect gas law and identify the repulsive and attractive terms.

   (4 marks)

   iii) Calculate the potential energy of a dipolar interaction between a water molecule (μ=1.85 D) and an ammonia molecule (μ=1.47 D) separated by a distance of 4.0 nm. The angle between the dipoles is 180˚.

   $$1D = 3.33564 \times 10^{-30} \text{ C m},$$
   $$\varepsilon_0 = 8.85 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1} \text{ and e} = 1.602 \times 10^{-19} \text{ C}$$

   (5 marks)

   iv) Sketch a phase diagram for a typical material (simple solid, liquid and vapour phases) indicating the triple point and critical point.

   (3 marks)

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

   i) Briefly explain, with the help of suitable diagrams, the process of X-ray diffraction. State Bragg's law, defining all terms used.

   (6 marks)

   ii) A reflection from the (2,2,2) plane of a cubic crystal is observed with x-rays of λ = 156 pm at an incident angle of 13.6˚. Calculate the length of the side of the unit cell.

   (4 marks)

c) Draw a cartoon of an AFM, identifying its components. Give a brief description of its mode of operation and indicate its typical resolution in the lateral and vertical directions. What is the typical force sensitivity of an AFM in Newtons? Under what environmental conditions can AFM's operate?

   (10 marks)

1P3 – Quantum Chemistry

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

a) For the quantum mechanical model of a *particle in a one-dimensional box*, the allowed energy levels are given by

$$E = \frac{n^2 h^2}{8ma^2}$$

   i) Explain (using a diagram) why the quantum number n must be an integer.
   (2.5 marks)

   ii) Why is $n = 0$ not allowed? Physically, why must the particle have a minimum kinetic energy ($n = 1$) that cannot be removed? Explain why values of $n < 0$ are not considered.
   (3 marks)

   iii) The Heisenberg uncertainty principle states that

   $$\Delta x \Delta p_x \geq \frac{h}{4\pi}$$

   where Δx is the uncertainty in a particle's position along the x axis, and Δp_x is the corresponding uncertainty in momentum. For an electron confined in a one-dimensional box of length $a = 1.0$ Å, what are the minimum uncertainties in its momentum and velocity? Briefly explain any assumption you make in your calculations.
   (3 marks)

   iv) For a particle confined to a *two-dimensional square box* of side a, the wavefunctions and corresponding energy levels are given by

   $$\psi = N \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right)$$

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

   Show that its ground state is non-degenerate, whereas the first excited state is doubly degenerate. Explain what will happen to this degeneracy if the square box is distorted into a rectangle such that side $a \neq b$.
   (4 marks)

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

A particle confined to move around a ring of constant potential energy and radius r obeys the Schrödinger equation:

$$-\frac{\hbar^2}{2mr^2}\frac{d^2\psi}{d\phi^2} = E\psi$$

i) What is the boundary condition for ψ in this case, and why is such a boundary condition required?

(2 marks)

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

(4.5 marks)

iii) Why is $m_l = 0$ an acceptable solution? Explain why energy levels with $|m_l| \neq 0$ are degenerate.

(2 marks)

iv) This *particle on a ring* model can be used to describe π-electrons in conjugated cyclic hydrocarbons. For benzene, modelled as a ring of radius 1.40 Å, calculate the wavelength of radiation that would generate the first excited electronic state.

(4 marks)

c) For a free particle travelling in the $+x$ direction, the wavefunction is

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

where $k = \dfrac{2\pi}{\lambda}$.

i) Show that this wavefunction contains no information about the position of the particle, and explain why.

(3 marks)

ii) Give the de Broglie relationship, defining all terms used. Why are the wavelengths predicted by this relationship important for electrons?

(3 marks)

iii) Show that the free particle wavefunction is an eigenfunction of the momentum operator

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

Show also that the resulting eigenvalue must correspond to the momentum p (using the de Broglie relation and $\hbar = h/2\pi$).

(3.5 marks)

iv) Show that the free particle wavefunction is an eigenfunction when the momentum operator operates on it twice. Hence determine the kinetic energy of a free particle of mass m.

(3 marks)