

NATURAL SCIENCES TRIPOS Part IB

Friday 2nd June 2006 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.

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<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 *all* parts of the question

- (a) What is meant by the statement that a wavefunction ψ is an eigenfunction of an operator \hat{Q} ? Explain the importance of eigenfunctions in quantum mechanics.
- (b) Show that $\psi = xe^{-\frac{1}{2}\alpha x^2}$ is an eigenfunction of the hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$$

for a suitable value of α , and find α and the eigenvalue.

- (c) Why is it possible to say, without doing any further calculations, that this is not the lowest-energy eigenfunction?

Approximate division of marks: (a) 15%, (b) 75%, (c) 10%.

A2

Answer *all* parts of the question

- (a) Describe the Pauli antisymmetry principle, and explain, with appropriate mathematical details, how it leads to the exclusion principle, that a single orbital can be occupied by two electrons only if they have paired (singlet) spins.
- (b) Explain what is meant by a ‘Fermi hole’, and explain the implications of this idea for many-electron systems.
- (c) Consider an octahedral transition-metal complex, in which the transition-metal d orbitals comprise a set of three orbitals with the same energy, and a pair of orbitals at energy Δ higher. Consider a d^5 state Ψ_1 in which all 5 electrons are in the lower set of three orbitals, and a state Ψ_2 in which each of the five orbitals contains one electron, all with parallel spin. Assuming that the energy is lowered by an amount K ($K > 0$) for each pair of electrons with parallel spins, show that Ψ_2 has a lower energy than Ψ_1 if $K > \frac{1}{3}\Delta$.
- (d) If there are now 4 electrons occupying these d orbitals, what is the condition for the ground state to be one in which all the electrons have the same spin?

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

A3

Answer **all** parts of the question

- (a) What is the *variation principle*? Explain its importance in quantum mechanics.
- (b) Consider the wavefunction $\psi = N e^{-\frac{1}{2}\alpha^2 r^2}$ as a trial function for the hydrogen atom, where the nucleus is assumed to be clamped at the origin and the electron position is described by spherical polar coordinates (r, θ, ϕ) . Show that

$$\hat{H}\psi = \left(\frac{3\alpha^2}{2} - \frac{r^2\alpha^4}{2} - \frac{1}{r} \right) \psi.$$

You may assume that for a wavefunction ψ that is independent of θ and ϕ , $\hat{H}\psi$ is given in atomic units by

$$\hat{H}\psi = \left(-\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{1}{r} \right) \psi.$$

- (c) Calculate the expectation value of the Hamiltonian operator for this wavefunction, which you may assume to be normalized when $N = (\alpha^6/\pi^3)^{1/4}$, and find the value of α which optimizes the wavefunction in accordance with the variation principle, and the corresponding energy.
- (d) What is the exact energy of the ground state of the hydrogen atom, in atomic units? Comment on the energy obtained from your calculation in relation to this exact value.

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

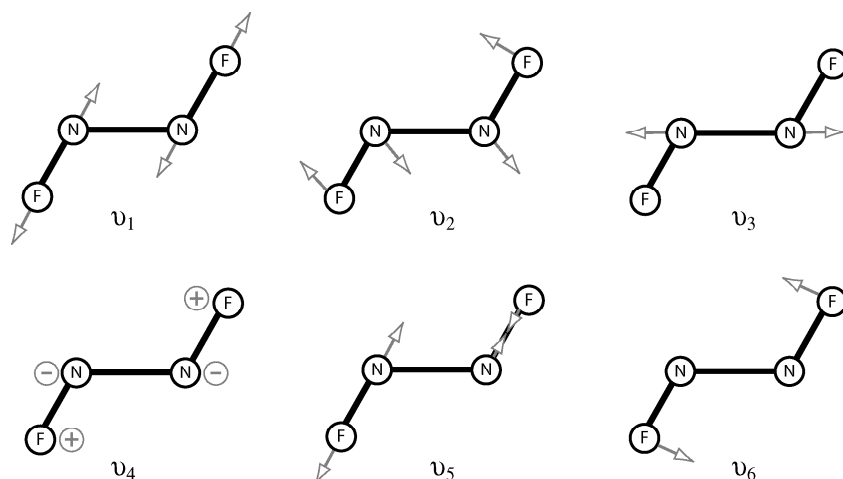
A4

Answer *all* parts of the question

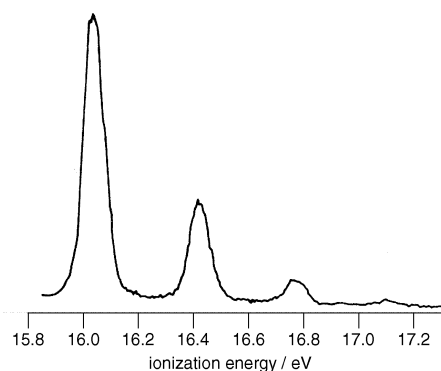
- (a) State the *rule of mutual exclusion*, and explain how you would use it to differentiate between the cis and trans forms of the planar molecule N_2F_2 .



- (b) Shown below are sketches of the atomic displacements for the normal modes of trans N_2F_2 . Giving your reasons, which of the normal modes would you expect to give rise to absorptions in the IR spectrum?



- (c) Shown below is the band with the lowest ionization energy from the photoelectron spectrum of HF



[TURN OVER]

[Continuation of Qu. A4]

The three strong peaks occur at 16.044, 16.430 and 16.790 eV.

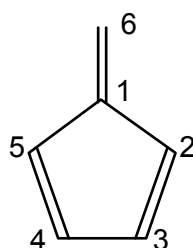
- (i) Using an MO picture of the bonding in HF, and the Franck Condon Principle, deduce the MO from which an electron is being ionized in the above band.
- (ii) What vibrational quantum numbers of HF^+ correspond to the above three peaks? Find *approximate* values for $\tilde{\omega}_e$ and $\tilde{\omega}_e x_e$ (in cm^{-1}) for the electronic state of HF^+ involved in the photoionisation transition. Any formulae needed may be quoted without proof.
- (iii) The photoelectron spectrum of HF also shows a band at an ionization energy of 19 eV. In contrast to the band at around 16 eV, the band at 19 eV shows an extensive progression of vibrational peaks. Suggest, giving your reasons, from which MO of HF the electron is being ionized to give the band at 19 eV.

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

A5

Answer *all* parts of the question

- (a) Write down the general form of the secular equations and explain how they are used to compute approximate molecular orbitals and energy levels in Hückel theory.
- (b) Using Hückel theory, construct the 6×6 secular determinant describing the π -bonding in fulvene:



- (c) Assign the point group of fulvene and construct normalized symmetry-adapted combinations of the $2p$ orbitals perpendicular to the plane of the molecule.
- (d) Use these combinations to compute the pair of molecular orbitals which are symmetric with respect to a rotation about 180° . [Give the coefficients of the orbitals numerically, to 3 significant figures.]

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

[TURN OVER

A6

Answer *all* parts of the question

- (a) Explain using symmetry arguments why the ‘rule of mutual exclusion’ holds in infrared and Raman spectroscopy.
- (b) Use group theory to predict (i) the number of infrared active modes and (ii) the number of Raman active vibrational modes in ethylene.
- (c) One of the vibrational modes of ethylene, $\nu_{inactive}$, is both infrared and Raman inactive. Explain why a transition from the vibrational ground state to a state in which both $\nu_{inactive}$ and any one of the infrared active modes is singly excited is detectable by Raman spectroscopy.

Approximate division of marks: (a) 25%, (b) 60%, (c) 15%.

A7

Answer *all* parts of the question

- (a) Explain, using orbital sketches and energy-level diagrams, how the degeneracy of a set of metal d-orbitals is split by a crystal field which has (i) octahedral and (ii) square planar symmetry.
- (b) What are the limitations of crystal-field theory, and how are these improved on by ligand-field theory?
- (c) For the square planar $[\text{Ni}(\text{CN})_4]^{2-}$ complex, use ligand-field theory to predict which symmetric linear combinations of the ligand σ -orbitals are able to mix with which metal d-orbitals. [You will find it convenient to locate the complex in the xy -plane, placing the ligands on the x and y axes.]
- (d) Which, if any, of the metal d-orbitals remain non-bonding when ligand π -orbitals are also included?

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

[END OF PAPER]

NATURAL SCIENCES TRIPOS Part IB

Wednesday 7th June 2006 1.30 to 4.30

CHEMISTRY A: PAPER 2

*There are seven questions on this paper.
Candidates should attempt any FIVE questions.*

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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.

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A8

Answer *all* parts of the question

- (a) Starting from the ‘bridge’ relationship

$$A = -kT \ln Q_N,$$

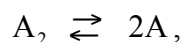
show that the chemical potential of an ideal gas is given by

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

where q is the molecular partition function, and N is the number of molecules (or atoms).

Explain how this expression can be modified to give the chemical potential of component i of a mixture of ideal gases.

- (b) Show that for a gas-phase equilibrium of the form

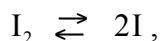


the equilibrium constant is given by

$$K_c = \frac{f_{\text{A}}^2}{f_{\text{A}_2}} \left(\frac{1}{c^0} \right) \exp \left(\frac{-D_e}{kT} \right),$$

where c^0 is the standard concentration, expressed in terms of molecules (or atoms) per unit volume, D_e is the dissociation energy of A_2 (measured from the bottom of the potential energy well) and f_i is the volume-independent partition function.

- (c) Given the data below, calculate K_c at 800 K for



Mass of I 127 amu, $\theta_{\text{rot}} = 0.054$ K, $\theta_{\text{vib}} = 308$ K, $D_e = 12,540$ cm⁻¹; the I_2 molecule has a singlet electronic ground state and the I atoms are in their electronic ground states. You may quote any further formulae you need without proof.

Approximate division of marks: (a) 25%, (b) 25%, (c) 50%.

A9Answer *all* parts of the question

- (a) Starting from the 'bridge' relationship

$$A = -kT \ln Q_N,$$

show that the entropy of N non-interacting indistinguishable atoms or molecules is given by

$$S = Nk \ln q - Nk \ln N + Nk + \frac{U}{T},$$

where U is the internal energy. Hence show that the translational contribution to the entropy is given by

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

whereas the rotational, vibrational or electronic contributions are given by

$$S_{\text{rot, vib, elec}} = Nk \ln q_{\text{rot, vib, elec}} + \frac{U_{\text{rot, vib, elec}}}{T}.$$

- (b) Use the following data to calculate the standard molar entropy of gaseous acetylene (ethyne, HCCH) at a temperature of 150 K. Comment on any approximations you make. [Any formulae you need can be quoted without proof]

Moment of inertia = 2.37×10^{-46} kg m²; molecular mass 26 amu; vibrational frequencies of the normal modes: 799 cm⁻¹ (doubly degenerate), 882 cm⁻¹ (doubly degenerate), 2247 cm⁻¹, 3607 cm⁻¹ and 3719 cm⁻¹.

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

[TURN OVER]

A10

Answer *all* parts of the question

- (a) Starting from the canonical probability distribution function

$$P_m = \frac{1}{Q_N} \exp(-E_m/kT),$$

derive the following expression for the internal energy, U , of a system consisting of N indistinguishable particles:

$$U = NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V.$$

In your answer, make clear the difference between the partition functions Q_N and q .

- (b) When a diatomic molecule is weakly adsorbed onto a surface it is possible that the molecule can still rotate about an axis perpendicular to the surface. The energy levels of such a two-dimensional rotor are given by

$$\varepsilon_J = BJ^2 \quad J = 0, 1, 2 \dots \quad \text{where} \quad B = \frac{\hbar^2}{2I},$$

B is the rotational constant and I is the moment of inertia. The energy levels are all two-fold degenerate, with the exception of $J = 0$ which is non-degenerate.

Write down the first four terms of the series you would need to sum in order to determine the partition function for this two-dimensional rotor.

Assuming that $kT \gg B$, find a simple expression for q , commenting on any approximations you make.

Make a sketch of q as a function of $\frac{kT}{B}$, pointing out any features of interest.

- (c) Determine the internal energy, U , of N such rotors in the low and high temperature limits, commenting on your answers. Hence, draw a sketch of how U varies with temperature, and a sketch of how the corresponding heat capacity, C_V , varies with temperature.

Compare your results with those expected for a freely rotating diatomic molecule in the gas phase.

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

A11

Answer *all* parts of the question

- (a) A certain solid, **X**, is an excellent electronic conductor yet has a very small electronic heat capacity. Explain *concisely* how this can be so.
- (b) The valence electrons in **X** are described well by free electron theory and are characterized by a Fermi temperature (T_F) of 10,000 K. Make numerical estimates of (i) the molar electronic heat capacity of **X** at 300 K and (ii) the temperature coefficient (γ) of the molar electronic heat capacity of **X**.
- (c) By considering the flow of electrons through a sample of **X** placed in a uniform magnetic field, derive a value for its Hall coefficient (R_H), making clear any approximations you use.
- (d) The table shows observed γ and R_H values for a variety of elements. Corresponding values calculated on the basis of free electron theory are also shown. Explain *briefly* how the various levels of agreement between observed and theoretical values may be understood.

	Na	Ge		Na	Cs	Be
γ (observed)	1.4	0	R_H (observed)	-25	-78	+25
γ (free electron) (mJ mol ⁻¹ K ⁻²)	1.1	1.0	R_H (free electron) (m ³ C ⁻¹ /10 ¹¹)	-24	-73	-3

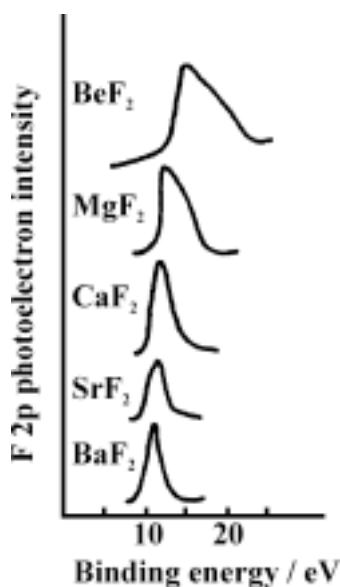
Approximate division of marks: (a) 20% (b) 30% (c) 30% (d) 20%.

[TURN OVER

A12

Answer *all* parts of the question

- (a) State Bloch's Theorem and explain concisely its significance in the theory of the electronic structure of crystalline solids. Show how it may be used to determine the number of allowed quantum states within an energy band, thus providing a basis for a classification scheme for solid state electronic structure.
- (b) Indicate how photoelectron spectroscopy may be used to investigate the density of occupied electronic states in a solid. Sketch the expected experimental result for potassium, pointing out salient features. How may this result be used to estimate the average energy of the valence electrons?
- (c) Explain qualitatively how the valence and conduction bands in potassium chloride arise.
- (d) The figure below shows the photoelectron spectra of a series of metal fluorides. Account for the differences between these spectra.



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

A13

Answer *all* parts of the question

- (a) One definition of a metal is: "a material having a part-filled band of electron states". In the light of this definition, and bearing in mind the particular valence-electron configurations of the atoms involved, would you expect the following elemental, crystalline solids to be metals or non-metals: i) Rb; ii) Ca; iii) Ge; iv) Ar?
- (b) If, in reality, any of the above materials (i-iv) do **not** obey your prediction, give an explanation of why this is so, providing a suitable drawing illustrating your answer.
- (c) Give another definition of a metal, in terms of the temperature behaviour of the electrical conductivity.
- (d) In the light of these two definitions, would you expect crystalline Ge, doped substitutionally with As atoms, to exhibit semiconducting or metallic behaviour?

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

A14

Answer *all* parts of the question

- (a) Sketch the conventional cubic unit cell of the body-centred-cubic (bcc) crystalline lattice, showing the positions of the atoms. On this figure, indicate, by suitable shading, the (100) and (111) crystal planes. In a separate figure, sketch the (100) and (111) crystal planes, indicating where contact is made between atoms in this cubic close-packed structure.
- (b) Cs crystallises in the bcc structure. Calculate the free-electron concentration of this material, given that the radius of a Cs atom is 260 pm. Give your answer in electrons per m^3 .
- (c) Cs undergoes a bcc – fcc (face-centred-cubic) structural transition at a pressure of 22 kbar. Assuming that the lattice constant is the same for bcc and fcc phases, would you expect the free electron concentration to increase, decrease or remain constant during the transition? Why?
- (d) Explain how some ionic crystal structures can be generated from the fcc structure. Give *two* examples, clearly explaining how the positions of cations and anions respectively relate to the underlying fcc structure in each case. Describe the geometry of the coordination polyhedra comprising cations and anions for each of the two structures.

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

[END OF PAPER]