NATURAL SCIENCES TRIPOS Part IB

Friday 28th May 2004   **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.

> 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) Write down the 1s orbital for a hydrogen-like (one-electron) atom with nuclear charge Z. Show that it obeys Schrödinger's equation. The normalisation constant is not required; use atomic units and spherical polar coordinates.

(b) From this 1s orbital, construct an approximate form for the $\sigma_g 1s(r)$ and $\sigma_u 1s(r)$ orbitals for H_2, again without normalisation.

(c) Evaluate the ratios $\sigma_g 1s(M)/\sigma_g 1s(A)$ and $\sigma_u 1s(M)/\sigma_u 1s(A)$, where M is the bond midpoint, and A is one of the protons, for the bond length $1.40a_o$. Sketch the form of these orbitals as functions of position along the internuclear axis.

(d) Repeat the calculation for an approximate $\sigma_g 1s$ orbital for O_2 ($Z = 8$), for which the bondlength is 2.29 a_o. Hence comment on the bonding characteristics of 1s orbitals.

(e) Give the electronic configuration of the ground state of O_2 in terms of molecular orbitals.

Approximate division of marks: (a) 20% (b) 5% (c) 25% (d) 25% (e) 25%.

A2

Answer *all* parts of the question

(a) Write down the Schrödinger equation for the harmonic oscillator, described as a particle of mass m moving on the x-axis in a potential $\frac{1}{2}m\omega^2 x^2$. Substitute the trial function e^{-ax^2} to derive the exact wavefunction and energy of the ground state.

(b) Sketch the harmonic potential, and on the same sketch show the lowest four energy levels and their corresponding wavefunctions. For each of these levels, find the values of x for which the classical momentum is zero. Hence explain the difference between the quantum and classical description of the harmonic oscillator.

(c) Obtain the probability that the particle is in the classically forbidden region for the ground state. [Use the substitution $x\sqrt{2a} = y$, with

$$\frac{2}{\sqrt{\pi}}\int_1^\infty e^{-y^2}\,dy = 0.158 \text{ and } \int_{-\infty}^\infty e^{-2ax^2}\,dx = \sqrt{\frac{\pi}{2a}}]$$

(d) Do you think this probability will be larger or smaller for the other states? Why?

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

A3

Answer *all* parts of the question

(a) What is the Pauli principle? Using the spin functions α, β write down the triplet and singlet combinations which are possible for two electrons, giving the quantum labels. Write down also the symmetric and antisymmetric combinations of products of two spatial orbitals φ_a, φ_b, again for two electrons. Hence write down possible space-spin wavefunctions which obey the Pauli principle.

(b) Obtain the possible term symbols for the atomic configuration $2s^2 2p^2$.

(c) Give an energy-level diagram which shows the terms and levels for the carbon atom in its $2s^2 2p^2$ configuration.

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

A4

Answer *all* parts of the question

(a) Sketch the form of a Morse potential energy function for a diatomic molecule and superimpose on this the first four vibrational energy levels ($v = 0$ to 3). Label the energies of each level in terms of $\tilde{\omega}$ and $\tilde{\omega}x_e$.

(b) Explain, indicating on your diagram as appropriate, the meaning of the terms *fundamental, first overtone* and '*hot band*' transitions. Find an expression for the frequency of each of these in terms of $\tilde{\omega}$ and $\tilde{\omega}x_e$.

(c) Show diagramatically that in the analysis of a rotation-vibration spectrum, the rotational constant in the lower vibrational state may be found by taking combinations of lines from the P and R branches according to the equation:

$$R_{(J-1)} - P_{(J+1)} = 2B(2J + 1)$$

Find an analogous expression which enables B in the upper state to be calculated.

The following lines have been observed in the high-resolution rotation-vibration infrared absorption spectrum of $^{81}Br^{35}Cl$.

$v' \leftarrow v''$	transition	wavenumber / cm^{-1}
$1 \leftarrow 0$	P(32)	428.496
	P(31)	428.845
	P(30)	429.191
	R(30)	447.494
$2 \leftarrow 1$	P(29)	425.890
	P(28)	426.231
	P(27)	426.572
	R(27)	442.993
$3 \leftarrow 2$	P(28)	422.557
	R(28)	439.485

(d) By taking the differences between suitable pairs of lines, find B_0, B_1, B_2 and B_3.

[QUESTION A4 CONTINUES ON THE NEXT PAGE]

[CONTINUATION OF QUESTION A4]

(e) By plotting an appropriate graph, determine B_e and hence calculate r_e, the internuclear separation at the bottom of the potential well.

(f) Calculate the vibrational band origins for each of the transitions $1 \leftarrow 0$, $2 \leftarrow 1$, and $3 \leftarrow 2$. Hence calculate $\tilde{\omega}$ and $\tilde{\omega}x_e$ for $^{81}Br^{35}Cl$ and an estimate of its dissociation energy in kJ mol^{-1}.

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

A5

Answer *all* parts of the question

1

2

$Re_2Cl_8^{2-}$
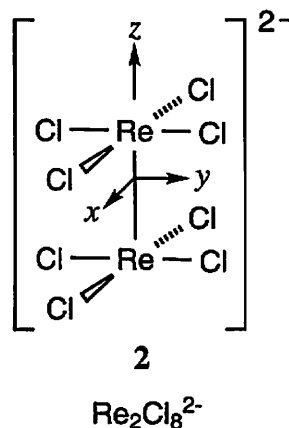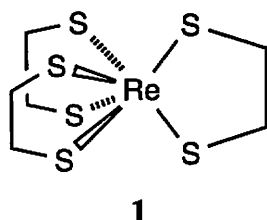
(a)   What are the point groups of molecules **1** and **2**?

(b)   The "site symmetry" of an atom is the subgroup of symmetry operations for which the atom is invariant. What are the site symmetries of the Re atoms in molecules **1** and **2**?

(c)   Using the subgroups found in (b), or otherwise, find the characters of the representations spanned by the Re 6s, 6p and 5d orbitals in each molecule. Reduce these representations.

(d)   Find the characters of the representations spanned by the eight chloride donor orbitals in $Re_2Cl_8^{2-}$. Reduce this representation.

(e)   What are the infra-red and Raman activities of the Re–Cl stretch modes in $Re_2Cl_8^{2-}$? Why are none of the stretches active in both infra-red and Raman?

(f)   If $Re_2Cl_8^{2-}$ can be described in terms of eight Re–Cl sigma bonds and a Re–Re quadruple bond formed from in-phase contributions of d_{z^2}, d_{xy}, d_{xz} and d_{yz} Re orbitals, predict the symmetries of the occupied molecular orbitals.
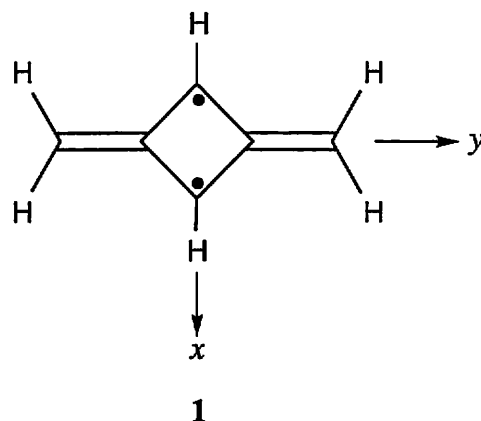
Distribution of marks: all parts carry the same weight.

[TURN OVER

A6

Answer *all* parts of the question

In the hypothetical diradical **1** all the C atoms are sp^2 hybridised, and each one contributes a single p^π orbital and one electron to the π system.

H
H   H
$\longrightarrow y$
H   H
H
$\downarrow$
x

1

(a)   What is the point group of this molecule?

(b)   Construct symmetry orbitals for the π system.

(c)   Calculate the energy levels of this π system in the Hückel approximation, noting that the secular equations can be reduced to 3×3, 2×2 and 1×1 determinants.

(d)   What is the delocalisation energy of **1**?

Distribution of marks: all parts carry the same weight.

A7

Answer *all* parts of the question

1   **2**   **3**

(a) What is the point group of the phosphazene molecule **1**?

(b) Find the characters of the representations spanned by the nitrogen p orbitals and the phosphorus d orbitals indicated in **2** and **3**.

(c) Construct symmetry orbitals for **2** and **3** and sketch them for **2**.

(d) If $\alpha_N = \alpha_P + \beta$, where $\alpha_N = \langle p^N | \hat{H} | p^N \rangle$, $\alpha_P = \langle d^P | \hat{H} | d^P \rangle$ and $\beta = \langle p^N | \hat{H} | d^P \rangle$ for in-phase $p^\pi - d^\pi$ overlap, calculate the energies of the six π molecular orbitals formed from sets **1** and **2** in the Hückel approximation. Note that it is only necessary to calculate the energy for one component of a degenerate pair of orbitals. Sketch an energy level diagram.

(e) Predict the Raman and infra-red activities of the P–Cl stretching modes.

Distribution of marks: all parts carry the same weight.

[END OF PAPER]

NATURAL SCIENCES TRIPOS Part IB

Wednesday 2nd June 2004   1.30 to 4.30

CHEMISTRY A: PAPER 2

There are seven questions on this paper.

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A8

Answer *all* parts of the question

(a) Contrast the *Boltzmann* and *Fermi–Dirac* distributions; in your answer make it clear how the two distributions differ at absolute zero and at a finite temperature, and define the *Fermi energy*. Give an example of a system for which the Boltzmann distribution is appropriate and an example of a system for which the Fermi–Dirac distribution is appropriate.

(b) Show that for a freely-translating, non-interacting particle of mass m occupying a volume V, the number of states with energy less than or equal to ε, $W(\varepsilon)$, is given by

$$W(\varepsilon) = \frac{\pi}{6}\left(\frac{8m\varepsilon}{h^2}\right)^{\frac{3}{2}} V \ .$$

Hence derive an expression for the Fermi energy for an arrangement consisting of N electrons occupying volume V.

(c) Given that the density of potassium metal is 0.86 g cm^{-3}, estimate the Fermi energy (in eV) and the Fermi temperature. Use your value of the Fermi energy to estimate the contribution which the electrons make to the molar heat capacity of the metal at 298 K.

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

A9

Answer *all* parts of the question

(a) The internal energy, U, is given in terms of the partition function Q_N, by

$$U = kT^2 \frac{1}{Q_N}\left(\frac{\partial Q_N}{\partial T}\right)_V .$$

Show how this expression can be modified for the case of N non-interacting molecules so as to give U in terms of the molecular partition function, q.

(b) At low temperatures, *para* hydrogen behaves as if it were a two level system, with the two levels being the rotational states with $J = 0$ and $J = 2$. Assuming that the rotational states can be modelled using the rigid rotor energy levels, show that the molecular partition function is given by

$$q = 1 + 5\exp\left(\frac{-6B}{kT}\right),$$

where B is the rotational constant. For this two-level system, what value does q take at low temperatures (meaning $B \gg kT$) and high temperatures (meaning $B \ll kT$)? Sketch a graph of how q varies with T, labelling the axes.

(c) Show that for this two level system the internal energy for N molecules is given by

$$U = \frac{30NB}{\exp\left(\frac{6B}{kT}\right) + 5} .$$

Determine the values of U for this two-level system at low and high temperatures; comment on the values you obtain. Make a labelled sketch plot of how U varies with temperature.

(d) Obtain an expression for the constant-volume heat capacity of the two-level system, explore its values at low and high temperatures, and make a labelled sketch plot of how the heat capacity varies with temperature.

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

A10

Answer *all* parts of the question

(a) What do you understand by the *equipartition principle* and when can it be applied? Use the principle to estimate the different contributions (translational, rotational, vibrational and electronic) to the internal energy of $F_2(g)$.

(b) For a harmonic oscillator the energy levels, measured relative to the ground state, are $E_v = vh\upsilon_0$, where $v = 0, 1, 2 \ldots$ and υ_0 is the vibrational frequency. Determine the vibrational partition function and hence show that the vibrational internal energy of N oscillators is given by

$$U'_{vib} = \frac{Nh\upsilon_0}{\exp\left(\dfrac{h\upsilon_0}{kT}\right) - 1} .$$

(c) Calculations made for the anion F_2^- predict it to have a vibrational frequency of 450 cm^{-1} and a rotational constant of 0.49 cm^{-1}. The electronic ground state is found to be doubly degenerate.

Calculate the translational, rotational, vibrational and electronic contributions to the standard molar entropy at 298 K. Any further formulae you need can be quoted without proof.

$\left[\text{The translational entropy is given by } S_{trans} = NK \ln q_{trans} - Nk \ln N + Nk + \dfrac{U_{trans}}{T}\right]$

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

A11

Answer *all* parts of the question

(a) The equilibrium constant, K_c, for the reaction

$$2 A \rightarrow B$$

can be computed from statistical thermodynamics using the expression

$$K_c = \frac{f_B c^0}{f_A^2} \exp(-\Delta\varepsilon_o / kT) .$$

Explain carefully what f_i, c^0 and $\Delta\varepsilon_o$ represent.

(b) Use *transition state theory* and the expression for K_c from part (a), to show that the second-order rate constant, k_{2nd}, for the bimolecular reaction $2 A \rightarrow$ products is given by

$$k_{2nd} = \frac{kT}{h} \frac{f_{TS}'}{f_A^2} \exp(-\Delta\varepsilon_o^{\ddagger} / kT) ,$$

explaining carefully what f_{TS}' and $\Delta\varepsilon_o^{\ddagger}$ represent.

(c) In the gas phase, ClO reacts with itself to produce $Cl_2 + O_2$. The reaction is thought to take place in a single bimolecular step:

$$2\, ClO \rightarrow [\text{transition state}] \rightarrow Cl_2 + O_2$$
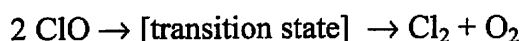
The geometry of the transition state Cl_2O_2 has been determined by theoretical calculations. Use the data below to compute k_{2nd} for this reaction at 400 K, giving the units of your answer. Also give k_{2nd} in units of $mol^{-1}\ dm^3\ s^{-1}$.

ClO: molecular weight 51, rotational temperature 0.94 K, vibrational temperature 1151 K, the ground electronic state is two-fold degenerate. Cl_2O_2: rotational partition function at 400 K $= 4.11 \times 10^3$, vibrational partition function (measured from the bottom of the potential energy well) at 400 K $= 2.75 \times 10^{-3}$, the electronic ground state is not degenerate, $\Delta\varepsilon_o^{\ddagger} = 0$.

Approximate division of marks: (a) 15% (b) 40% (c) 45%.

A12

Answer *all* parts of the question

(a) One-electron Bloch wavefunctions Ψ_k for a linear chain of N atoms separated by distance a may be written in the form:

$$\Psi_k = e^{ikx} u(x)$$

Show that, when periodic boundary conditions are applied, there are N allowed values of the wavevector k within the first Brillouin zone; $-\pi/a \leq k < \pi/a$.

(b) Within the LCAO approximation, the wavefunction Ψ_k for a one dimensional chain may be written as

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

where χ_n is an atomic orbital on the nth atom of the chain and a is the repeat distance of the chain, $-\pi/a \leq k < \pi/a$. Demonstrate that states outside this range of k are identical to states within the first Brillouin zone.

(c) Consider a binary chain of Ag and Cl atoms in which the interacting orbitals are $Ag(4d_{xz})$ and $Cl(3p_z)$ respectively, as indicated below.
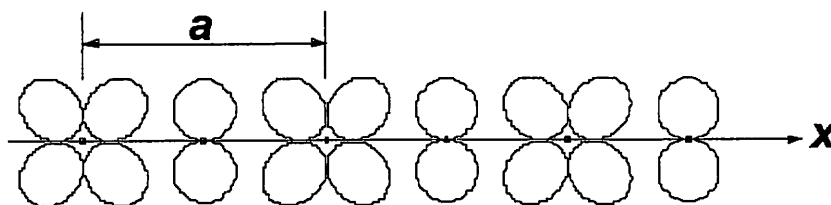
If it assumed that the energy of the $Ag(4d_{xz})$ is lower than that of the $Cl(3p_z)$ draw trial wavefunctions for the wavevector values $k = 0$ and $k = \pi/a$. Give reasons for your choice and hence sketch the energy band diagram for the first Brillouin zone. What is the consequence of this calculation for the electronic structure of AgCl?

[QUESTION A12 CONTINUES ON THE NEXT PAGE]

[CONTINUATION OF QUESTION A12]

(d) An LCAO calculation for a chain of $Cl(3p_z)$ orbitals, for which the repeat distance $a = 0.28$nm, yields a Huckel parameter $\beta = -0.25$ eV. Calculate the effective mass for an electron occupying a state in this band with $k = \pi/a$ and comment upon the value that you obtain. Equations may be quoted without proof. Give your answer in units of m_e.

Approximate distribution of marks: (a) 15% (b) 15% (c) 40% (d) 30%.

A13

Answer *all* parts of the question

(a) Explain by means of a suitable diagram how orbital hybridisation results in the formation of a band gap for diamond. Explain the factors that cause a band gap to form in diamond also offer a rationalisation for the properties of tin.

(b) Show how classical statistical thermodynamics may be used to obtain an equilibrium constant K_c for electron-hole pair formation in an intrinsic semiconductor. (The formula for K_c may be quoted without proof). Identify any approximations that are made in the derivation and provide justifications for their validity.

(c) Calculate the intrinsic concentration of electrons at 300K in the direct gap semiconductor GaAs for which $m_e^* = 0.07m_e$, $m_h^* = 0.68m_e$ and $E_g = 1.43$ eV.

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

A14

Answer *all* parts of the question

(a) Starting from the expression for the force **F** upon a particle with charge q moving with velocity **v** in a magnetic field **B**,

$$\mathbf{F} = q\,\mathbf{v} \times \mathbf{B}$$

define the Hall coefficient R_H in terms of measurable quantities and derive an expression for R_H in terms of the charge and density of the moving particle.

(c) A sample of a doped semiconductor 5 mm wide (y direction) and 2 mm thick (z direction) is placed in a magnetic field 0.2 T (z direction). When a current of 1 mA passes through the sample (x direction) a Hall Voltage of -0.3×10^{-4} V is observed. Identify the type and concentration of dopant.

(c) At 300K the electron concentration in an intrinsic semiconductor was found to be 1.5×10^{16} m^{-3}. If the mobilities of the electrons and holes are 0.13 and 0.05 m^2 V^{-1} s^{-1} respectively, calculate the conductivity at 300K. At 275K the conductivity of this sample has been found to be 5.83×10^{-5} S^{-1} m^{-1}. Using this information estimate the band gap. Identify any assumptions and approximations which you make.

Approximate division of marks: (a) 40% (b) 25% (c) 35%.

[END OF PAPER]