



UNIVERSITY OF CAMBRIDGE

NATURAL SCIENCES TRIPOS Part IB

Friday 2nd June 2017

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.

<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>
--

A1

Answer **all** parts of the question.

- (a) (i) Normalise the function

$$\Psi = (2q^2 - 1)e^{-q^2/2} \quad (1)$$

in the interval $-\infty < q < \infty$.

- (ii) Show that Ψ is an eigenfunction of the harmonic-oscillator hamiltonian

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

and determine its eigenvalue.

- (iii) Sketch Ψ (showing its asymptotic behaviour, and the precise locations of its nodes and turning points) and assign a quantum number.
- (b) (i) Give a general equation defining an expectation value in quantum mechanics.
- (ii) By evaluating appropriate expectation values, show that the system described by Ψ in part (a) is consistent with the Heisenberg uncertainty principle $\Delta q \Delta p \geq 1/2$, where Δq and Δp are the uncertainties in position q and momentum p [in the units of Eq. (1) for which $\hbar = 1$].
- (iii) What does your answer to (b)(ii) predict about possible experimental measurements of q and p ?
- (c) (i) Define quantum tunnelling (a very brief answer will suffice).
- (ii) Use the correspondence principle and the integral

$$\int_1^\infty e^{-q^2} dq = 0.1394$$

to estimate an upper bound to the tunnelling probability of a particle described by Ψ .

Approximate division of marks:

(a)(i) 15%, (ii) 10%, (iii) 15%; (b)(i) 5%, (ii) 30% (iii) 5%; (c)(i) 5%, (ii) 15%.

A2

Answer **all** parts of the question.

- (a) The spatial part of the wavefunction of a hydrogen atom can be written as

$$|nlm\rangle = R_{nl}(r)Y_{lm}(\theta, \phi).$$

- (i) Evaluate and sketch the radial probability density for a 2p orbital. Indicate on your sketch the most likely distance from the nucleus of finding a 2p electron.
 - (ii) Without further calculation, add to your sketch an estimate of the 2s radial probability distribution, explaining how the difference in shape of the two distributions leads to a splitting between the 2s and 2p energy levels in multi-electron atoms.
 - (iii) Write down expressions for the ($2p_x$, $2p_y$, $2p_z$) orbitals in terms of $|nlm\rangle$. Show, by evaluating the fewest number of integrals necessary, that these orbitals are mutually orthogonal.
- (b) When the hydrogen-atom spectrum is measured using a plane-polarized laser field aligned along the z -axis, the absorption intensity is proportional to the transition-dipole moment

$$T(n'l'm' \leftarrow nlm) = |\langle n'l'm' | \hat{\mu}_z | nlm \rangle|^2$$

where $\hat{\mu}_z = z = r \cos \theta$.

- (i) Use the symmetry of the integrand to determine which transition(s) between $n = 1$ and $n' = 2$ are allowed.
- (ii) How would the answer to (b)(i) change if the laser field were instead aligned along the x -axis, and why?

[You may use:-

$$R_{10}(r) = 2e^{-r}, \quad R_{20}(r) = \frac{1}{\sqrt{8}}(2 - r)e^{-r/2}, \quad R_{21}(r) = \frac{1}{\sqrt{24}}re^{-r/2}]$$

Approximate division of marks: (a)(i) 20%, (ii)20%, (iii)20%; (b)(i) 25%, (ii) 15%.

[TURN OVER

A3

Answer *all* parts of the question.

- (a) State and explain the selection rules for (i) pure rotational and (ii) vibrational transitions for diatomic molecules.
- (b) The $J = 0 \rightarrow J = 1$ rotational transition of BF in its vibrational ground state has been observed at 90369.8 MHz. Use this information to calculate the value of the rotational constant, \tilde{B} , and the bond length, r_0 , of BF.

You can assume integer masses (B = 11 amu; F = 19 amu).

- (c) The table below lists a number of IR transitions in the electronic emission spectrum of the BF molecule from the first electronic excited state to the ground electronic state.

λ/nm	v'' in electronic ground state	v' in electronic excited state
191.10	0	1
196.27	1	1
201.64	2	1

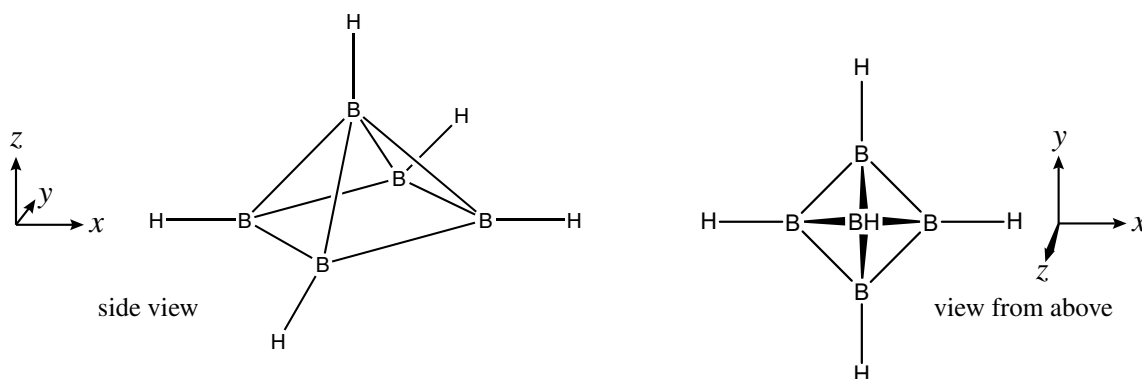
- (i) Use a diagram to sketch the transitions between the rotational-vibrational levels in the electronic ground and excited states of BF given above and give expressions for the energies of these transitions, assuming the Morse potential.
- (ii) From these data, determine $\tilde{\omega}$ and $\tilde{\omega}x_e$ for the ground electronic state and use these data to calculate the bond dissociation energy, D_e , of BF in kJ mol^{-1} . State any assumptions made.
- (d) Estimate how many vibrational levels exist in the electronic ground state of BF, based on the information above.

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

A4

Answer *all* parts of the question.

The molecular ion $B_5H_5^{4-}$ has the square-based pyramidal structure given below.



With the exception of the B–H unit at the top vertex of the pyramid, you may assume all the other atoms lie in the xy plane. All boron atoms can be considered to be sp -hybridized, with one sp -hybrid orbital on each boron pointing radially inwards, and the other towards the attached hydrogen.

- (a) The bonding electrons may be split into those involved in B–H bonds and the remainder involved in ‘cage-bonding’. The electrons and orbitals involved in the B–H bonding can be ignored when considering the bonding making up the boron cage.
 - (i) How many electrons are involved in ‘cage-bonding’?
 - (ii) The radial sp -hybrids and the remaining boron p -orbitals can be split into five sets, one of which is a p_z orbital for each of the borons at the base of the pyramid. Looking down the z -axis, sketch the orbitals in each of the remaining sets.
 - (iii) Classify each set of orbitals according to the point-group symmetry of the molecule, and sketch the resulting symmetry orbitals from each of the sets.
- (b) An approximate molecular-orbital diagram can be drawn by considering the energy of each of the symmetry orbitals from Hückel theory. Assuming that $\alpha_{sp} = \alpha$, $\alpha_p = \alpha - 2\beta$, and for nearest neighbours, $\beta_{sp,sp} = 2\beta$ and $\beta_{p,p} = \beta$, calculate the energy of each **symmetry** orbital and sketch and label an approximate molecular-orbital diagram.

[Qu. 4 continued on next page]

[TURN OVER]

[Continuation of Qu. 4]

- (c) A more detailed estimate may be made by allowing the symmetry orbitals to interact to form **molecular** orbitals. With the additional assumption that the interaction integral between the axial sp-hybrid and a basal p-orbital is $\beta_{\text{sp,p}} = \sqrt{2}\beta$:
- (i) Show that the Hückel hamiltonian for the totally symmetric irreducible representation can be written as:
- $$\begin{pmatrix} \alpha + 4\beta & 4\beta & 0 \\ 4\beta & \alpha & 2\sqrt{2}\beta \\ 0 & 2\sqrt{2}\beta & \alpha \end{pmatrix}$$
- (ii) Show that one of the totally symmetric orbitals has energy $E = \alpha - 4\beta$ and determine the energy of the remaining totally symmetric orbital(s).
- (d) Given that 4− is the most stable charge for this molecular ion, sketch an approximate molecular-orbital energy diagram, and suggest a value for the Fermi level.

Approximate distribution of marks:

- (a)(i) 5%, (ii) 15%, (iii) 20%; (b) 20%; (c)(i) 15%; (ii) 15%; (d) 10%.

A5

- (a) (i) Compare the electronic structures of the transition metal complexes $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{CN})_6^{3-}$
- (ii) Giving reasons, determine where the monodentate azide ligand, N_3^- , is likely to be found in the spectrochemical series.
- (b) Complexes with the formulae $\text{Mn}(\text{CO})_n^+$ [$n = 1$ to 6] have been formed in the gas phase and studied by infrared spectroscopy.
- (i) For each $n = 1$ to $n = 4$, predict the likely structure of the complex and give its point group. Draw a labelled MO energy diagram to show the splitting of the five orbitals dominated by the metal d orbitals. By adding the relevant number of electrons to each, suggest a likely spin multiplicity.
- (ii) Determine the symmetry of the CO stretching modes of the complex for $n = 5$ and $n = 6$, and predict the number of peaks in the IR spectrum.

Approximate distribution of marks: (a)(i) 25%, (ii) 10%; (b)(i) 45%, (ii) 20%.

END OF PAPER



UNIVERSITY OF CAMBRIDGE

NATURAL SCIENCES TRIPOS Part IB

Wednesday 7th June 2017

13.30 to 16.30

CHEMISTRY A: PAPER 2

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.

<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>
--

A6

Answer *all* parts of the question.

- (a) (i) Use the bridge relationship, $A = -k_B T \ln Q_N$, to show that the translational entropy of an ideal gas, S_{trans} , is given by

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

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

- (ii) Explain how the expression for the rotational entropy for a diatomic gas, S_{rot} , is different to the expression given above.
- (b) Using the following data, calculate the standard molar entropy of NO(g) at 298 K, explaining any approximations you make.
- Mass of NO: 30 amu
 Rotational temperature: $\theta_{\text{rot}} = 2.45$ K
 Vibrational temperature: $\theta_{\text{vib}} = 2719$ K

Approximate division of marks: (a)(i) 35%, (ii) 15%; (b) 50%.

A7

Answer *all* parts of the question.

The compound 2,2-diphenyl-1-picrylhydrazyl (DPPH) has a single unpaired electron in each molecule. Here we consider the behaviour of DPPH in an external magnetic field B . We assume that the unpaired electrons are all independent and only interact with the external magnetic field.

- (a) The spin of the electron is associated with a magnetic dipole μ . The energy of the dipole when aligned with the field is $-\mu B$ and when the orientation of the dipole and the field is antiparallel, the dipole energy is μB . Calculate the magnetic field dependent partition function Q_N for N molecules of DPPH.
- (b) By using the bridge relationship, compute the Helmholtz free energy.
- (c) By differentiating the free energy with respect to the temperature T , find an expression for the entropy of the system.
- (d) Give the low-temperature ($T \rightarrow 0$) and high-temperature ($T \rightarrow \infty$) limits of the entropy. By recalling the statistical definition of entropy $S = k_B \ln(\Omega)$, where Ω is the number of states accessible to the system, give Ω in both these limits and provide a qualitative explanation of the values that you have found.
- (e) Make a sketch of the entropy as a function of temperature.
- (f) We now consider the magnetisation of the system. The magnetisation M is defined as the total magnetic moment generated by the material and can be calculated as $M = N\langle\mu\rangle$ where $\langle\mu\rangle$ is the average magnetic moment from a single DPPH molecule. By considering the probability for a single spin to orient itself up and down in a field, provide an expression for $\langle\mu\rangle$ and hence M .
- (g) Show that at high temperatures ($k_B T > \mu B$) the magnetisation follows approximately the law

$$M \approx N \frac{\mu^2 B}{k_B T}.$$

The value of μ for a free electron is given by $\mu_B = 9.27 \times 10^{-24} \text{ J T}^{-1}$. How strong a magnetic field is needed to generate 10% magnetisation, $\langle\mu\rangle/\mu_B = 0.1$, in DPPH at a temperature of 50 K?

Approximate division of marks:

(a) 10%; (b) 10%; (c) 10%; (d) 25%; (e) 15%; (f) 15%; (g) 15%.

A8

Answer *all* parts of the question.

- (a) Consider the adsorption of atoms of type A onto a surface from the gas phase. The number of arrangements of N_A atoms on a surface with M binding sites is $Q_{N_A} = M!/(N_A!(M - N_A!))$. Assume that there are no interactions between the sites.

By using the approximation $\ln(N!) \approx N \ln(N)$ derive an expression for the Helmholtz free energy A , and for the chemical potential of the adsorbed atoms $\mu_{\text{ads}} = (\partial A / \partial N_A)_{V,T}$.

- (b) The chemical potential of the atoms in the gas phase is given by:

$$\mu_{\text{gas}} = -k_B T \ln(k_B T / (p_A \Lambda^3)) + \varepsilon_0$$

where p_A is the partial pressure of A, Λ is the thermal wavelength of the atoms A, and ε_0 is the energy difference between the gaseous and adsorbed states.

Derive an expression for the surface coverage, $\theta_A = N_A/M$, at equilibrium as a function of ε_0 .

- (c) The same result as in (b) may be derived from kinetic arguments. The rate of adsorption, r_A^+ , is given by $r_A^+ = k_A^+(M - N_A)p_A$ and the rate of desorption, r_A^- , is given by $r_A^- = k_A^- N_A$ where k_A^+ and k_A^- are the rate constants for adsorption and desorption, respectively.

Show that the equilibrium surface coverage can be written as $\theta_A = K_A p_A / (1 + K_A p_A)$ and determine an expression for K_A in terms of the rate constants.

- (d) Consider the simultaneous adsorption of atoms A and different atoms B. Show, by following a similar argument as in (c), that at equilibrium the following relationships are satisfied: $(1 - \theta_A - \theta_B)K_A p_A = \theta_A$ and $(1 - \theta_A - \theta_B)K_B p_B = \theta_B$ and hence that $\theta_A = K_A p_A / (1 + K_A p_A + K_B p_B)$. Give an analogous equation for θ_B .

- (e) Assume that A and B can undergo a bimolecular reaction when they adsorb to the surface as governed by transition-state theory:



where AB^\ddagger is the transition state on the surface, and k_1 is a first-order rate constant.

Using the result from (d), find an expression for the rate of the reaction, stating any assumptions you make.

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

A9

Answer *all* parts of the question.

- (a) Explain briefly how the electronic structure of the semiconductor, crystalline silicon (c-Si), changes on substitutional doping with small concentrations of: i) As; or ii) Ga. What are the dominant electronic charge carriers for (i) and (ii), respectively?
- (b) The bandgap of pure c-Si is 1.1 eV. Estimate a value for the electrical-conductivity activation energy of c-Si, making clear any assumptions made.
- (c) Now consider silicon, substitutionally doped with arsenic, c-Si:As. Making clear any assumptions and approximations made, give estimates for the electrical-conductivity activation energy of c-Si:As at: i) low temperature; ii) high temperature. (You may quote any equation used without proof, and may assume that the effective mass of electrons and holes in c-Si is $m_{e,h}^* = 0.3 m_e$, where m_e is the rest mass of the electron, and that the relative permittivity of c-Si is $\epsilon_r = 11.7$. Take the Rydberg energy to be 13.6eV.)
- (d) At approximately what temperature, T^* , is there a cross-over between high- and low-temperature behaviour of the electrical conductivity of c-Si:As?
- (e) What would be the effect on the temperature dependence of the electrical conductivity of c-Si if it were simultaneously substitutionally doped with equal (but small) concentrations of As and Ga dopants?
- (f) Why would the temperature dependence of the electrical conductivity of c-Si at low temperature change if substitutionally doped with a sufficiently high concentration of a dopant (As or Ga)? At approximately what dopant concentration would this cross-over between low- and high-concentration behaviour occur? (You may take the Bohr radius of the hydrogen atom to be 53 pm.)

Approximate division of marks: (a) 20%, (b) 10%, (c) 30%, (d) 5%, (e) 10%, (f) 25%.

A10

Answer *all* parts of the question.

- (a) Explain what is meant by a Bloch electron state in a crystal. Write down two different, but equivalent, forms of Bloch's theorem. Consider the case of a rectangular 2-dimensional (2D) lattice, with unit-cell vectors \mathbf{a} and \mathbf{b} ($|\mathbf{a}| > |\mathbf{b}|$) in the x - and y -directions, respectively.
- (b) Write down an expression for the electron wavefunction, in the linear-combination-of-atomic-orbitals (LCAO) approximation, which satisfies Bloch's theorem, for electrons propagating in this 2D rectangular lattice.
- (c) Assuming that the AOs at each lattice site are 1s-like, draw graphical representations for the Bloch states, in terms of circles (representing the 1s AOs), coloured black or white (representing opposite phases, ± 1), located at lattice sites of the 2D rectangular lattice, for the wavevector (k_x, k_y) values corresponding to the corner and mid-edge points in the first Brillouin zone. Sketch the shape of the first Brillouin zone in reciprocal space.
- (d) The electron energy, $E(k_x, k_y)$, for the case of the 2D square lattice, with unit-cell parameter, a , is $E(k_x, k_y) = \alpha + 2\beta[\cos(k_x a) + \cos(k_y a)]$. Describe briefly how this expression may be obtained, and explain what are the quantities α and β .
- (e) Generalize the above expression for $E(k_x, k_y)$ for a 2D square lattice to the case of the rectangular lattice.
- (f) Evaluate $E(k_x, k_y)$ for the 2D rectangular lattice for k -values corresponding to high-symmetry points in the first Brillouin zone. Hence, sketch the form of the band-structure, $E(k)$, for the 2D rectangular lattice for trajectories in k -space from the Γ -point to the corner and to the mid-edge points in the first Brillouin zone. What is the width, W , of the 1s LCAO band for this lattice?

Approximate division of marks: (a) 15%, (b) 5%, (c) 20%, (d) 15%, (e) 10%, (f) 35%.

END OF PAPER