# NATURAL SCIENCES TRIPOS Part IB

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**Friday 1st June 2007      1.30 to 4.30**

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## 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 x 4 sheets
Lined paper
Rough work pad
Cover sheets

**SPECIAL REQUIREMENTS**
Department of Chemistry Data Book
Master cover sheet

> 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

**A1**

Answer ***all*** parts of the question.

(a)  (i) Define, using equations, the terms *expectation value* and *uncertainty* used in quantum mechanics, and explain what these quantities predict about possible experimental measurements.
(ii) Under what conditions is it possible to predict an experimental measurement precisely?

(b)  Write down the Hamiltonian, unnormalised eigenfunctions $\Psi_n(x)$, and energy levels $E_n$, of a particle of mass $m$ confined to a 1-dimensional box of length $a$. Derive expressions, as a function of $n$, for:
(i)   the normalised eigenfunctions,
(ii)  the expectation value of the position $\langle x \rangle$,
(iii) the expectation value of the momentum $\langle p_x \rangle$,
(iv)  the uncertainty in the momentum $\Delta p_x$.

(c)  State the Heisenberg uncertainty principle, and use it to predict a lower limit for the uncertainty $\Delta x$ of a particle occupying the $n$th energy level of a 1-dimensional box.

(d)  Prove that the Hamiltonian of part (b) is a Hermitian operator, and demonstrate that the $\Psi_n(x)$ have the properties one would expect of the eigenfunctions of such an operator.

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

**A2**

Answer **all** parts of the question.

When expressed in atomic units, the radial part of a hydrogen 2p orbital has the form $R_{2p}(r) = \sqrt{\frac{1}{24}}\, r \exp(-r/2)$.

(a) Show that $R_{2p}(r)$ is an eigenfunction of the effective radial Schrödinger equation,
$$-\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R_{2p}(r) + \frac{1}{r^2}R_{2p}(r) - \frac{1}{r}R_{2p}(r) = E_{2p}R_{2p}(r),$$
and determine its eigenvalue $E_{2p}$.

(b) (i) Write down an expression for the probability of finding a 2p electron in a spherical shell of radius $r$ and thickness $dr$.

    (ii) At what distance from the nucleus is this electron most likely to be found?

(c) Prove that $R_{2p}(r)$ is normalised.

(d) The corresponding angular part of the 2p orbital can take one of the forms:
$$Y_{1,0}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta$$
$$Y_{1,\pm 1}(\theta,\phi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\exp(\pm i\varphi)$$

    (i) What is the meaning of the subscripts "1,0", "1,-1" and "1,1"?

    (ii) Which linear combinations of these functions must be taken in order to generate $2p_x$ and $2p_y$ orbitals?

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

**A3**

Answer **all** parts of the question.

(a) Explain how a trial wave function $\widetilde{\psi}$ and its approximate energy

$$\widetilde{E} = \frac{\langle \widetilde{\psi} | \hat{H} | \widetilde{\psi} \rangle}{\langle \widetilde{\psi} | \widetilde{\psi} \rangle}$$

can be systematically improved using the variational method.

(b) The electronic wave function of a diatomic molecule can be approximated as
$\widetilde{\psi} = c_a \phi_a + c_b \phi_b$, where $\phi_a$ and $\phi_b$ are atomic orbitals centred on each of the two atomic nuclei.

(i) Show that

$$\widetilde{E} = \frac{c_a^2 \alpha_a + c_b^2 \alpha_b + 2 c_a c_b \beta}{(c_a^2 + c_b^2) + 2 c_a c_b S} ,$$

where you should define (but not evaluate) the integrals $\alpha_a$, $\alpha_b$, $\beta$, $S$.

(ii) Assuming that $\alpha_a = \alpha_b = \alpha$, and $S = 0$, show that the best trial wave function and energy are obtained when

$$\begin{pmatrix} \alpha - \widetilde{E} & \beta \\ \beta & \alpha - \widetilde{E} \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}.$$

(c) (i) Explain how this last equation leads to the concept of bonding and anti-bonding orbitals in a diatomic molecule.

(ii) How and why do the energy levels and wave functions change when allowance is made for the overlap of $\phi_a$ and $\phi_b$?

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

**A4**

Answer *all* parts of the question.

(a) Write down an expression for the Morse potential, $V_M(r)$, explaining the meaning of the terms involved. Sketch the function $V_M(r)$, labelling it with key parameters. Show that the equilibrium dissociation energy is given by $\tilde{D}_e = \omega_e^2/4\omega_e x_e$ for the Morse potential, making clear any assumptions.

(b) The IR spectrum of the molecule RbH shows a very strong absorption peak at 908.5 cm$^{-1}$ and a much weaker one at 1788.7 cm$^{-1}$. Identify the likely origin of the vibrational transitions responsible for these two peaks. Hence show that the experimental dissociation energy is $\tilde{D}_o = 15040$ cm$^{-1}$, and obtain an estimate for the bond force constant, $k_m$, making clear any assumptions.

(c) If the equilibrium bond length of RbH is $r_e = 236.7$ pm, find an estimate for the value of the rotational quantum number, $J_{max}$, for which the rotational kinetic energy is equal to $\tilde{D}_o$ of this molecule. What would happen to the molecule if this condition could be reached? What is the population (relative to the $J = 0$ level) of the rotational state $J_{max}$ at 300 K? Comment on your answer.
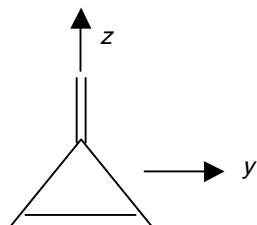
[m(Rb) = 85.47 amu]

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

**A5**

Answer *all* parts of the question.

(a)  What is the point group of the $C_4H_4$ molecule shown in the figure below?



(b)  Construct appropriate symmetry orbitals for this molecule from the four $p^\pi$ orbitals. Use the axis system in the Figure.

(c)  Using the symmetry orbitals deduced in part (b), construct the secular determinants for each symmetry species. Find the molecular-orbital energy corresponding to the smallest determinant in terms of the usual Hückel integrals $\alpha$ and $\beta$.

(d)  What is the sum of the molecular orbital energies for this molecule? Given that two of the other molecular orbital energies are $\alpha+0.311\beta$ and $\alpha-1.481\beta$, find the energy of the remaining molecular orbital. What is the delocalisation energy of this molecule?

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

**A6**

Answer *all* parts of the question.

(a) What is the point group of cyclopropane, $C_3H_6$?

(b) Classify the vibrations of cyclopropane using the point group identified in part (a). Which modes would be active in vibrational and Raman spectra?

(c) How many features would you expect to find for cyclopropane in the C-H stretching region of the above spectra?

(d) How many transitions would you expect to see in the C-H stretching region for transitions from the ground state to doubly-excited, singly-degenerate vibrational states?

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

**A7**

Answer *all* parts of the question.

(a)  What is the point group for the staggered configuration of ethane?

(b)  Using a basis set of $sp^3$ hybrid orbitals for carbon, construct symmetry orbitals for all the carbon valence orbitals primarily involved in CH bonding in ethane. Sketch a rough molecular-orbital energy-level diagram for ethane. Your diagram should include symmetry labels and a conventional classification in terms of bonds and antibonds.

(c)  The site symmetry of an atom in a molecule is the group containing all the point-group operations that do not change the position of the atom.
(i)   What is the site symmetry for the hydrogen and carbon atoms in ethane?
(ii)  Using your answer to part (i), or otherwise, deduce the characters of the representation spanned by the empty carbon 3d orbitals. Which of the occupied molecular orbitals can these 3d orbitals mix with?

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

# NATURAL SCIENCES TRIPOS Part IB

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## Wednesday 6th June 2007     1.30 to 4.30

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## CHEMISTRY A:  PAPER 2

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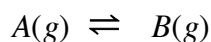
**A8**

Answer **all** parts of the question

(a) The chemical potential of an ideal gas can be written as:

$$\mu = -k_B T \ln\left[\frac{q}{N}\right],$$

where $q$ is the molecular partition function and $N$ is the number of molecules. Explain how this expression can be modified to give the chemical potential for species $i$ in a mixture, and to take into account the fact that different molecules have different ground-state electronic energies.

(b) For the equilibrium
$$A(g) \rightleftharpoons B(g)$$
show that the equilibrium constant (expressed in terms of concentrations) is given by

$$K_c = \frac{f_B}{f_A} e^{-\Delta E_o / k_B T},$$

where $f_i$ is the volume-independent partition function of species $i$ and $\Delta E_o$ is the difference between the electronic ground-state energies of B and A.

(c) Under what circumstances might $K_c$ be greater than unity for an endothermic reaction?

(d) Use the following data to compute $K_c$ at 700 K for the isomerization equilibrium
$$HCN(g) \rightleftharpoons HNC(g)$$

HCN : $\tilde{B}$ = 1.478 cm$^{-1}$; normal-mode frequencies (cm$^{-1}$) 3311, 2097, 712*
HNC : $\tilde{B}$ = 1.512 cm$^{-1}$; normal-mode frequencies (cm$^{-1}$) 3653, 2024, 464*
(where * indicates a doubly-degenerate vibration)
$\Delta E_o$ = 14.8 kJmol$^{-1}$
[$k_B$ = 0.695 cm$^{-1}$K$^{-1}$]

Approximate division of marks: (a) 10%, (b) 30%, (c) 10%, (d) 50%

**A9**

Answer *all* parts of the question

(a) Starting from the 'bridge relationship'

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

derive an expression for the molar entropy of a non-interacting gas in terms of the molecular partition function $q$ and the internal energy $U$.

Explain why a slightly different expression is used for calculating the translational entropy than is used for calculating the contribution to the entropy of the internal degrees of freedom (rotation, vibration, electronic).

(b) Consider a two-level system in which the ground state has a degeneracy of 2 and the excited state (at energy $\Delta$ above the ground state) has a degeneracy of 4.

Write down the partition function for this system and use it to show that
$$U = \frac{4N\Delta}{2e^{\Delta/k_B T} + 4} \ .$$
Discuss the limiting values of $U$ at low and high temperatures.

Hence derive an expression for the entropy contributed by this two-level system.

(c) The ground electronic state of NO is doubly degenerate, and an excited state lying 120 cm$^{-1}$ above the ground state has a degeneracy of 4. Compute the electronic contribution to the standard molar entropy of NO at 298 K.

(d) Compute the translational and rotational contributions to the standard molar entropy of NO at 298 K, given that $\theta_{rot} = 2.4$ K (use integer masses).
[$k_B = 0.695$ cm$^{-1}$K$^{-1}$]

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

**A10**

Answer *all* parts of the question

(a) Outline the key assumptions in the transition-state theory (TST) for the calculation of rate constants using statistical thermodynamics. Take the reaction

A + B-C → products
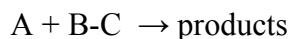
as an example.

[A proof is *not* required.]

(b) TST gives the second-order rate constant for the above reaction as

$$k_{2nd} = \frac{k_B T}{h} \frac{f'_{TS}}{f_A f_{BC}} e^{-\Delta E_o^{\ddagger} / k_B T} .$$

Explain briefly what $f'_{TS}, f_A, f_{BC}$ and $\Delta E_o^{\ddagger}$ each represent.

(c) Consider the reaction between two identical atoms, each of mass $m$. Assuming that the transition state is a diatomic with bond length $R$, obtain an expression for the pre-exponential factor for the reaction, using the expression in (b) above.

(d) Evaluate your expression for the case of the reaction between two iodine atoms at 298 K. Take the bond length in the transition state to be 3.76Å.

(e) In simple collision theory, the pre-exponential factor is given by:

$$A = \sigma \left( \frac{16 k_B T}{\pi m} \right)^{1/2}$$

where σ is the collision cross-section.

Use your value of $A$ from (c) to find an estimate for σ.

[$m(I) = 127$amu]

Approximate division of marks: (a) 15%, (b) 15%, (c) 40%, (d) 15%, (e) 15%

**A11**

Answer *all* parts of the question.

(a) What criteria justify the statement: *"the properties of the valence electrons in crystalline potassium metal are described satisfactorily by free-electron theory"*? Formulae may be quoted without derivation.

(b) Consider a one-dimensional crystal of $10^{-2}$ m length consisting of a chain of potassium atoms. Estimate the difference in energy between the highest occupied orbital and the lowest unoccupied orbital, making clear any assumptions or approximations that you use. Take the spacing between K atoms as 235 pm.
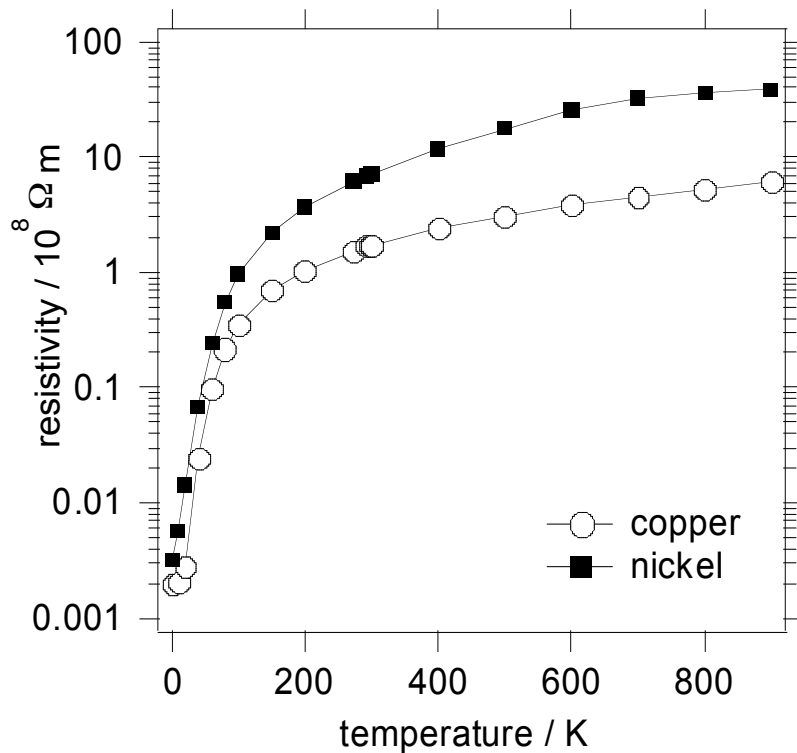
$$\left[ \frac{\hbar^2}{2m_e} = 6 \times 10^{-39} \, \text{m}^4 \text{kgs}^{-2} \right]$$

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

**A12**

Answer *all* parts of the question.

(a) Define the term *Brillouin zone*. Use this term to illustrate the transition from free-electron to LCAO theory.

(b) Lithium has a lattice constant of 3.49 Å and a free-electron density of $4.7 \times 10^{28} \text{m}^{-3}$. How many Brillouin zones are occupied by the Fermi surface of lithium?

(c) Sketch $N(E)$, the density of states as a function of electron energy, for Cu and Ni. How does $N(E)$ explain experimental results for the resistivity of Cu and Ni shown below?



(d) Explain how the *density of occupied states* $Z(E)$ is derived from $N(E)$. How can $Z(E)$ be measured?

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

**A13**

Answer *all* parts of the question

(a) Explain, by reference to appropriate energy-band diagrams, what is meant by: (i) a *direct* bandgap; (ii) an *indirect* bandgap, in an intrinsic semiconductor. Indicate, on these two diagrams, optically-induced electronic transitions satisfying the vertical selection rule. How does the threshold optical transition occur in the indirect-gap case?

(b) Estimate how 'vertical', in terms of wavevector, is the purely photon-induced threshold transition of a semiconductor **A**, with a direct bandgap of $E_g = 1eV$ and a unit-cell parameter of $a = 3Å$, by calculating the ratio of the difference in final and initial electron wavevectors, $\Delta k_e$, to the size of the Brillouin zone.

(c) What is an exciton? Draw a sketch of the expected optical-absorption spectrum of **A** if exciton formation occurs.

(d) Calculate the threshold energy for optical absorption in **A** in the case of exciton formation, if the dielectric constant of **A** is $\varepsilon = 10$ and the exciton reduced mass is $\mu = 0.5m_e$, where $m_e$ is the free-electron mass.

$[R_H = 13.6 \text{ eV}]$

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

**A14**

Answer *all* parts of the question

(a) By means of an appropriate electron-energy diagram, explain how the addition of phosphorus impurities, substituting for silicon atoms in the lattice of crystalline Si, can have a marked effect on the electrical conductivity of Si.

(b) An intrinsic semiconductor, **X**, exhibits an optical-absorption threshold at a wavelength of 1.77μm.  If its electrical conductivity at 400 K is $\sigma = 2.94 \times 10^{-2}\,\Omega^{-1}\mathrm{m}^{-1}$, estimate the value of the conductivity at 300 K, making clear your assumptions.

(c) If the electron mobility of **X** at 300 K is $\mu_e = 0.36\,\mathrm{m^2V^{-1}s^{-1}}$, and the total intrinsic carrier concentration is $2 \times 10^{16}\,\mathrm{m^{-3}}$, calculate a value for the hole mobility, $\mu_h$.

(d) Calculate a value for the conductivity of extrinsic **X** doped with $10^{24}\mathrm{m^{-3}}$ of donor atoms, making clear your assumptions.

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