

NATURAL SCIENCES TRIPOS Part IB

Thursday 29th May 2003 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>
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[TURN OVER

A1

Answer *all* parts of the question

- (a) Write down the Hamiltonian $\hat{H}(x, p)$ for a one-dimensional harmonic oscillator of mass m and spring constant k . If $\omega = \sqrt{k/m}$ is the characteristic frequency of the oscillator, write down the energy levels ε_n of this oscillator without proof.
- (b) The oscillating particle is now assumed to carry an electric charge q ; the Hamiltonian in the presence of an electric field E is:

$$\hat{H}'(x, p) = \hat{H}(x, p) - qEx \quad .$$

Show that \hat{H}' may be written in the form:

$$\hat{H}'(x, p) = \hat{H}(\xi, p) + C \quad ,$$

where $\xi = (x - x_0)$, x_0 is a new equilibrium position of the oscillator in the presence of the electric field and C is a constant. Determine x_0 and C . Show that the energy eigenvalues of the Hamiltonian \hat{H}' are shifted relative to those of \hat{H} by a constant amount $\Delta\varepsilon$.

The ground-state wavefunction of \hat{H}' is $(\alpha/\pi)^{1/4} e^{-\alpha\xi^2/2}$. Determine α . Compute the expectation values $\langle \xi \rangle$, $\langle x \rangle$ and $\langle p \rangle$.

Conclude from the result for $\langle x \rangle$ that the electric field induces a mean dipole moment μ of the oscillator and give the expression for μ .

- (c) Consider finally the three-dimensional harmonic oscillator made up of three independent harmonic oscillators vibrating along the three cartesian axes x, y, z , with identical masses m and spring constants k . Write down the corresponding hamiltonian $\hat{H}(\mathbf{r}, \mathbf{p}) = \hat{H}(x, y, z; p_x, p_y, p_z)$. Write down the ground-state energy of this three-dimensional oscillator and the corresponding ground-state wavefunction $\psi_0(x, y, z)$. What is the energy of the first excited state? What is the degeneracy of this energy level?

Approximate division of marks: (a) 10%; (b) 50%; (c) 40%.

A2

Answer *all* parts of the question

- (a) Write down the Hamiltonian $\hat{H}(\mathbf{r}, \mathbf{p})$ for an electron in a He^+ ion. The kinetic energy operator can be separated into radial and angular parts:

$$\frac{\hat{\mathbf{p}}^2}{2m} = \frac{p_r^2}{2m} + \frac{\hat{\mathbf{L}}^2}{2mr^2} ,$$

where $\hat{\mathbf{L}}^2$ is the square of the angular momentum operator. Explain briefly why any wavefunction ψ which is a solution of the Schrödinger equation $\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$ factorizes into a radial factor and an angular factor, $\psi(\mathbf{r}) = R(r)\Phi(\theta, \varphi)$. Specify the quantum numbers that characterize the eigenfunctions of \hat{H} .

- (b) Write down the eigenvalue equations of the operators $\hat{\mathbf{L}}^2$ and \hat{L}_z . Use the former to derive the Schrödinger equation for the radial wavefunction $R(r)$. On which quantum numbers does $R(r)$ depend?

- (c) In atomic units, the Schrödinger equation for the ground-state wavefunction reads:

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{Z}{r} \right] R(r) = \varepsilon R(r) ,$$

where r is in units of the Bohr radius, a_0 , ε is in Hartrees and Z is the nuclear charge. The ground-state wavefunction is of the form $R(r) = Ae^{-\lambda_1 r}$ where A is a normalization constant. Determine λ_1 and the ground-state energy ε_1 by direct substitution.

- (d) If the electron is in a state described by the (unnormalized) wavefunction:

$$\psi(\mathbf{r}) = \psi(x, y, z) = (x + y + z)e^{-\frac{\lambda_1}{2}\sqrt{x^2+y^2+z^2}} ,$$

calculate the probability that a simultaneous measurement of $\hat{\mathbf{L}}^2$ and \hat{L}_z will yield the values 2 and 0 (all variables are expressed in atomic units).

$$\left[\int_0^\pi \cos^2 \theta \sin \theta d\theta = \frac{2}{3} \right]$$

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

A3

Answer *all* parts of the question

- (a) Write down the Hamiltonian for a Li^+ ion. Which ground-state configuration would you expect in terms of one-electron orbitals?
- (b) Specify the possible values of the total angular momentum quantum numbers j and m in the ground state (characterized by zero *orbital* angular momenta of the electrons). Write down the four possible angular momentum eigenstates in terms of the single-spin functions α and β .
- (c) Combine these spin states with the single-electron orbital wavefunctions $\varphi_a(\mathbf{r}_1)$ and $\varphi_b(\mathbf{r}_2)$ to construct the total wavefunctions of the Li^+ ion compatible with the Pauli principle. Consider the special case of the ground state and show why the electrons are necessarily in a singlet spin state in that case.
- (d) Keeping in mind that for a hydrogenic atom the Schrödinger equation for the ground state reads, in atomic units:

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{Z}{r} \right) R(r) = \varepsilon R(r)$$

with $\varepsilon = -Z^2/2$ and $R(r) = Ae^{-Zr}$, calculate the expectation value of the energy of the Li^+ ion in the singlet ground state obtained in (c) when the electron-electron interaction is neglected. Explain briefly how the proper inclusion of the latter interaction would affect the expectation value.

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

A4

Answer *all* parts of the question

- (a) How do the potential energy functions for the harmonic oscillator and the Morse oscillator differ? Considering only the vibrational energy levels, how do the resulting absorption spectra differ between the two models?
- (b) For the Morse oscillator, show that the value for the vibrational quantum number with the greatest vibrational energy, v_{\max} , is given by:

$$v_{\max} = \frac{1}{2x_e} - \frac{1}{2},$$

where x_e is the anharmonicity constant. Use this result to find an expression for:

(i) the depth of the potential well, D_e , and (ii) the dissociation energy, D_0 , of a diatomic molecule.

- (c) In a study of the electronic absorption spectrum of argon gas under pressure, transitions were detected indicating the possible existence of a diatomic argon molecule, Ar_2 . A number of progressions were observed from the electronic ground state to various excited electronic states. The table below gives the *wavelengths* in \AA ($1\text{\AA} = 10^{-10}\text{ m}$) for one such progression from different vibrational levels in the electronic ground state to a fixed vibrational level in an electronically excited state.

v'	v''	$\lambda / \text{\AA}$
1	0	1051.424
1	1	1051.704
1	2	1051.928

where v' is the vibrational quantum number in the electronically excited state and v'' is the vibrational quantum number in the electronic ground state.

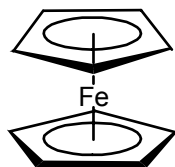
- (i) Draw a schematic diagram to illustrate these transitions.
- (ii) Calculate, for the electronic ground state, $\tilde{\omega}$, $\tilde{\omega}x_e$, and \tilde{D}_e . Calculate D_0 in both cm^{-1} and kJ mol^{-1} and comment on your value.
- (iii) Estimate how many vibrational levels exist in the electronic ground state of Ar_2 .

Approximate division of marks: (a) 20%; (b) 10%; (c): i) 10%; ii) 50%; iii) 10%.

A5

Answer *all* parts of the question

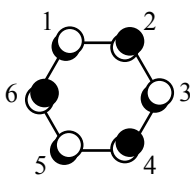
- (a) Identify the point group for each of the following molecules: H_2O , NH_3 , BH_3 , and the staggered form of ferrocene (whose structure is shown below).



ferrocene

- (b) What are the characters of the representations generated by the following bases:

- (i) the two hydrogen $1s$ orbitals in H_2O ;
- (ii) the two O-H σ bonds in H_2O ;
- (iii) the three $\text{N } 2p$ orbitals in NH_3 ;
- (iv) the B-H stretching vibrations in BH_3 ;
- (v) the linear combination $p_z(1) - p_z(2) + p_z(3) - p_z(4) + p_z(5) - p_z(6)$ in benzene (shown schematically below);



- (vi) the $2p_z$ orbitals of the cyclopentadiene ligands in ferrocene?

Reduce all of the above representations.

- (c) Assuming that the molecule AB_n has point group C_{nv} , derive the representation matrix corresponding to the transformation of a set of three p orbitals on the A atom under rotation through $2\pi/n$ about the principal axis. What is the character for this operation?

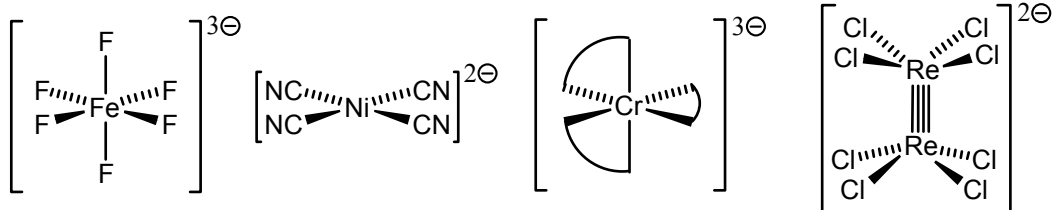
Approximate division of marks: (a) 10%; (b) 60% equally divided between parts (i)-(vi); (c) 30%.

A6

Answer *all* parts of the question

- (a) What are the point groups of the following transition metal compounds, whose structures are shown below:

(i) FeF_6^{3-} , (ii) $\text{Ni}(\text{CN})_4^{2-}$, (iii) $\text{Cr}(\text{ox})_3^{3-}$, (iv) $\text{Re}_2\text{Cl}_8^{2-}$?



The detailed structure of the bidentate oxalate ligand, $(\text{ox})^{2-}$, is not shown.

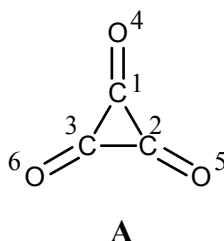
- (b) Which irreducible representations are contained in the representations defined by the metal d orbitals in each of the four molecules above?
- (c) Sketch a qualitative molecular-orbital energy-level diagram for an octahedral first-row transition metal complex ML_6 , where the ligand is a simple σ donor. How would your diagram change for: (i) π acceptor ligands, and (ii) π donor ligands?
- (d) How many features would you expect to see in the M–L stretching region of the infrared and Raman vibrational spectra for the above ML_6 complex? Sketch the M–L vibrational displacements for this complex.

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

A7

Answer *all* parts of the question

- (a) Outline the assumptions and approximations of Hückel theory.
- (b) For the hypothetical planar molecule, **A**, shown below:
- find the character of the representation generated by the basis of carbon p_π orbitals ϕ_1 , ϕ_2 and ϕ_3 , and find its irreducible components;
 - construct a symmetry orbital for each irreducible representation;
 - write down the symmetry orbitals constructed from the oxygen p_π orbitals ϕ_4 , ϕ_5 and ϕ_6 ;
 - set up and solve the secular equations to obtain the orbital energies for each symmetry, given that $\beta_{CO} = \beta_{CC} = \beta$, and $\alpha_O = \alpha_C + 2\beta_{CC} = \alpha + 2\beta$;
 - calculate the total π -orbital energy and comment on the stability of this molecule.



Approximate division of marks: (a) 20%; (b): i) 20%; ii) 20%; iii) 10%;
iv) 20%; v) 10%.

[END OF PAPER]

NATURAL SCIENCES TRIPOS Part IB

Wednesday 4th June 2003 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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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.

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[TURN OVER

A8

Answer *all* parts of the question

- (a) Starting from the ‘bridge relationship’

$$A = -k_B T \ln Q_N ,$$

which relates the Helmholtz energy, A , to the partition function, Q_N , show that the translational entropy of an ideal gas, S_{trans} , is given by

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

where N is the number of molecules, q_{trans} is the molecular translational partition function and U_{trans} is the translational internal energy.

Derive a similar expression for the rotational entropy, S_{rot} , explaining why it is different in form from the expression for S_{trans} .

- (b) Use the following data to calculate the standard molar entropy of NO gas at 298 K, explaining any assumptions you make.

Mass of NO: 30 amu, $\theta_{\text{rot}} = 2.45 \text{ K}$, $\theta_{\text{vib}} = 2719 \text{ K}$, electronic ground state $^2\Pi$.

Approximate division of marks: (a) 60%; (b) 40%.

A9

Answer *all* parts of the question

- (a) Starting from the ‘bridge relationship’

$$A = -k_B T \ln Q_N ,$$

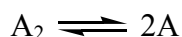
which relates the Helmholtz energy, A , to the partition function, Q_N , show that the chemical potential, μ , of an ideal gas is given by

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

where N is the number of molecules and q is the molecular partition function.

Explain how this expression for the chemical potential is modified for the case of a mixture of ideal gases, such as would be encountered in chemical equilibrium.

- (b) For the dissociation of a diatomic gas



write down an expression which you could use to compute the equilibrium constant in terms of partial pressures, K_p , from a knowledge of the partition functions of one mole of A and A_2 in the standard state, q_A^0 and $q_{A_2}^0$, and the dissociation energy, D_e , of A_2 , measured from the bottom of the potential energy well. (A derivation is not required.)

Use the following data to calculate K_p for the dissociation of $I_2(g)$ into iodine atoms at 1200 K, explaining any assumptions you make.

Data for I: mass 127 amu, atomic term symbol $^2P_{3/2}$,

Data for I_2 : $\theta_{\text{rot}} = 0.054$ K, $\theta_{\text{vib}} = 307$ K, electronic ground state $^1\Sigma$,

$D_e = 12447$ cm $^{-1}$.

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

A10

Answer *all* parts of the question

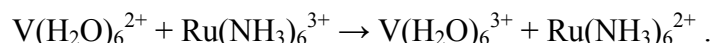
- (a) Starting from the Eyring expression for a second-order rate constant, k_{2nd} ,

$$k_{2nd} = \left(\frac{1}{c_0} \right) \frac{k_B T}{h} K^\ddagger ,$$

where c_0 is the standard concentration and K^\ddagger is the equilibrium constant for the formation of the transition state, show how k_{2nd} can be related to the enthalpy and entropy of activation, $\Delta_r H^\ddagger,0$ and $\Delta_r S^\ddagger,0$ respectively. Hence describe a graphical method for determining the values of these activation parameters.

For a reaction in solution, how is $\Delta_r H^\ddagger,0$ related to the activation energy?

- (b) For reactions in solution, both positive and negative values of $\Delta_r S^\ddagger,0$ have been observed. How do you interpret such observations?
- (c) The following reaction has been studied in aqueous solution using a flow system:



Second-order rate constants have been determined for this reaction as a function of temperature:

T / K	290	300	310	320
$10^{-4} \times k_{2nd} / \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$	2.61	2.82	3.02	3.23

Use a graphical method to determine values for the enthalpy and entropy of activation. What does the value of the entropy of activation imply about the mechanism for this reaction?

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

A11

Answer *all* parts of the question

- (a) Explain, using a diagram showing the relevant electron energy levels, how the substitutional incorporation of phosphorus atoms into the lattice of crystalline silicon causes an increase in the conduction-electron concentration, n .
- (b) (i) A semiconductor is transparent to light with wavelengths longer than $1.77 \mu\text{m}$. Calculate the bandgap energy of the semiconductor.
- (ii) The electron effective mass and dielectric constant of the semiconductor are, respectively, $m_e^* = 0.15 m_e$ and $\epsilon_r = 16$. Calculate the electron binding energy for donor atoms substitutionally doped into the semiconductor.
- (iii) The semiconductor has a total intrinsic charge-carrier concentration of $2.4 \times 10^{19} \text{ m}^{-3}$ at 300K. Calculate the hole concentration, p , when the material is substitutionally doped with $5 \times 10^{20} \text{ m}^{-3}$ of donor atoms. Explain and justify any assumptions used.
- (iv) Indicate on a suitably labelled energy diagram, with calculated numerical values of appropriate energies marked on the diagram, how the Fermi level of the doped semiconductor moves with temperature.

All equations used may be quoted without proof.

[The Rydberg constant, $R_H = 13.6 \text{ eV}$]

Approximate division of marks: (a) 15%; (b): (i) 15%; (ii) 10%; (iii) 45%; (iv) 15%.

A12

Answer *all* parts of the question

The graphite allotrope of carbon has a two-dimensional (2D) crystal structure, each layer consisting of an hexagonal net of atoms.

- (a) Describe the bonding in this structure.
- (b) Draw the primitive 2D unit cell, superimposed upon the hexagonal net. How many atoms does the unit cell contain?
- (c) Sketch the π -band structure (for representative trajectories in \mathbf{k} -space between high-symmetry \mathbf{k} -points of the function $E(\mathbf{k})$), and the corresponding density of states, for an ideal layer of graphite. Sketch the form of the Bloch wavefunctions, superimposed on three connected hexagons of the hexagonal net, for electron states at the middle, and at both extremities, of the band.
- (d) What is the electrical-conductivity behaviour of pure graphite? How does it change when lithium, or bromine, is intercalated between the layers?
- (e) Explain, by means of a suitable energy-band diagram, how the different electron-orbital hybridization, and resulting atomic structure, adopted by the diamond allotrope of carbon changes the electronic structure.

Approximate division of marks: (a) 10%; (b) 10%; (c) 45%; (d) 20%; (e) 15%.

A13

Answer *all* parts of the question

- (a) Explain what is meant by the term *Fermi level*. Indicate, on a suitable diagram, the position of the Fermi level, with respect to the highest-lying electron state, for:
i) a metal; ii) an intrinsic semiconductor. Give reasons for these placements.
- (b) Obtain an equation for: i) the Fermi energy, E_F , and ii) the density of states, for a free-electron gas. Would you expect the *average* energy per electron of a free-electron gas to be greater than, equal to, or less than $\frac{1}{2}E_F$? Give reasons for your answer.
- (c) The atomic structure of crystalline aluminium is face-centred cubic, with unit-cell parameter $a = 4.05\text{\AA}$. Obtain a value for the Fermi energy of this material.

Approximate division of marks: (a) 20%; (b) 55%; (c) 25%.

A14

Answer *all* parts of the question.

- (a) Draw a perspective, labelled, diagram of the rocksalt (NaCl) structure. How may this structure alternatively be regarded in terms of a packing of one type of ion with the interstitial holes filled by the other type of ion?
- (b) What types of point defect are prevalent in NaCl? Obtain an approximate expression for the concentration, n_d , of such defects in terms of the enthalpy of defect creation, h_d , starting from the Boltzmann equation for entropy. If $h_d = 2.3$ eV / atom, calculate the fractional concentration of such defects at 1500K.
- (c) What is the effect on the point-defect concentration in NaCl when CaCl_2 is incorporated into the rocksalt lattice?
- (d) Write down an expression for the ionic electrical conductivity in terms of the defect concentration and mobility, μ . If 10^{-3} mol% of CaCl_2 is dissolved into a crystal of NaCl (with unit-cell parameter $a = 5.7 \text{ \AA}$), and the doped crystal has a value of electrical conductivity $\sigma = 10^{-3} \text{ S m}^{-1}$ at 500K, obtain a value for the defect mobility at this temperature.
- (e) If the conductivity activation energy is $E_\sigma = 1.65 \text{ eV}$ at 1500K and $E_\sigma = 0.5 \text{ eV}$ at 500K, what is the activation energy for the defect mobility, E_μ ? Give reasons for your answer.

Approximate division of marks: (a) 15%; (b) 30%; (c) 10%; (d) 30%; (e) 15%.

[END OF PAPER]