

**SECOND PUBLIC EXAMINATION
Honour School of Chemistry**

CHEMISTRY PART IB

GENERAL PAPER 1: PHYSICAL CHEMISTRY

TRINITY TERM 2012

SAMPLE PAPER

Saturday 5th June, 9:30 am – 12:00 noon

Candidates should answer **FOUR** questions

Please start each question in a separate booklet

The numbers in square brackets indicate the approximate marks that the examiners intend to assign to each part of the question.

Attention is drawn to the table of constants provided on page 2 of this booklet.

Guide to questions

1. Atomic and molecular spectroscopy
2. Statistical mechanics
3. Soft condensed matter
4. Valence
5. Magnetic resonance
6. Rate processes

Do not turn over this page until you are told to do so.

Fundamental Constants

Speed of light	c	$2.998 \times 10^8 \text{ m s}^{-1}$
Planck constant	h	$6.626 \times 10^{-34} \text{ J s}$
	\hbar	$1.054 \times 10^{-34} \text{ J s}$
Boltzmann constant	k_B	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	R	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	F	$9.649 \times 10^4 \text{ C mol}^{-1}$
Elementary charge	e	$1.602 \times 10^{-19} \text{ C}$
Electron mass	m_e	$9.109 \times 10^{-31} \text{ kg}$
Proton mass	m_p	$1.673 \times 10^{-27} \text{ kg}$
Vacuum permittivity	ϵ_0	$8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Avogadro constant	N_A	$6.022 \times 10^{23} \text{ mol}^{-1}$
Atomic mass unit	u	$1.661 \times 10^{-27} \text{ kg}$
Bohr magneton	μ_B	$9.274 \times 10^{-24} \text{ J T}^{-1}$

Other conventions

$p^\ominus = 1 \text{ bar} = 10^5 \text{ Pa}$	$1 \text{ atm} = 101.325 \text{ kPa} = 760 \text{ Torr}$	
$1 \text{ Da} = 1 \text{ g mol}^{-1}$	$1 \text{ L} = 1 \text{ dm}^3$	$1 \text{ M} = 1 \text{ mol L}^{-1}$

1. Atomic and molecular spectroscopy

- (a) (i) The electronic *terms* of diatomic molecules are characterised by a quantum number Λ , whereas the terms of atoms (in Russell-Saunders coupling) are characterised by the quantum number L . Explain the difference between these two quantum numbers and why L is not a good quantum number in a diatomic molecule. [4]
- (ii) State the selection rules for change in Λ and for the change of rotational quantum number J for an electronic transition of a diatomic molecule. [2]
- (b) The table below lists the wavenumbers of a few of the rotational lines observed for the 0-0 vibrational band in the electronic spectrum of the CH^+ cation, which has a $^1\Sigma^+$ ground state. [Note that J'' is the ground state rotational quantum number and that transitions involving J'' less than 2 and greater than 5 are not shown.]

J''	$R(J'')/\text{cm}^{-1}$	$Q(J'')/\text{cm}^{-1}$	$P(J'')/\text{cm}^{-1}$
2	23650.445	23581.732	23536.252
3	23658.072	23566.526	23498.544
4	23660.450	23546.194	23455.915
5	23657.479	23520.671	23408.358

- (i) Comment on the observation of P, Q and R branches in the spectrum in relation to the selection rules in (a) (ii) and sketch the transitions on an energy level diagram. [4]
- (ii) The wavenumbers of the R branch are given by

$$\tilde{\nu}_J = \tilde{\nu}_0 + (B' + B'')(J'' + 1) + (B' - B'')(J'' + 1)^2$$

with rotational constants B' in the upper state and B'' in the lower state (ignoring centrifugal distortion). Explain what is meant by a 'band head' in the electronic spectrum and derive an expression for the J'' value corresponding to the band head in terms of the two rotational constants. [4]

- (iii) Using the method of combination differences with the aid of your diagram from b(i) (or otherwise) determine the ground state and excited state rotational constants B'' and B' . Determine also the position of the band origin $\tilde{\nu}_0$. [5]

Question continues, turn over.

- (iv) What do the values obtained for B'' and B' indicate about the change of bonding on excitation? **[2]**
- (v) Use your rotational constants obtained in part (iii) and the formula from part (ii) to predict the J'' quantum number at the R branch band head and compare this prediction with the data given in the table. **[4]**

2. Statistical mechanics

(a) The partition function for a monatomic van der Waals gas is

$$Q(N, V, T) = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} (V - Nb)^N \exp\left(\frac{aN^2}{Vk_B T} \right)$$

where a and b are the van der Waals constants.

(i) Comment on the form of $Q(N, V, T)$ in relation to that expected for an ideal gas. [3]

(ii) The internal energy, U , may be related to the canonical partition function by the equation

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V, N}$$

Using this relationship derive an expression for the internal energy of a monatomic van der Waals gas and compare it with that for a monatomic ideal gas, $U = 3/2RT$.

[4]

(b) The two lowest-energy electronic levels of atomic iodine are the $^2P_{3/2}$ and $^2P_{1/2}$ levels with energies of 0 and 7603 cm^{-1} respectively. You may assume that these are the only states that need be considered.

(i) Derive an expression for the electronic partition function, q_{el}^0 . [3]

(ii) What temperature is required to ensure that the population of the excited level relative to that of the lower level is 1:50? [4]

(iii) Calculate the maximum value of the electronic internal energy. [3]

Question continues, turn over

- (c) The absolute entropy of a system, S , is related to the canonical partition function, Q , as follows:

$$S = k_B \ln Q + \frac{U}{T}$$

where U is the internal energy of the system. The entropy of 1 mole of helium gas at 400 K and 1.0×10^{-3} bar is $21.89R$.

- (i) Given that $U = 3/2RT$ for a mole of ideal monatomic gas, calculate a value for $\ln Q$ for a mole of He at 400 K and 1.0×10^{-3} bar pressure.

[3]

- (ii) For an ideal gas of N identical indistinguishable particles, Q is related to the molecular partition function, q , as follows

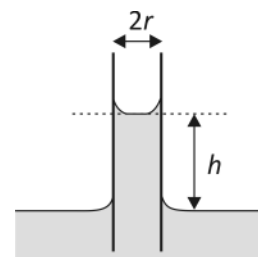
$$Q = \frac{q^N}{N!}$$

By using Stirling's approximation, $\ln N! \approx N \ln N - N$, and letting $N = N_A$, calculate q and comment on its value.

[5]

3. Soft condensed matter

The setup shown in the diagram can be used to measure surface tension γ from the capillary rise in a glass tube with radius r in contact with an aqueous solution. The pressure drop across the interface is given by $2\gamma/r$ (the contact angle between the aqueous solution and glass is 0°) and the hydrostatic pressure of a liquid column is equal to $\Delta\rho gh$, where $\Delta\rho$ is the density difference between water and air.



- (a) (i) By constructing the appropriate pressure balance, show that the height h to which the liquid rises is given by

$$h = \frac{2\gamma}{\Delta\rho gr} \quad [5]$$

- (ii) The interfacial tension of pure water at 298 K is 0.072 N m^{-1} and the density difference between water and air is 0.98 g mL^{-1} . Calculate the radius of the glass tube which will support a height, h , of 15 cm of water.

[Note that $g = 9.8 \text{ m s}^{-2}$]. [4]

- (b) The apparatus in (a) was used to make measurements of the capillary rise h as a function of concentration c for a solution of a non-ionic surfactant. The resulting data are given in the table below. The density of the aqueous phase does not depend on the surfactant concentration.

$\ln c$	-18.50	-16.75	-13.60	-11.00	-10.00	-9.25	-6.20
h / cm	14.6	14.0	12.3	9.5	8.0	6.7	6.7

Plot h against $\ln c$ and explain the shape of the curve. [6]

- (c) Use the Gibbs adsorption equation,

$$\Gamma = - \frac{d\gamma}{d\mu}$$

with Γ the adsorption density (surface excess) and μ the chemical potential of the surfactants (ideally dilute) to carry out the following:

- (i) Using the relationship between the chemical potential and the surfactant concentration, obtain an expression for Γ in terms of h and c . [4]

- (ii) Determine Γ and the area occupied by a single surfactant molecule for a saturated surface at 298 K. Use your value of r from part (a) (ii). [6]

Turn over

4. Valence

- (a) Explain how the *orbital approximation* leads to the concept of a *molecular orbital*. [4]
- (b) State the main assumptions of the Hückel theory of electronic structure. Write down the secular equations in Hückel theory for the π electrons of an ethene molecule. Solve the equations to obtain:

(i) the energy levels; and

(ii) the stabilization energy for the π electrons. [7]

- (c) (i) Write down the general form of the secular equations in Hückel theory for the π orbitals of a cyclic polyene with N carbon atoms, and by making a substitution $x = (\alpha - E)/\beta$, show that a general row of the matrix equation gives a set of simultaneous equations for the molecular orbital coefficients of the form:

$$c_{n-1} + xc_n + c_{n+1} = 0 \quad [4]$$

- (ii) For even-membered rings ($N = 2\ell$ where ℓ is an integer) a general solution for the wavefunction is found to have the form $c_n^k = e^{ik2\pi n/N}$, where k is a label for each molecular orbital and takes integer values from 0 to $N-1$. Using the equation above, show that this leads to the energy level expression

$$E_k = \alpha + 2\beta \cos\left(\frac{2k\pi}{N}\right) \quad [5]$$

- (iii) Determine the molecular orbital energies of a 4-membered polyene ring and calculate the stabilization energy of a cyclobutadiene molecule. Comment on the result obtained in relationship to your result in (b) (ii). [5]

5. Magnetic resonance

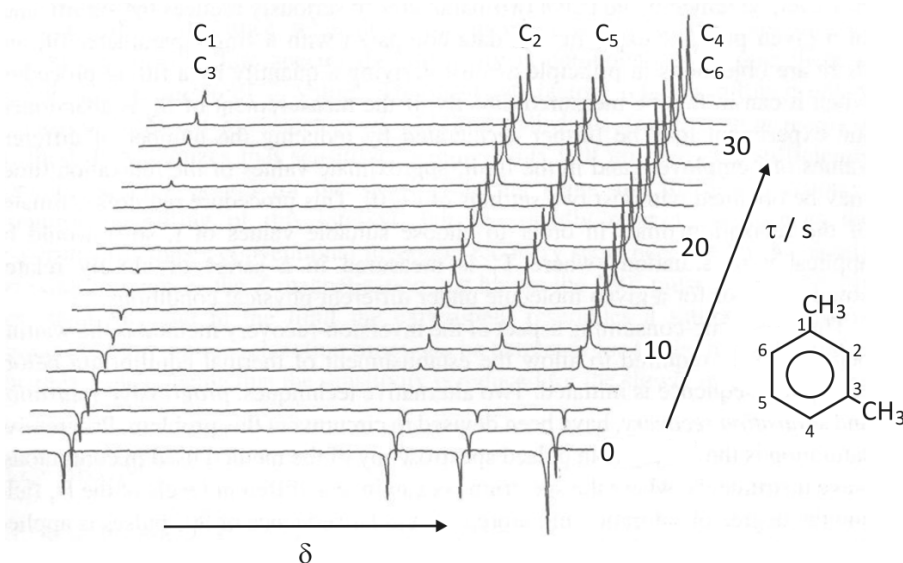
Relaxation processes are fundamental to the phenomenon of Nuclear Magnetic Resonance.

- (a) Briefly describe the physical origin of *spin-lattice* (or *longitudinal*) *relaxation* in solution. **[4]**
- (b) Spin-lattice relaxation is typically investigated using the method of *inversion recovery* by applying the following pulse sequence,

$$\pi_x - \tau - (\pi/2)_x$$

in which the magnetization vector is first inverted and then rotated after a time delay τ into the x - y plane, where the magnetization signal is measured.

The figure below illustrates the results of such an experiment for the aromatic region of the ^{13}C NMR spectrum of *m*-xylene.



- (i) Comment briefly on the number of peaks observed in the $\tau = 0$ spectrum. **[2]**
- (ii) Assuming exponential relaxation, the observed magnetization $M_z(\tau)$ in such an inversion recovery experiment can be described by

$$M_z(\tau) = M_z(0) [1 - 2 \exp(-\tau/T_1)]$$

where T_1 is the spin-lattice relaxation time. Derive an expression for the time τ at which the observed magnetization is zero. **[3]**

Question continues, turn over

(iii) Use your answer to (ii) to obtain a rough estimate of T_1 for:

$^{13}\text{C}_1$ and $^{13}\text{C}_3$;

$^{13}\text{C}_2$;

$^{13}\text{C}_5$;

$^{13}\text{C}_4$ and $^{13}\text{C}_6$

from the data provided in the Figure (graphs not required).

[4]

(iv) Using values in the table below, determine a more precise value for the relaxation time of the aromatic $^{13}\text{C}_4$ and $^{13}\text{C}_6$ nuclei in *m*-xylene.

[4]

τ/s	$M_z(\tau)/M_z(0)$ for C_4 and C_6
0	-1.00
3	-0.32
6	+0.13
9	+0.43
12	+0.62

(v) Explain why the spin lattice relaxation time of carbons C_1 and C_3 is very different from those of C_2 , C_5 and C_4 and C_6 .

[4]

(c) Consider a solution containing a mixture of benzene ($T_1(^{13}\text{C})$ of benzene = 23 s) and *m*-xylene. At what time delay would the signal from the inversion recovery experiment only show the spectrum of *m*-xylene? Sketch the spectrum obtained for the aromatic region.

[4]

6. Rate processes

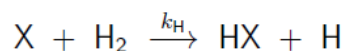
Transition state theory gives the following expression for the rate of a gas phase bimolecular reaction between reactants A and B:

$$k(T) = \frac{k_B T}{h} \frac{q^\ddagger}{q_A q_B} \exp\left(-\Delta E_0^\ddagger / RT\right).$$

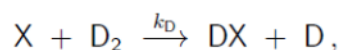
- (a) Briefly outline the assumptions of transition state theory, and define the terms q and ΔE_0^\ddagger appearing in the above equation.

[6]

- (b) Consider the two reactions



and



where X is an unidentified atom.

- (i) Explain what is meant by the term kinetic isotope effect. Using transition state theory, write down an expression for the rate constant ratio, k_H/k_D , in terms of the partition functions for the species involved and ΔE_0^\ddagger for each reaction.
- (ii) Estimate the contribution of the reactant partition functions to the rate constant ratio, k_H/k_D , assuming that the vibrational partition functions are unity. Identify and comment on any further assumptions you make.

[6]

[7]

[Take the masses of H and D to be 1 u and 2 u, respectively.]

- (iii) Discuss qualitatively what other factors might contribute to the kinetic isotope effect for the reactions given above.

[6]

END OF PAPER