

NATURAL SCIENCES TRIPOS Part IB

Friday 30th May 2008 13.30 to 16.30

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.

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.

STATIONERY REQUIREMENTS

Graph paper × 4 sheets

Lined paper

Rough work pad

Cover sheets

SPECIAL REQUIREMENTS

Department of Chemistry Data Book

Master cover sheet

<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>

A1

Answer *both* parts of the question.

- (a) The Hamiltonian operator for a harmonic oscillator has the form

$$\hat{H} = -\frac{1}{2} \frac{d^2}{dq^2} + \frac{1}{2} q^2$$

where q is a scaled position coordinate. The ground and first excited state eigenfunctions are given by $\psi_0(q) = \exp(-q^2/2)$ and $\psi_1(q) = q \exp(-q^2/2)$.

Normalise these functions, prove that they are eigenfunctions of \hat{H} and determine their eigenvalues.

- (b) Compute the expectation values over $\psi_0(q)$ and $\psi_1(q)$ of the following operators:

- (i) the position operator \hat{q} ,
- (ii) the operator \hat{q}^2 ,
- (iii) the kinetic energy operator \hat{T} ,
- (iv) the momentum operator \hat{p} .

Hence show that the uncertainty product $\Delta p \Delta q$ is greater in the first excited state of a harmonic oscillator than in the ground state. What is special about the value of $\Delta p \Delta q$ in the ground state?

Approximate division of marks: (a) 30%, (b) 70%.

A2

Answer *all* parts of the question.

- (a) State the Pauli principle, referring in your answer to the total wave function $\Psi(1,2)$ of a two electron system.
- (b) Consider a He atom in its $1s2s$ configuration, for which suitable primitive spatial wave functions are $\psi_{1s}(1)\psi_{2s}(2)$ and $\psi_{1s}(2)\psi_{2s}(1)$.
- (i) Write down all combinations of these spatial functions and the associated spin functions that are consistent with the Pauli principle.
- (ii) Use these functions to show that the triplet energy levels in He($1s2s$) are stabilised by an amount $2K$ with respect to the singlet energy level, where

$$K = \iint \psi_{1s}(1)\psi_{2s}(2) \frac{1}{r_{12}} \psi_{2s}(1)\psi_{1s}(2) d^3r_1 d^3r_2.$$

- (iii) What is the physical justification for the result obtained in (ii)?
- (c) Why is the first ionisation energy of an O atom lower than the first ionisation energy of an N atom? Does the same relation hold for the second ionisation energies?

Approximate division of marks: (a) 15%, (b) 70%, (c) 15%.

A3

Answer *all* parts of the question.

- (a) (i) State the variation principle relating the approximate ground state energy \tilde{E} obtained from a trial wave function $\tilde{\Psi}$ to the exact ground state energy E .
 (ii) Explain how to find the best trial wave function in the case that $\tilde{\Psi}$ depends on a parameter α which can be varied.
- (b) The following functions are proposed as ground-state trial wave functions over the region $0 \leq x \leq a$ for a particle-in-a-box of length a ,

$$\tilde{\Psi}_A(x) = x(a-x) \qquad \tilde{\Psi}_B(x) = x^2(a-x)$$

- (i) Pretend that you do not know the exact solution for this system, and use the variation principle to demonstrate that $\tilde{\Psi}_A(x)$ is a better approximation to the ground state wave function than $\tilde{\Psi}_B(x)$.
- (ii) Write down the exact ground state wave function $\Psi(x)$ for this system and rationalise your answer to (i) by sketching $\tilde{\Psi}_A(x)$, $\tilde{\Psi}_B(x)$ and $\Psi(x)$.
- (c) Suggest modifications to $\tilde{\Psi}_A(x)$ which would make suitable trial functions for the first and second excited states of the particle-in-a-box system.

Approximate division of marks: (a) 20%, (b) 60%, (c) 20%.

A4

Answer *all* parts of the question.

Whilst the stable fluoride of boron is the trifluoride BF_3 , the monofluoride BF is of interest since it has the same number of electrons as molecules such as N_2 and CO . Only limited spectroscopic data exist for BF due to the harsh conditions needed for its formation.

- (a) In the microwave spectrum of $^{11}\text{B}^{19}\text{F}$, the $J = 0 \rightarrow J = 1$ rotational transition has been observed with a frequency of 90369.8 MHz.
- Calculate the value of the rotational constant B for $^{11}\text{B}^{19}\text{F}$. Express your answer in both Hz and cm^{-1} .
 - Calculate a value for the bond length in $^{11}\text{B}^{19}\text{F}$.
- (b) The following vibrational transitions have been detected in the electronic emission spectrum of $^{11}\text{B}^{19}\text{F}$; each transition is from the same electronic excited state to the electronic ground state.

ν'' in electronic ground state	ν' in electronic excited state	$\lambda / \text{\AA}$
0	1	1911.0
1	1	1962.7
2	1	2016.4
3	1	2072.1

- Draw a schematic diagram to show the vibrational energy levels in the electronic ground state, and in the electronic excited state. Show these transitions on your diagram.
- Mark on your diagram, expressions for the first four vibrational energy levels in the electronic ground state in terms of ω and ωx_e .
- With the aid of your diagram, or otherwise, determine ω and ωx_e for the electronic ground state of BF . Give your answers in cm^{-1} .
- Calculate, in cm^{-1} and kJ mol^{-1} , the bond dissociation energy, D_e for BF . There is no need to derive the equation you use.

[Question A4 continues over the page]

[TURN OVER]

A4 continued

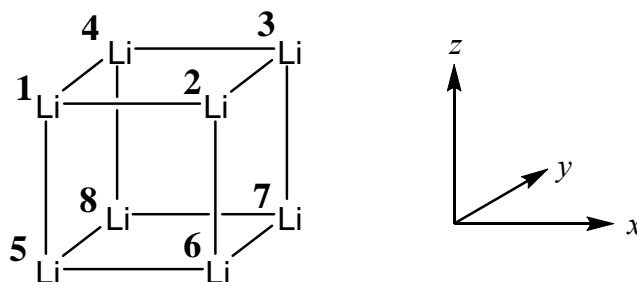
- (c) A single line from the *P*-branch has been detected in the IR spectrum of $^{11}\text{B}^{19}\text{F}$ at 1343.48 cm^{-1} .
- (i) Using your answers from part (b), calculate the frequency of the band origin, ω_0 , for the fundamental IR stretch of $^{11}\text{B}^{19}\text{F}$. Give your answer in cm^{-1} .
- (ii) Using your value of the rotational constant B from part (a), suggest the most likely transition which gives rise to absorption in the *P*-branch at 1343.48 cm^{-1} (i.e. assign the value of J'' for the transition).

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

A5

Answer *all* parts of the question.

In this question you will analyse the bonding in a hypothetical Li_8 cluster where the Li atoms occupy the vertices of a cube.



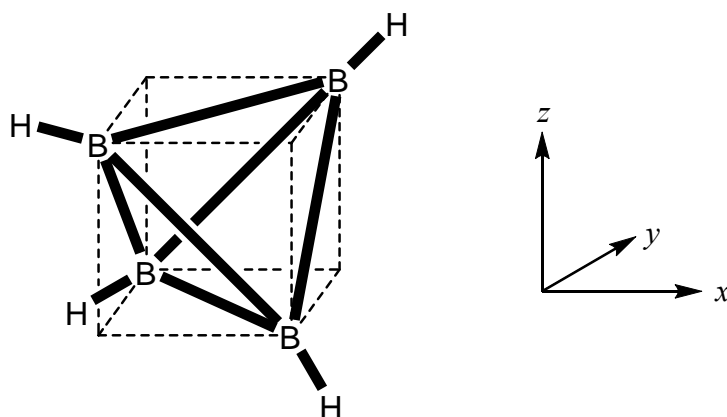
- What is the point group of this structure?
- How does the function xyz transform in this point group?
- Write out the full 8×8 Hückel secular matrix for this molecule using the Li 2s orbitals and the numbering scheme shown above. Briefly state how symmetry helps to simplify problems like this.
- Construct symmetry orbitals from the Li 2s orbitals. You may find it helpful to make use of the result from part (b).
- Calculate the expectation value of the Hückel Hamiltonian for one symmetry orbital corresponding to each irreducible representation. Hence plot a labelled molecular orbital energy level diagram for Li_8 .

Approximate division of marks: (a) 5%, (b) 5%, (c) 20%, (d) 50%, (e) 20%.

A6

Answer *all* parts of the question.

- (a) What is the point group of the B_4H_4 cluster shown below inscribed in the dashed cube?



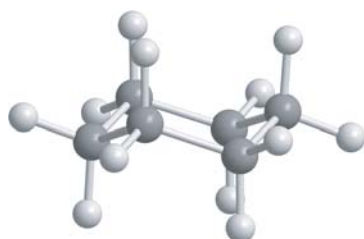
- (b) Predict the symmetries of the molecular orbitals corresponding to B–H σ and σ^* orbitals.
- (c) Calculate the characters of the representation spanned by a basis of sp^3 hybrids on each B atom using the three hybrids on each site that are not primarily involved in B–H bonding. Reduce this representation. These twelve sp^3 hybrids could also be used to form localised σ bonding and antibonding orbitals corresponding to each B–B contact. Calculate the characters of the two corresponding representations and reduce them. Construct symmetry orbitals for the six B–B bonding orbitals and sketch them. [Hint: the required coefficients can be obtained by evaluating appropriate functions of x , y and z at the centre of each B–B bond (or use the projection operator).]
- (d) Draw a labelled molecular orbital energy level for B_4H_4 . What charge state would Wade's rules predict for the system in this geometry? What charge state would you expect if all the bonding orbitals are filled?

Approximate division of marks: (a) 10%, (b) 25%, (c) 40%, (d) 25%.

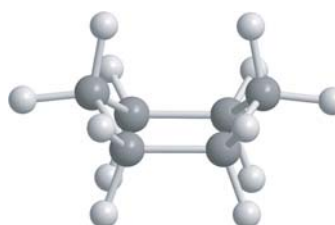
A7

Answer *all* parts of the question.

- (a) What are the point groups of cyclohexane in its boat and chair conformations shown below?

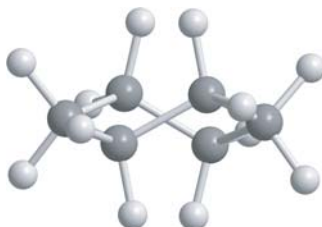


Chair



Boat

- (b) How many distinct features would you expect to see in the C–H stretching region for infra-red and Raman spectra of these two molecules?
- (c) How many coincidences would there be in the infra-red and Raman spectra of each molecule? Comment on your result.
- (d) The twist-boat conformation of cyclohexane is shown below:



Twist boat

What is the point group of this molecule? [Hints: the chemically equivalent carbon atoms occur in sets of four and two; the conformation is chiral.]

How many fundamental infra-red and Raman active C–H stretching modes does the twist-boat possess?

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

[END OF PAPER]

NATURAL SCIENCES TRIPOS Part IB

Wednesday 4th June 2008 13.30 to 16.30

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.

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.

STATIONERY REQUIREMENTS

Graph paper \times 4 sheets

Lined paper

Rough work pad

Cover sheets

SPECIAL REQUIREMENTS

Department of Chemistry Data Book

Master cover sheet

<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

A8

Answer *all* parts of the question.

- (a) Starting from the ‘bridge’ relationship between the Helmholtz energy A and partition function of the system Q_N

$$A = -kT \ln Q_N$$

show that the translational contribution to the entropy of N molecules of a non-interacting gas is given by

$$S_{\text{trans}} = Nk \ln q_{\text{trans}} - Nk \ln N + Nk + \frac{U_{\text{trans}}}{T},$$

where q_{trans} is the translational partition function for one molecule and U_{trans} is the translational contribution to the internal energy.

Derive a similar expression for the rotational contribution to the entropy in terms of the rotational partition function q_{rot} and the rotational contribution to the internal energy U_{rot} .

- (b) Explain how, at normal temperatures, the equipartition principle can be used to provide good estimates for U_{trans} and U_{rot} for both linear and non-linear molecules.
- (c) The rotational partition function for a non-linear molecule is given by:

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\theta_{\text{rot},a} \theta_{\text{rot},b} \theta_{\text{rot},c}} \right)^{1/2},$$

where σ is the symmetry number and $\theta_{\text{rot},a}$ is the rotational temperature associated with rotation about the a axis, and likewise for the b and c axes.

Using the following data, compute the standard molar entropy of $\text{H}_2\text{O}(\text{g})$ at 298 K, explaining any approximations you make.

Rotational temperatures: $\theta_{\text{rot},a} = 40.1 \text{ K}$, $\theta_{\text{rot},b} = 20.9 \text{ K}$, $\theta_{\text{rot},c} = 13.4 \text{ K}$

$\sigma = 2$ for H_2O

Vibrational temperatures of the three normal modes:

$\theta_{\text{vib},1} = 5360 \text{ K}$, $\theta_{\text{vib},2} = 5160 \text{ K}$, $\theta_{\text{vib},3} = 2290 \text{ K}$

Use integer masses.

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

A9

Answer *all* parts of the question.

- (a) The chemical potential of N molecules of an ideal gas is given by

$$\mu = -kT \ln \frac{q}{N}$$

where q is the molecular partition function. Show how this expression can be developed to give the following expression for the chemical potential of species i in a mixture of ideal gases

$$\mu_i = -kT \ln \frac{f_i}{c_i} + \varepsilon^{0,i}$$

where f_i is the volume independent partition function, c_i is the concentration in molecules per unit volume and $\varepsilon^{0,i}$ is the energy of the electronic ground state of i . Be careful in your answer to explain how f_i is defined and why it is necessary to include the term $\varepsilon^{0,i}$.

- (b) Show that the equilibrium constant for the gas-phase equilibrium between the diatomic species A_2 , B_2 and AB ,



is given by

$$K = \frac{f_{AB}^2}{f_{A_2} f_{B_2}} \exp(-\Delta\varepsilon_0/kT)$$

carefully defining what is meant by $\Delta\varepsilon_0$.

- (c) Use the following data to compute the equilibrium constant at 298 K for



Cl_2 : mass 70 amu, rotational temperature 0.35 K, vibrational temperature 800 K

Br_2 : mass 160 amu, rotational temperature 0.12 K, vibrational temperature 470 K

$BrCl$: mass 115 amu, rotational temperature 0.22 K, vibrational temperature 640 K

$$\Delta\varepsilon_0 = 2.0 \text{ kJ mol}^{-1}$$

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

[TURN OVER

A10

Answer *all* parts of the question.

- (a) Given the following values of the partition function for $^{16}\text{O}_2$ at 298 K, estimate the corresponding values for $^{16}\text{O}^{17}\text{O}$. Be sure to explain your logic carefully

$$f_{\text{trans}} = 1.75 \times 10^{32} \text{ m}^{-3} \quad q_{\text{rot}} = 72 \quad q'_{\text{vib}} = 1.00 \quad q'_{\text{el}} = 3.00$$

[f_{trans} is the volume independent partition function; use integer masses]

- (b) The standard molar entropy of $^{16}\text{O}_2(\text{g})$ is $205 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K. *Estimate* the corresponding value for $^{16}\text{O}^{17}\text{O}(\text{g})$.
- (c) Estimate the constant volume molar heat capacity (C_V) for $^{16}\text{O}_2(\text{g})$ and for $^{16}\text{O}^{17}\text{O}(\text{g})$ at 298 K.
- (d) In the rotational Raman spectrum of $^{16}\text{O}^{17}\text{O}$ the first line is displaced by $\sim 8.4 \text{ cm}^{-1}$ from the laser line, and subsequent lines are separated by $\sim 5.6 \text{ cm}^{-1}$. In the corresponding spectrum of $^{16}\text{O}_2$ the first line is displaced by $\sim 14 \text{ cm}^{-1}$ and subsequent lines are separated by $\sim 11 \text{ cm}^{-1}$. Discuss the origin of the differences between these two spectra.

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

A11

Answer *all* parts of the question.

- (a) What do you understand by the terms fermion, Fermi-Dirac distribution, Fermi energy? Formulae may be quoted without proof. Under what conditions would you expect an assembly of ^3He atoms to behave like fermions?
- (b) Sketch the form of the Fermi-Dirac distribution (i) at the absolute zero of temperature and (ii) at some finite temperature. Explain concisely what consequences this behaviour has for the properties of the valence electrons in a metal.
- (c) Show, neglecting experimental details, how you could directly observe the Fermi Dirac distribution of the valence electrons in a metal such as potassium.
- (d) For a free electron solid the Fermi energy is given by

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

and the average energy per electron is given by

$$\langle E \rangle = \frac{3}{5} E_F$$

Use these relations to obtain an expression for the bulk modulus (B).

- (e) Comment on the experimentally observed and calculated (free electron approximation) values of B shown in the table below.

	B (obs) / Pa	B (calculated) / Pa
Cs	1.5×10^{-19}	1.5×10^{-19}
Ag	100×10^{-19}	35×10^{-19}

Approximate division of marks (a) 15%, (b) 25%, (c) 20%, (d) 25%, (e) 15%.

A12

Answer *all* parts of the question.

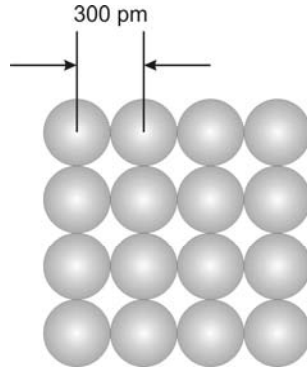
- (a) By reference to the concept of orbital hybridization, explain concisely why *amorphous* silicon exhibits a band gap. In the case of *crystalline* silicon, specify and explain the location of the Fermi level.
- (b) How does the position of the Fermi level change when pure crystalline silicon is n-doped with donor atoms such as phosphorous? How do you envisage the electronic structure of such donor species when embedded in the Si lattice?
- (c) Explain why in the simplest view the donor ionization energy in a semiconductor is independent of the chemical identity of the donor atom. Sketch and explain the temperature dependence of the carrier concentration and the Fermi level in n-doped silicon.
- (d) Given the Bohr radius of the hydrogen atom ($a_0 = 53 \text{ pm}$), the electron effective mass at the bottom of the Si conduction band ($m_e^* = 0.2 m_e$, where m_e is the electron rest mass) and the relative permittivity of Si ($\epsilon_r = 12$) estimate the donor concentration at which the localized donor orbitals begin to overlap.

Approximate division of marks (a) 20%, (b) 15%, (c) 35%, (d) 30%.

A13

Answer *all* parts of the question.

A two-dimensional crystal of metallic lithium was made by depositing a square array of Li atoms on a flat quartz surface that may be regarded as inert in every respect, serving merely to support the sheet of lithium atoms as illustrated below



- (a) By working in the free electron approximation, estimate the energy of the highest occupied electronic orbitals in this two-dimensional metal. Recall that for a one-dimensional solid of length L quantization of the wavevector (k) is given by

$$k = n \frac{2\pi}{L}; \quad n = 0, \pm 1, \pm 2, \dots$$

- (b) How would you verify your estimate by means of experiment?
- (c) Using the extended zone scheme, sketch the form of the first and second Brillouin zones that correspond to the two-dimensional crystal shown above.
- (d) If Be were to be used instead of Li to make the two-dimensional crystal, explain what changes in electronic properties might occur.

$$\frac{\hbar^2}{2m_e} = 6 \times 10^{-39} \text{ m}^4 \text{ kg s}^{-2}$$

Approximate division of marks (a) 35%, (b) 25%, (c) 15%, (d) 25%.

[TURN OVER

A14

Answer *all* parts of the question.

- (a) Explain how the concept of electron effective mass (m_e^*) arises. Sketch $E(k)$ for a one-dimensional crystal with lattice parameter a for $-\pi/a < k < \pi/a$ and consider an electron initially at $k = 0$ in this otherwise empty band. Explain how the electron would respond to a constant externally applied electric field that tends to increase its momentum in the direction $k > 0$.
- (b) Pure polyacetylene, $(\text{CH})_x$, may be regarded as a one-dimensional crystal. At room temperature it is non-metallic with a bandgap of ~ 2 eV. Explain in detail why this is so.
- (c) Are there any circumstances in which polyacetylene exhibits metallic behaviour?

Approximate division of marks (a) 45%, (b) 35%, (c) 20%.

[END OF PAPER]