



UNIVERSITY OF CAMBRIDGE

NATURAL SCIENCES TRIPOS Part IB

Friday 31st May 2013

13:30 to 16.30

CHEMISTRY A: PAPER 1

Candidates should attempt all 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.

STATIONERY REQUIREMENTS

Graph paper (4 sheets)

Lined paper

Rough work pad

SPECIAL REQUIREMENTS

Chemistry master cover sheet

Department of Chemistry Data Book

Calculator – students are permitted to bring an approved calculator.

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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> |
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A1

Answer *all* parts of the question.

- (a) (i) What is the significance in quantum mechanics of an operator \hat{Q} and its associated expectation value $\langle \hat{Q} \rangle$?
- (ii) Write down expressions for $\langle \hat{Q} \rangle$ for (I) a non-normalised and (II) a normalised wave function.
- (iii) Give expressions for the uncertainty ΔQ , and explain (in one sentence) its significance.
- (iv) Which condition has to be met to ensure that $\Delta Q = 0$?
- (b) The Hamiltonian for a harmonic oscillator can be written in scaled coordinates q as

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

and the ground state wave function is

$$\Psi = \exp(-q^2/2).$$

- (i) Calculate the ground state expectation values of the operators \hat{q} and \hat{q}^2 and hence obtain the uncertainty in position Δq .
- (ii) The momentum operator in scaled coordinates is $\hat{p} = -id/dq$. Calculate the ground state expectation values of \hat{p} and \hat{p}^2 , and hence obtain the uncertainty in momentum Δp .
- (c) (i) Define the commutator $[\hat{A}, \hat{B}]$ of two operators \hat{A} and \hat{B} .
- (ii) Evaluate the expectation value of the commutator $[\hat{p}, \hat{q}]$ for the case of the harmonic oscillator in its ground state, and thus verify the uncertainty relation

$$\Delta p \Delta q \geq \left| \frac{1}{2} \langle [\hat{p}, \hat{q}] \rangle \right|$$

- (iii) How might your answer to part (ii) change for an excited state of the harmonic oscillator?

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

A2

Answer *all* parts of the question.

- (a)
 - (i) State the Pauli principle for electrons.
 - (ii) Consider a helium atom represented by an approximate wave function $\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2)$, where $\mathbf{r}_1, \mathbf{r}_2$ are the positions of electrons 1 and 2. Give equations showing how this wave function must be combined with spin wave functions and modified in order to give approximate wave functions that are consistent with the Pauli principle.
 - (iii) Use your answer to (ii) to justify the Pauli *exclusion* principle (that two electrons with the same spin cannot occupy the same orbital).
 - (iv) Use your answer to (ii) to justify Hund's first rule for the case of He; [you are not expected to make use of integrals in your answer].
- (b)
 - (i) Show, using the example of C($1s^2 2s^2 2p^2$) how the use of Hund's rules allows one to make predictions about the nature of the ground state wave function of an atom. Your answer should make use of term symbols.
 - (ii) Explain why N($1s^2 2s^2 2p^3$) has a greater first ionization energy than O($1s^2 2s^2 2p^4$).
 - (iii) Obtain and order the three lowest electronic energy levels of Ti([Ar] $4s^2 3d^2$). How would the ordering of these levels change for the case of Ni([Ar] $4s^2 3d^8$) and why?

Approximate division of marks: (a) 45%, (b) 55%.

A3

Answer *all* parts of the question.

- (a) Giving your reasons, outline the principal differences between the vibrational spectra which you would expect to observe for harmonic and anharmonic oscillators.
- (b) Giving your reasons, suggest how you might expect the bond length, and thus the rotational constant, of a diatomic molecule to change as it is excited into:
- a higher *vibrational* state
 - a higher *electronic* state.
- (c) Spectroscopic measurements were made for the electronic transition from the ground state, X, ($^2\Sigma^+$) to the first allowed excited state, A, of the molecule $^{12}\text{C}^{14}\text{N}$. Rotational fine structure for the $v'' = 0$ to $v' = 0$ transition were assigned as below (in cm^{-1}).

| R_0 | R_1 | P_1 | P_2 |
|---------|---------|---------|---------|
| 9118.00 | 9121.05 | 9110.81 | 9106.66 |

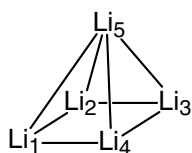
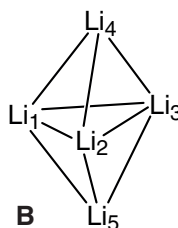
- Draw a schematic diagram to show these transitions.
 - Use the information to obtain the rotational constants and thus the bond lengths in the X and A states (assume integer atomic masses).
 - In light of your answers to (ii), suggest the electronic configuration and term symbol for the A state.
 - Indicate, with reasons, how you might expect the vibrational frequencies of the X and A states to differ.
- (d) Further measurements showed the presence of an electronic transition at approximately 26000 cm^{-1} . Detailed measurements allowed a rotational constant to be determined of 1.96 cm^{-1} . Assuming the transition is from the ground state, suggest, with reasons, an electronic configuration and term symbol for the excited state which is consistent with this observation.

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

A4

Answer *all* parts of the question.

Structures **A** and **B** are proposed as possible configurations of the Li_5 cluster: square-based pyramidal, and trigonal bipyramidal respectively.

**A****B**

- What is the point group of each structure?
- Considering the Li $2s$ orbitals, construct symmetry orbitals for both structures.
- Using Hückel theory, for each structure calculate the molecular orbital energies and draw a symmetry-labelled molecular orbital energy diagram. You should assume that all nearest neighbour Li-Li bond distances are the same, and only consider the interactions explicitly shown. *The individual coefficients in the MOs are not required.*
- These clusters may have an overall charge. For what values of total charge is structure **A** more stable than **B**?

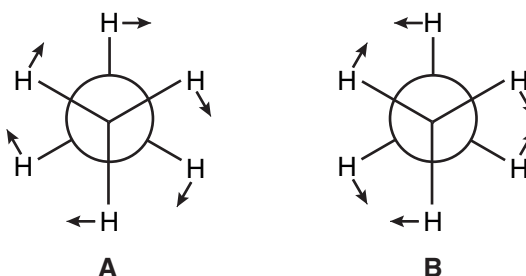
Approximate division of marks: (a) 10%, (b) 20%, (c) 60%, (d) 10%.

A5

Answer **all** parts of the question.

- (a) Give the point group of the molecule and determine the irreducible representation(s) spanned by each of the following, and comment on the origins of any degenerate representations:

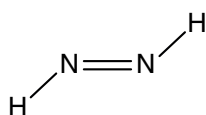
- (i) the rotations **A** and **B** of the methyl groups in the staggered conformation of ethane;



- (ii) the electronic wavefunction of the lowest excited state of N_2 where an electron has been promoted from a $\pi \rightarrow \pi^*$ orbital
- (iii) the U 5*f* orbitals f_{xyz} , $f_{z(x^2-y^2)}$, f_z^3 , f_{xz^2} , and f_{yz^2} in *trans*- UF_4Cl_2 in which the overall coordination of uranium is octahedral.

[The *f*-functions are labelled with their principal Cartesian components which are sufficient to determine the symmetry of the orbitals.]

- (b) For the following structure of diazene:



- (i) Determine the symmetries of the normal modes of this molecule.
- (ii) By considering the symmetries of the in-plane N–H stretches and N=N–H bends, or otherwise, sketch the displacements involved in each of the infrared active normal modes.

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

END OF PAPER



UNIVERSITY OF CAMBRIDGE

NATURAL SCIENCES TRIPOS Part IB

Wednesday 5th June 2013

13.30 to 16.30

CHEMISTRY A: PAPER 2

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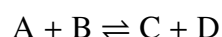
A6

Answer *all* parts of the question.

- (a) Given that the chemical potential of an ideal gas in a mixture of gases is given by :

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

where q_i is the molecular partition function and N_i is the number of moles, show that the equilibrium constant of the gas phase reaction :

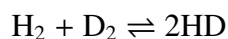


can be expressed as :

$$K_c = \frac{f_C f_D}{f_A f_B} \exp(-\Delta\varepsilon^{\circ}/kT),$$

where f_A , f_B , f_C and f_D are the volume independent partition functions (*i.e.* q_i/V) of the species present. What is the significance of the individual $\varepsilon^{\circ,i}$ terms and how are they combined into $\Delta\varepsilon^{\circ}$?

- (b) If θ_{rot} and θ_{vib} for H_2 are 85.4 and 5987 K respectively, estimate the equilibrium constant K_c at 300 K for the reaction :



You should state any assumptions you may make.

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

A7

Answer *all* parts of the question.

- (a) From a consideration of simultaneous adsorption and desorption of gas molecules at a solid surface, show that the fraction of the available sites occupied, θ , is related to an adsorption constant K_{ads} and the gas pressure P according to the equation :

$$\theta = \frac{K_{\text{ads}}P}{1 + K_{\text{ads}}P}$$

- (b) This relationship may also be explored via statistical mechanics. By equating the chemical potentials of adsorbed and gaseous species, show that for a monatomic gas the same equation may be derived, and that K_{ads} may then be written as

$$K_{\text{ads}} = \frac{\Lambda^3}{kT} \exp\left(\frac{-\Delta\epsilon}{kT}\right),$$

where Λ is the thermal wavelength and $\Delta\epsilon$ is the energy difference between the ground electronic states of the adsorbed and gaseous atoms.

- (c) Given the expression derived for K_{ads} , would you expect the fraction of adsorbed atoms to be greater with xenon than argon ?

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

A8

Answer *all* parts of the question.

- (a) Derive an expression for the internal energy of a system U in terms of its partition function q . For a molecule with translational, rotational and vibrational partition functions q_{trans} , q_{rot} and q_{vib} , show that their respective contributions to the molar energy and heat capacity must be additive.
- (b) (i) Making clear your reasoning, show that at sufficiently high temperatures, the rotational partition function of a heteronuclear diatomic molecule can be expressed as

$$q_{\text{rot}} = \frac{T}{\theta_{\text{rot}}}.$$

- (ii) Explain how this expression changes for a homonuclear diatomic molecule and derive expressions for the rotational contributions to the molar entropy and the molar heat capacity of $^1\text{H}_2$ in the high temperature limit.
- (c) At low temperatures, the rotational contribution to the molar heat capacity for $^1\text{H}_2$ deviates from the expression obtained in (b). Explain the nature of these effects. Making clear your assumptions *estimate* the molar heat capacity of $^1\text{H}_2$ at 100 K. Comment on your result.

[The rotational constant for H_2 is 60.80 cm^{-1} .]

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

A9

Answer *all* parts of the question.

A free-electron gas is characterised by its valence electron density, n_e , which may be related to the Fermi wavenumber, k_F , by the equation

$$k_F^3 = 3\pi^2 n_e.$$

- (a) Show that the density of states, $D(\epsilon)$, of this free-electron gas may be expressed as

$$D(\epsilon) = \frac{LV_c}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} \epsilon^{1/2}$$

where ϵ is the electron energy, m_e the mass of an electron, L the number of distinct primitive unit cells in the solid, and V_c the volume of each primitive unit cell.

[You may assume that the reciprocal-space density of \mathbf{k} -points permitted by the Born–von Karman boundary conditions is $LV_c/(2\pi)^3$.]

- (b) If the densities of solid Cu and Zn are 8920 kg m^{-3} and 7140 kg m^{-3} respectively, calculate their Fermi wavenumbers and Fermi energies within the free-electron model
[Assume that each Cu atom contributes one valence electron and each Zn atom two.]
- (c) Calculate the free-electron density of states per unit volume at the Fermi level for both Cu and Zn.
- (d) A uniform alloy is formed from equal numbers of Cu and Zn atoms, having a density precisely midway between those of the parent metals. What is its free-electron density of states per unit volume at the Fermi level, and would one predict on this basis that its properties should be more similar to those of Cu or of Zn?

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

A10

Answer *all* parts of the question.

The alloy $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ displays a direct band gap of 1.8 eV and a relative permittivity (dielectric constant) of 12.05. The effective masses of electrons and holes in this material are 0.088 and 0.245 respectively, in units of the true electron mass.

- (a) Outline the significance of direct and indirect band gaps when considering semiconducting materials for use in optoelectronic applications.
- (b) Estimate the concentration of electrons and holes in $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ at 300 K, assuming it to be intrinsic.
- (c) Estimate the electron mobility in $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$, given that the measured conductivity at 300 K is $10^{-10} \Omega^{-1}\text{m}^{-1}$, assuming that the hole mobility is negligible.
- (d) Estimate the binding energy of the most tightly bound exciton in $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$.

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

END OF PAPER