

## NATURAL SCIENCES TRIPOS Part IB

---

**Friday 3rd June 2005      1.30 to 4.30**

---

### CHEMISTRY A: PAPER 1

*There are seven questions on this paper.*

*Candidates should attempt any FIVE questions.*

Where a question is divided into sections, the *approximate* division of marks between sections is indicated at the end of the question.

Linear graph paper is available if required.

A Periodic Table, the structures of the amino acids and nucleotide bases, the values of physical constants, character tables and selected mathematical formulae will be found in the data book provided.

Write on ONE side of the paper only.

The answers to each question should be returned separately.

A separate cover sheet for each question should be completed.

<p>You may not start to read the questions printed on the subsequent pages of this question paper until instructed that you may do so by the Invigilator.</p>
---

[TURN OVER

**A1**

Answer *all* parts of the question

- (a) Explain, with mathematical definitions, what is meant by the terms  
(i) *expectation value*, (ii) *uncertainty*, (iii) *eigenfunction* and (iv) *eigenvalue*.
- (b) Show that the uncertainty in a physical observable such as energy or momentum is zero for a state that is an eigenfunction of that observable.
- (c) Consider a harmonic oscillator with wavefunction  $\exp(-\frac{1}{2}\alpha x^2)$ . Show that the expectation values of momentum and position are both zero. Find the uncertainties in position  $x$  and momentum  $p$  for this wavefunction, and show that  $\Delta x \Delta p = \frac{1}{2} \hbar$  for any value of  $\alpha$ .

Approximate division of marks: (a) 30%, (b) 20%, (c) 50%.

**A2**

Answer *all* parts of the question

- (a) Explain what is meant by (i) the Pauli principle, (ii) a Fermi hole and (iii) Hund's first rule, and explain the connections between them.
- (b) Explaining the procedure that you use, obtain the term symbol for the ground state of each of the atoms Li, Be, B, C, N, O, F and Ne. (You need not give the  $J$  value.)
- (c) Assuming that there is a contribution to the energy of  $-K$  for each pair of parallel-spin  $2p$  electrons, where  $K > 0$  is roughly constant, obtain the total energy arising from this effect for the ground states of the atoms B, C, N, O, F and Ne and their positive ions, and hence explain why the ionisation energy is less for the O atom than for the N atom.

Approximate division of marks: (a) 40%, (b) 30%, (c) 30%.

**A3**

Answer *all* parts of the question

- (a) State the variation principle for the expectation value of the Hamiltonian, and explain why it is important.
- (b) A LiH molecule lies on the  $z$  axis, with  $z_{\text{H}} > z_{\text{Li}}$ . The wavefunction for the  $\sigma$  bond can be expressed as a linear combination of the lithium  $2s$  and  $2p_z$  orbitals and the hydrogen  $1s$  orbital, i.e. as

$$\psi = c_{2s}\phi_{2s} + c_{2p}\phi_{2p} + c_{1s}\phi_{1s}.$$

Set up the secular equations for this problem and solve them for the molecular orbital energies, assuming that  $\alpha_{2s} = \alpha_{2p} = \alpha$ ,  $\alpha_{1s} = \alpha + \beta$ ,  $\beta_{2s1s} = \beta_{2p1s} = \beta$  and  $\beta_{2s2p} = 0$ .

- (c) Find the molecular orbital coefficients for the occupied orbital, and show that it involves an  $sp$  hybrid on the Li atom.

Approximate division of marks: (a) 15%, (b) 55%, (c) 30%.

A4

Answer *all* parts of the question

- (a) The moment of inertia of a linear triatomic molecule XYZ is given by

$$I = m_x r_{xy}^2 + m_z r_{yz}^2 - \frac{(m_x r_{xy} - m_z r_{yz})^2}{M}$$

where  $r_{xy}$  and  $r_{yz}$  are internuclear distances and  $M$  is the total mass,

$$M = m_x + m_y + m_z.$$

The frequency of the  $J = 0 - 1$  rotational transition of  $^{16}\text{O}^{12}\text{C}^{32}\text{S}$  is 12163 MHz. The ratio of the bond lengths in OCS is  $r_{\text{co}}/r_{\text{cs}} = 0.7478$ . Calculate the frequency of the same transition in  $^{18}\text{O}^{12}\text{C}^{32}\text{S}$ . Use integral masses in your calculation, making clear any assumptions you use.

- (b) Lines in the pure rotational *Raman* spectrum of the linear molecule cyanogen,  $\text{N} \equiv \text{C} - \text{C} \equiv \text{N}$ , are separated by  $0.63 \text{ cm}^{-1}$ . Calculate the moment of inertia of cyanogen. If the C-N bond length in cyanogen is 0.1165 nm, calculate the C-C bond length. Use integral masses in your calculation.
- (c) The photoelectron spectrum of hydrogen shows a progression of lines to the  $\nu' = 0, 1, 2, \dots$  vibrational levels of the ground electronic state of the  $\text{H}_2^+$  ion. The separations between the first three lines are  $2190.9$  and  $2065.2 \text{ cm}^{-1}$ . Assuming a Morse potential, calculate  $\omega_e$ ,  $\omega_{\text{ex}}$  and  $D_e$  for the ground electronic state of  $\text{H}_2^+$ . Give your answers in  $\text{cm}^{-1}$ . Formulae may be quoted without proof.

The values of  $\omega_e$  and  $D_e$  for  $\text{H}_2$  are  $4396 \text{ cm}^{-1}$  and  $38300 \text{ cm}^{-1}$  respectively. Comment on the magnitude of these values in comparison to  $\text{H}_2^+$ .

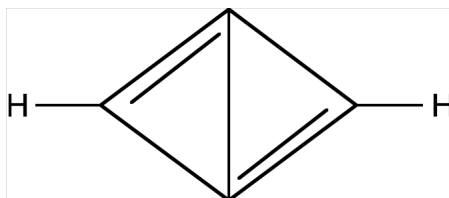
Approximate division of marks: (a) 40% (b) 30% (c) 30%

[TURN OVER]

**A5**

Answer *all* parts of the question

- (a) What is the point group of bicyclobutadiene, shown below?



- (b) Derive the symmetry orbitals for the  $\pi$  system of this molecule.
- (c) Set up and solve the secular equations to obtain the molecular orbital energies using the symmetry orbitals derived above and the simplest Hückel approximations.
- (d) Calculate the delocalisation energy of this molecule.

Approximate division of marks: (a) 10%, (b) 20%, (c) 50%, (d) 20%

**A6**

Answer *all* parts of the question

- (a) State Wade's rule for the number of skeletal electron pairs in a borane or carborane cluster.
- (b) Predict the structures of the following molecules: (i)  $C_2B_3H_5$ , (ii)  $B_5H_{11}$ , (iii)  $B_6H_{10}$ , (iv)  $C_2B_5H_7$ . How many distinct isomers would you expect to find for the two carboranes?
- (c) Use Wade's rules and the above results to deduce formulae for the total number of valence electrons in (i) *closo*, (ii) *nido*, and (iii) *arachno* boranes.
- (d) Deltahedral *closo*, *nido* and *arachno* clusters containing  $n$  transition metal atoms generally contain  $10n$  valence electrons more than the corresponding boranes. Using this fact, and the formulae derived above, predict the arrangement of the metal atoms in (i)  $Os_5(CO)_{15}^{2-}$ , (ii)  $Rh_6(CO)_{16}$ , (iii)  $Rh_{12}Sb(CO)_{27}^{3-}$ . You should assume that each carbonyl ligand donates two electrons to cluster bonding, and that the Sb atom in part (iii) lies at the centre of the cluster, and donates all its valence electrons to cluster bonding.

Approximate division of marks: (a) 10%, (b) 30%, (c) 30%, (d) 30%.

[TURN OVER

**A7**

Answer *all* parts of the question

- (a) Sketch the clusters  $\text{Li}_6$  and  $\text{BeLi}_6$ , if each one is assumed to have  $O_h$  point group symmetry.
- (b) Using the six  $2s$  Li orbitals as a basis, derive and sketch the corresponding symmetry orbitals.
- (c) Using the simplest Hückel approximation and the symmetry orbitals derived above, calculate the molecular orbital energies for the  $\text{Li}_6$  cluster, and draw an energy level diagram.
- (d) Using a symmetry analysis, explain how you would expect the energy level diagram for  $\text{Li}_6$  to change for  $\text{BeLi}_6$ . Hence suggest why  $\text{BeLi}_6$  exhibits a stable geometry with  $O_h$  symmetry, but  $\text{Li}_6$  does not.

Approximate division of marks: (a) 10%, (b) 20%, (c) 40%, (d) 30%.

[END OF PAPER]



## NATURAL SCIENCES TRIPOS Part IB

---

**Wednesday 8th June 2005      1.30 to 4.30**

---

### CHEMISTRY A: PAPER 2

*There are seven questions on this paper.*

*Candidates should attempt any FIVE questions.*

Where a question is divided into sections, the *approximate* division of marks between sections is indicated at the end of the question.

Linear graph paper is available if required.

A Periodic Table, the structures of the amino acids and nucleotide bases, the values of physical constants, character tables and selected mathematical formulae will be found in the data book provided.

Write on ONE side of the paper only.

The answers to each question should be returned separately.

A separate cover sheet for each question should be completed.

You may not start to read the questions printed on the subsequent pages of this question paper until instructed that you may do so by the Invigilator.

[TURN OVER

**A8**

Answer *all* parts of the question

- (a) In statistical thermodynamics, what do you understand by the terms *partition function of the system* and *molecular partition function*? Describe how these two quantities are related.
- (b) Molecules weakly adsorbed onto a surface can be thought of as behaving like a two-dimensional gas. Assuming that the molecules do not interact with one another, derive an expression for their translational molecular partition function; take the surface area to be  $A$ . Be sure to explain and comment on the various steps in your derivation.  
Evaluate the molecular partition function for the case of  $\text{N}_2$  molecules adsorbed onto an area of  $1 \text{ cm}^2$  at 298 K (use integer masses). Comment on your answer.
- (c) Using your expression for the molecular partition function, derive expressions for the translational contributions to the molar internal energy and the molar heat capacity of this two-dimensional gas. How does the internal energy of this two-dimensional gas compare with that expected for a normal (three-dimensional) gas?
- (d) Derive an expression for the density of (translational) states for this two-dimensional gas, being sure to explain any key steps in the derivation. Evaluate this expression for the system described in part (b), and comment on your answer.

Approximate division of marks: (a) 15% (b) 25% (c) 20% (d) 40%

A9

Answer **all** parts of the question

- (a) What do you understand by the *equipartition principle* and when can it be applied? Use this principle to estimate the constant volume molar heat capacities ( $C_V$ ) at 298 K of  $N_2(g)$ ,  $CO_2(g)$  and  $H_2O(g)$ , commenting on any assumptions that you find it necessary to make.
- (b) Show that the partition function for a harmonic oscillator of frequency  $\nu_0$  is given by

$$q'_{\text{vib}} = \frac{1}{1 - \exp(-h\nu_0/kT)};$$

in this expression, the energy levels are measured relative to the ground vibrational state. Hence derive an expression for the internal energy, and then use this to show that the constant volume molar heat capacity is given by

$$C_{V,\text{vib}} = \frac{N_A h^2 \nu_0^2}{kT^2} \frac{\exp(h\nu_0/kT)}{[\exp(h\nu_0/kT) - 1]^2}.$$

- (c)  $NO_2$  is a non-linear triatomic molecule, and so has three rotational constants which have the values 8.0, 0.43 and 0.41  $\text{cm}^{-1}$ . The three vibrational modes have frequencies of 750, 1320 and 1618  $\text{cm}^{-1}$ . Use these data to obtain a value for the constant volume molar heat capacity of  $NO_2(g)$  at 1000 K, commenting on any assumptions that you make.

Approximate division of marks: (a) 30% (b) 30% (c) 40%

[TURN OVER]

**A10**

Answer *all* parts of the question

- (a) What are the key assumptions made in *transition state theory*, used to calculate rate constants using the methods of statistical thermodynamics? (A derivation of the expression for the rate constant is **not required**.)

- (b) Starting from the *Eyring equation* for a second order rate constant,  $k_{2nd}$

$$k_{2nd} = \left( \frac{1}{c^0} \right) \frac{kT}{h} K^\ddagger,$$

where  $c^0$  is the standard concentration and  $K^\ddagger$  is the equilibrium constant for the formation of the transition state. Explain how this equation can be expressed in terms of the Gibbs energy, enthalpy and entropy of activation.

Describe a graphical method for determining the enthalpy and entropy of activation.

- (c) The second-order rate constant for the hydrogenation of ethene in the gas phase has been measured as a function of temperature, yielding the following data:

temperature / °C	$10^{10} \times k_{2nd} / \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
350	10.04
370	29.60
390	81.74
410	212.7
430	524.0
450	1228

Determine the enthalpy and entropy of activation. Comment on the magnitude and sign of the entropy of activation, given that for an atom—atom reaction, the entropy of activation is expected to be of the order of  $-70 \text{ J K}^{-1} \text{ mol}^{-1}$ .

Approximate division of marks: (a) 20% (b) 30% (c) 50%

**A11**

Answer *all* parts of the question

The quantum free electron theory of solids predicts that the allowed energy levels are given by the expression

$$E(k) = \hbar^2 k^2 / 2m_e$$

where  $k$  is the electron wavevector.

- a) Show how the wavevector  $k$  arises in the theory and explain its physical meaning.
- b) Define the Fermi energy and derive an expression for it in terms of electron concentration.
- c) Sodium has a body centred cubic lattice with unit cell parameter  $a = 4.230 \text{ \AA}$ . Calculate the Fermi energy  $E_F$  and electron velocity  $v_F$  at the Fermi level at 0K.
- d) What can you learn about the behaviour of a free electron gas by measuring its conductivity at 0K?

Approximate division of marks: (a) 20% (b) 35% (c) 20% (d) 25%

[TURN OVER

**A12**

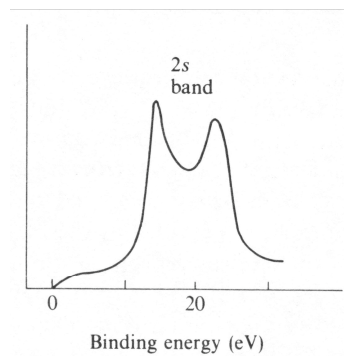
Answer *all* parts of the question

One-electron Bloch wavefunctions  $\Psi_k$  for a linear chain of atoms separated by a distance  $a$  may be written, using the LCAO approximation, in the form

$$\Psi_n = \sum_n e^{ikna} \chi_n$$

where  $\chi_n$  is an atomic orbital on the  $n^{\text{th}}$  atom of the chain.

- Assuming each atom contributes an s orbital identify the values of  $k$  at which the highest and lowest energy solutions will be obtained and sketch the form of the wavefunction at these values.
- Sketch the energy band diagram for this system and hence show how this can be used to explain the shape of the C2s region of the X-ray photoelectron spectrum for the linear hydrocarbon,  $\text{C}_{36}\text{H}_{74}$ , given below.



- Show how consideration of the wavefunction and energy band for this system would lead to the predictions that the linear hydrocarbon  $\text{C}_{36}\text{H}_{74}$  should be an electrical insulator but polyacetylene should be a metal.
- It is found experimentally that polyacetylene is an insulator; show how this can be explained by the band theory of a suitable linear chain.

Approximate division of marks: (a) 30% (b) 25% (c) 15% (d) 30%

**A13**

Answer *all* parts of the question

- a) By means of a suitable energy diagram, show how the addition of Ga impurities to silicon has a dramatic effect upon its electrical conductivity.
- b) Sketch a representative Arrhenius plot of the electrical conductivity of Ga-doped silicon. Identify any characteristic regions in this plot and explain their presence with reference to the behaviour of the Fermi level with temperature.
- c) The electrical conductivity of pure Ge increases by a factor of 6.9 between 300K and 350K. Calculate the bandgap noting any assumptions that you make.
- d) Estimate the conductivity at 300K of Germanium doped with  $10^{21} \text{ m}^{-3}$  Ga atoms assuming complete ionisation of the impurity atoms,  $\mu_h = 0.35 \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$ . How might the accuracy of this calculation be improved?

Approximate division of marks: (a) 25% (b) 45% (c) 15% (d) 15%

**A14**

Answer *all* parts of the question

- (a) Outline how X-ray photoelectron spectroscopy may be used to determine band energy ( $E$  versus  $k$ ) diagrams.

- (b) For sodium metal it is found that

$$E(k) = \hbar^2 k^2 / 2m_e^*$$

where  $m_e^* = m_e \times 1.28$ . Explain without mathematical details how the simplest free electron theory of solids may be extended to account for this behaviour.

What insight does this model offer to cohesion in metals?

- (c) For an electron in a Bloch wavefunction, the momentum is not proportional to the wavevector  $k$ . Starting from the equation

$$dE = f v dt$$

where  $dE$  is the change in energy of an electron in time  $dt$  due to an applied force  $f$ , derive the equation

$$f = \hbar \frac{dk}{dt}$$

Comment upon the significance of this expression. Hence derive an expression for the effective mass of an electron in a Bloch wavefunction.

- (d) Calculate the effective mass  $m_e^*$  of an electron in a 1D chain of atoms separated by distance  $a$ , assuming the Huckel approximation where

$$E_k = \alpha + 2\beta \cos ka$$

Sketch the variation of  $m_e^*$  with  $k$  in the first Brillouin zone and calculate the values of  $m_e^*$  at  $k=0$  and  $k=\pm\pi/a$ .

Approximate division of marks: (a) 25% (b) 25% (c) 30% (d) 20%

[END OF PAPER]