NATURAL SCIENCES TRIPOS Part 1B

Friday 28th May 2010   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.

Linear graph paper is available if required.

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 subsequent pages of this question paper until instructed to do so by the Invigilator.

STATIONERY REQUIREMENTS
Graph paper x 4 sheets
Lined paper
Rough work pad
Cover sheets

SPECIAL REQUIREMENTS
Chemistry master cover sheet
Department of Chemistry Data Book

A1 *Answer all parts of the question*

(a) The Hermitian conjugate $\hat{Q}^\dagger$ of an operator $\hat{Q}$ satisfies

$$\int \psi_n^* \hat{Q} \psi_m \, d\tau = \int (\hat{Q}^\dagger \psi_n)^* \psi_m \, d\tau \qquad (1)$$

for any two funtions ψ_n and ψ_m with the relevant boundary conditions.

(i) What is a Hermitian operator, and why are such operators important in quantum mechanics?

(ii) Express Eq. (1) in the Dirac bracket notation and show that nondegenerate eigenfunctions of a Hermitian operator are mutually orthogonal.

(iii) Find the Hermitian conjugate of the operator d/dq.

(b) The Hamiltonian of the harmonic oscillator in scaled coordinates is

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

(i) One eigenfunction of H is

$$\varphi = (2q^3 - 3q)e^{-q^2/2} .$$

Without detailed calculation, deduce the quantum number of this wavefunction and state its energy.

(ii) Consider the operator

$$\hat{Q} = q + \frac{d}{dq} .$$

Show that $(\hat{Q}\varphi)$ is also an eigenfunction of H and find its energy.

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

A2 *Answer all parts of the question*

(a) (i) Find the constant N that normalises the pair of hydrogen-like wavefunctions

$$\psi_\pm = N\, r^2\, e^{-Z\,r/3}\, \cos\theta \sin\theta\, e^{\pm\, i\,\phi},$$

where Z is the nuclear charge.

(ii) Write down the operator $\hat{l}_z$ for the z-component of the orbital angular momentum and use it to find the quantum numbers m_l of $\psi_\pm$.

(iii) To which atomic orbitals do $\psi_\pm$ correspond?

(b) (i) Write down the Hamiltonian of the helium atom in atomic units, explaining the meaning of the symbols you use.

(ii) It is convenient to write the spatial wavefunctions of many-electron atoms as (suitably symmetrised) products of hydrogen-like orbitals. Why are such wavefunctions necessarily approximate?

(iii) Give a concise account of the central field approximation and how it allows us to retain the concept of atomic orbitals in many-electron atoms.

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

A3 *Answer all parts of the question*

(a)   Give a concise statement of Hund's rules.

(b)   Justify Hund's first rule in terms of the Pauli principle and the concept of Fermi holes, using appropriate equations to make the argument clear.

(c)   Why is the ground electronic term of the chromium atom ^7S rather than ^5D?

(d)   What physical effect causes an electronic term to split into levels? What levels arise from the ground term of the vanadium atom and which lies lowest in energy?

(e)   The ground electronic term of the O_2 molecule is $^3\Sigma_g^-$. Explain the meaning of this term symbol. Predict the ground term of the O_2^+ molecular ion.

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

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A4 *Answer all parts of the question*

(a) (i) Write down expressions for the potential energy of the harmonic oscillator, $V_H(r)$, and for the Morse potential $V_M(r)$, explaining the meaning of the terms involved. Sketch both the functions, labelling any key parameters.

(ii) Give an equation for the energy levels of a Morse oscillator and use this to derive an expression for the bond dissociation energy, measured from the bottom of the potential energy well.

(b) The ground state electronic configuration, X, of Be_2 is $(2s\sigma_g)^2(2s\sigma_u)^2$. It is possible to promote an electron to give the excited state, B, with configuration $(2s\sigma_g)^2(2s\sigma_u)^1(2p\sigma_g)^1$. The following transitions have been observed for the transitions from state X to B:

transition / cm^{-1}	v''	v'
27860.3	0	0
28363.5	0	1
28854.7	0	2
27636.1	1	0
27466.0	2	0

(i) Sketch a diagram showing these observed transitions.

(ii) Calculate, in cm^{-1}, the values of ω and ωx_e and hence D_e and D_0 for both the ground and excited states of Be_2. Comment on the values of D_0 you obtain.

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

**A5** *Answer all parts of the question*
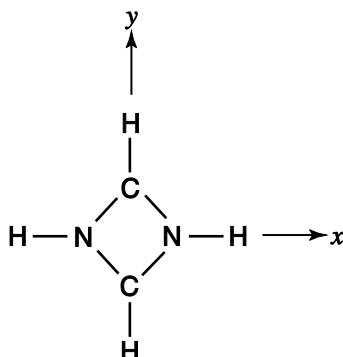
(a)   Identify the point group of the planar molecule in the figure.

(b)   Assume that the atoms in the ring are sp^2 hybridised, with a lone pair on each nitrogen atom in the *xy* plane. Construct symmetry orbitals from the p_z orbitals on the two carbon and the two nitrogen atoms, and specify how they transform.

(c)   Assume that $\alpha_N = \alpha_C + \beta$, where α_C is the Hückel α parameter for the carbon p_z orbitals, and the Hückel β parameters are β for the carbon–nitrogen integrals and zero otherwise.
Construct the secular equations for each symmetry species spanned by the p_z orbitals, and hence find the molecular orbital energies for the π system in this molecule.

(d)   Which of the molecular orbital energies change if $\beta_{CC} = \beta$ instead of zero for the interaction of the carbon p_z orbitals? Find the new energies for these orbitals.

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

A6 *Answer all parts of the question*
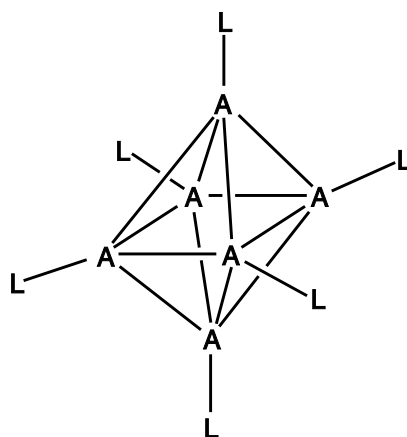
(a)   What is the point group for the structure shown above which is an octahedral cluster of six atoms, A, with identical structureless ligands, L, (treated as points)? Define what is meant by the site symmetry of an atom, and determine the site symmetry for the A and L sites.

(b)   Treating the A atoms as fixed, find the symmetries of the 18 fundamental vibrational normal modes involving motion of the ligands. Which of these modes are active in Raman and infra-red vibrational spectra? What are the activities of the A−L stretching modes?

(c)   Now suppose that one of the L ligands is substituted by a different ligand, M, also treated as a structureless point. What is the new point group for the A_6L_5M molecule? Identify the sites corresponding to distinct chemical environments and deduce the site symmetry for each. What are the Raman and infra-red activities of the A−L and A−M stretching modes in this molecule?

(d)   For the non-degenerate vibrational modes in part (c), identify the Raman and infra-red activity of all the overtone and combination transitions that start from the ground state.

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

A7 *Answer all parts of the question*

In this question we consider the carboxylate ion RCO_2^-, treating the alkyl group R as a pseudoatom (a single point mass).
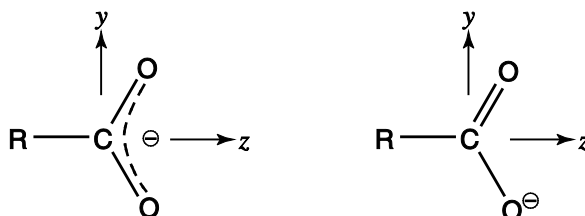
(a)   What is the point group for this ion (i) for the structure with equivalent C−O bonds and delocalised π bonding, and (ii) for the structure with inequivalent C=O and C−O⁻ bonds?

(b)   For the delocalised carboxylate ion shown in part (i) of the figure, construct symmetry orbitals from the p_x orbitals of the carbon and oxygen atoms in the π system.

(c)   Taking $\alpha_O = \alpha_C + \beta$, where α_C is the Hückel α parameter for the carbon p_x orbital, and β is the Hückel parameter corresponding to the carbon−oxygen p_x interaction, calculate the molecular orbital energies for the π system. Sketch the corresponding energy level diagram and calculate the total π electron energy.

(d)   For the localised description with inequivalent C=O and C−O⁻ bonds solve the two-level Hückel problem for the C=O double bond using the same parameters as in part (c). Hence calculate the delocalisation energy for the carboxylate group.

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

[END OF PAPER]

NATURAL SCIENCES TRIPOS Part 1B

Wednesday 2nd June 2010   13.30 to 16.30

CHEMISTRY A: PAPER 2

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A8 *Answer all parts of the question*

(a)   Starting from the 'bridge relationship' $A = -kT \ln Q_N$, derive an expression for the entropy of a system consisting of N non-interacting indistinguishable molecules with molecular partition function q. Be sure in your derivation to explain each step carefully. Go on to show that the contribution to the entropy due to translational degrees of freedom can be written

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

and derive a corresponding expression for the rotational contribution to the entropy.

(b)   As well as the contribution which the overall rotation of a molecule makes to its entropy there are also contributions from *internal rotations* such as that of a methyl group rotating about the bond which connects it to the rest of the molecule. If it is assumed that the barrier to this rotation is negligible, then the energy levels associated with this rotation are given by

$$\varepsilon_n = \frac{n^2 h^2}{8\pi^2 I} \qquad n = 0, \pm 1, \pm 2, \pm 3 \ldots,$$

where I is the moment of inertia of the CH_3 group about the axis of the bond connecting it to the rest of the molecule.
Assuming that the temperature is such that many energy levels contribute, show that the corresponding partition function $q_{\text{int. rot.}}$ is given by

$$q_{\text{int. rot.}} = \left(\frac{8\pi^3 IkT}{h^2}\right)^{\frac{1}{2}}.$$

(c)   Use this expression for $q_{\text{int. rot.}}$ to determine the contribution that free rotation of a methyl group makes to the molar entropy at 298 K taking the value of I to be 5.36×10^{-47} kg m^2.

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

**A9** *Answer all parts of the question*

(a)   The chemical potential μ_i of species i in a mixture of ideal gases is given by

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

where q_i is the molecular partition function, N_i is the number of molecules. Describe what the energy term $\varepsilon^{0,i}$ represents.
By expressing the partition function in terms of the volume independent partition function f_i (where $f_i = q_i / V$), show that the equilibrium constant for the reaction
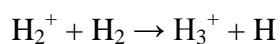
$$A + B \rightleftharpoons C + D$$
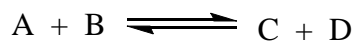
can be expressed as

$$K_c = \frac{f_C f_D}{f_A f_B} \exp\left(-\Delta\varepsilon^0 / kT\right).$$

In your answer, be sure to define $\Delta\varepsilon^0$.

[A9 continues over the page]

A9 continued

(b)   A spectroscopist who wishes to study the H_3^+ (which is found in great abundance in interstellar space) proposes to create the molecule by the gas-phase reaction between H_2^+ and H_2:

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

Use the data below to estimate the equilibrium constant for this reaction at 500 K, assuming that $\Delta\varepsilon^0$ is zero. You are advised to compute the values of the rotational and vibrational partition functions separately for each molecule. Use integer masses.

Data

H_2: $\theta_{rot} = 85.4$ K, $\theta_{vib} = 5987$ K

H_2^+: $\theta_{rot} = 41.6$ K, $\theta_{vib} = 3162$ K

H_3^+ is planar with the atoms forming an equilateral triangle. The rotational partition function is given by

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

where $\theta_{a,rot}$, $\theta_{b,rot}$ and $\theta_{c,rot}$ are the characteristic temperatures associated with rotation about the three principal axes: $\theta_{a,rot} = 59.6$ K, $\theta_{b,rot} = 59.6$ K and $\theta_{c,rot} = 29.8$ K. For this molecule the symmetry factor σ takes the value 3. H_3^+ has three normal modes. The first has a vibrational temperature of 4573 K and the other two are degenerate with vibrational temperatures of 3628 K.

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

A10   *Answer all parts of the question*

(a)   In the thermodynamic formulation of transition state theory the second-order rate constant for a reaction in solution can be expressed as

$$k_{2nd} = \frac{1}{[\,]^\circ} \frac{kT}{h} \exp\left(\frac{-\Delta_r G^{\circ,\ddagger}}{RT} \right)$$

where $[\,]^\circ$ is the standard concentration and $\Delta_r G^{\circ,\ddagger}$ is the standard Gibbs energy of activation. Show how this relationship can be developed so as to introduce the standard molar volume of activation $\Delta_r V^{\circ,\ddagger}$. Go on to describe a graphical method by which measurements of the rate constant as a function of pressure can be used to determine a value for the volume of activation. Why is the volume of activation only a useful concept for reactions in solution?

(b)   The pseudo first-order rate constant, k_{1st}, for the solvolysis of *t*-amyl chloride in ethanol has been measured at 34.2 °C as a function of pressure to give the following data:

pressure / atmosphere	1.00	340	680	1020	1360
$10^5 \times k_{1st} / s^{-1}$	4.50	5.69	7.36	9.58	11.7

Analyse these data graphically so as to obtain a value of $\Delta_r V^{\circ,\ddagger}$ for this reaction. Comment on the value you obtain.

[*t*-amyl chloride is 2-methyl-2-chlorobutane, and solvolysis is a reaction with the solvent itself]

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

A11 *Answer all parts of the question*

(a) Explain how the concept of reciprocal space is used to represent the wave-like properties of electrons in crystalline solids, with particular reference to the reciprocal lattice, the Brillouin zone, and the Born von Karman boundary conditions.

(b) Derive an expression for the density of electronic states in reciprocal space of a 3D solid.

(c) What is the physical interpretation of the Fermi energy? Derive an expression for the Fermi wave-vector of a crystalline solid, and thence the Fermi energy, assuming n electrons per unit volume.

(d) Derive an expression for the density of states at the Fermi level. *Estimate* the molar electronic heat capacity of Cu (density 8960 kg m^{-3}) at room temperature, making clear any assumptions used.

(e) Suggest and briefly explain two other experimental methods which would allow the free electron model to be tested.

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

A12   *Answer all parts of the question*

(a)   Outline qualitatively the significance of the *exchange interactions* in the magnetism of solid materials.

(b)   Assuming a spin unpolarised ground state with N electrons in volume Ω, and neglecting any exchange interactions, show that changing the spin orientations of δn electrons leads to an energy change $\Delta E = 2(\delta n)^2 / g$, where g is the density of states at the Fermi level.

(c)   Show how the expression for ΔE is modified in the presence of an external applied magnetic field H, and use this expression to show that the magnetisation M of a material can now be related to the applied magnetic field by:

$$M = \chi_p H$$

where χ_p is the paramagnetic susceptibility. Find an expression for χ_p.

(d)   Show how ΔE is again modified following the inclusion of electron exchange interactions and use this expression to derive the paramagnetic susceptibility:

$$\chi = \frac{\chi_p}{1 - gJ}$$

where J is the exchange integral and gJ is referred to as the 'Stoner Parameter'. Explain how the Stoner Parameter can be used to predict the magnetic properties of a material and why only some materials show ferromagnetism.

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

A13 *Answer all parts of the question*

(a)   What is meant by the term *electronic density of states* (EDOS)? Explain how the EDOS is related to the band structure $E(k)$ of a crystal.

(b)   What is a van Hove singularity in the EDOS of a crystal and what type of feature in $E(k)$ does it correspond to?

(c)   Sketch the EDOS for:

                    i) crystalline silicon

                    ii) graphite

Label relevant features of these sketches, and in each case indicate which type of atomic orbitals contribute predominantly in particular regions of the EDOS. With reference to the EDOS, account for the electrical behaviour of each material in the *intrinsic* state.

(d)   Indicate on EDOS diagrams how the incorporation of the impurities, arsenic in silicon and lithium in graphite, affects the states in the EDOS and their electron occupancy. In each case, mark the position of the Fermi level at $T = 0K$ on the EDOS diagram, and comment on how the electrical behaviour differs from that in case (c).

(e)   Give two examples of conditions under which *extrinsic* crystalline silicon containing arsenic impurities may, nevertheless, behave as an *intrinsic* material.

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

A14   *Answer all parts of the question*

(a)   The low-temperature optical absorption spectrum of crystalline GaAs reveals, with decreasing wavelength, a series of peaks the first being at $\lambda_1 = 8376$ Å, followed by a rise to a continuum at $\lambda_2 = 8266$ Å.

Deduce what you can about the properties of GaAs, given that the electron and hole effective masses can be taken to be $m^* = 0.5 \; m_e$. What happens to this spectrum with increasing temperature?

(b)   Describe the effects on the electronic structure of substitutionally doping GaAs with Ge impurity atoms.

(c)   Describe, as quantitatively as you can, the changes to the optical absorption spectrum of Ge-doped GaAs that you would expect at both high and low temperatures.

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

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

[END OF PAPER]