



UNIVERSITY OF CAMBRIDGE

NATURAL SCIENCES TRIPOS Part IB

Friday 1st June 2018 13:30 to 16:30

CHEMISTRY A: PAPER 1

Candidates should attempt all five questions

Each question is marked out of 20. Where a question is divided into parts, the *approximate* number of marks available for each part is indicated thus **[*n*]**

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.

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 the commutator $[\hat{A}, \hat{B}]$, where \hat{A} and \hat{B} are the operators corresponding to two observable physical quantities A and B . [1]
 (ii) What does $[\hat{A}, \hat{B}]$ predict about uncertainties in the measurements of A and B ? [2]

- (b) The operator \hat{J}_z , corresponding to the z -component of the angular momentum of a particle is

$$\hat{J}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

where $\hat{p}_x, \hat{p}_y, \hat{p}_z$ are the operators corresponding to linear momentum in the x, y, z directions.

- (i) Write down the operators \hat{J}_x, \hat{J}_y , corresponding to x - and y - components of the angular momentum. [2]
 (ii) By writing out $\hat{p}_x, \hat{p}_y, \hat{p}_z$ as differential operators (i.e. $\hat{p}_x = -i\hbar\partial/\partial x$, etc.), evaluate the commutators between all pairs of \hat{J}_x, \hat{J}_y , and \hat{J}_z . [5]
 (iii) Using your results to part (ii), prove that the commutator

$$[\hat{J}_z, \hat{J}^2] = 0$$

where $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$. [4]

- (iv) Using your answers to parts (ii) and (iii), predict which properties of the angular momentum of the electron in a hydrogen atom can be measured precisely. [2]
 (c) (i) Evaluate the effect of \hat{J}_z on the p_x and p_y orbitals

$$\psi_x = Nx e^{-r/2} \quad \psi_y = Ny e^{-r/2}$$

where $r = \sqrt{x^2 + y^2 + z^2}$ and N is a normalization constant (which you are not expected to determine). [3]

- (ii) Comment on your result in the light of your answers to part (b). [1]

A2

Answer *all* parts of the question.

- (a) (i) State the Pauli principle as it applies to the wavefunction of a multi-electron system. [1]
- (ii) Write down symmetrised and anti-symmetrised spatial and spin functions for the electronic wave function of a Helium atom in its $1s^1 2s^1$ configuration. [3]
- (iii) What restrictions does the Pauli principle impose on which He ($1s^1 2s^1$) spatial functions can be combined with which spin functions? [2]
- (iv) How would your answers to (ii) and (iii) be different for the case of He ($1s^2$)? [2]
- (b) For He ($1s^1 2s^1$), the *Coulomb integral* J and the *exchange integral* K are defined to be

$$J = \iint \phi_{1s}(\mathbf{r}_1) \phi_{2s}(\mathbf{r}_2) \frac{1}{r_{12}} \phi_{1s}(\mathbf{r}_1) \phi_{2s}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

$$K = \iint \phi_{1s}(\mathbf{r}_1) \phi_{2s}(\mathbf{r}_2) \frac{1}{r_{12}} \phi_{1s}(\mathbf{r}_2) \phi_{2s}(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2$$

where $\mathbf{r}_1, \mathbf{r}_2$ are the spatial coordinates of the two electrons, and r_{12} is the distance between them.

- (i) Using your answers to part (a), calculate the relative energies of the triplet and singlet states for He ($1s^1 2s^1$), and thus confirm that Hund's first rule is obeyed (which you should state). [You may assume that J and K are both positive.] [6]
- (ii) Use a sketch to give a physical justification for your answer to (i). [1]
- (c) (i) How does Hund's first rule generalize to systems with more than two electrons? [1]
- (ii) Construct the term symbol (including J value) for the ground state of the d^7 configuration. [4]

[TURN OVER

A3

Answer *all* parts of the question.

- (a) State the selection rules that apply to (pure) rotational Raman scattering from linear molecules. [2]
- (b) A rotational Raman spectrum was recorded for $^{14}\text{N}_2$ using a laser operating at a wavelength of 1064.0 nm. For technical reasons it is not possible to observe lines very close to the frequency of the laser, and in this experiment the first three lines that were clearly visible on the low-frequency side of the laser have the following wavenumbers

$$9346.77 \text{ cm}^{-1} \quad 9338.81 \text{ cm}^{-1} \quad 9330.85 \text{ cm}^{-1}$$

- (i) Assign these lines, giving brief reasons for your answer. [4]
- (ii) Determine a value for the rotational constant of this molecule and hence estimate the bond length of $^{14}\text{N}_2$; give your answer in pm.
[The mass of ^{14}N is $14.0031 m_u$.] [2]
- (iii) Calculate the wavenumbers of the three lines that appear closest to and on the high-frequency side of the laser line; in your answer be sure to state the quantum numbers of the states involved. [4]

[Qu. 3 continued on next page]

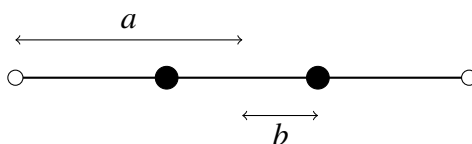
[Continuation of Qu. 3]

- (c) Raman spectra have been recorded on two isotopologues of ethyne (acetylene) giving the following values for the rotational constant

$$\tilde{B}_{\text{H}} = 1.181 \text{ cm}^{-1} \text{ for } {}^1\text{H}-{}^{12}\text{C} \equiv {}^{12}\text{C}-{}^1\text{H}$$

$$\tilde{B}_{\text{D}} = 0.851 \text{ cm}^{-1} \text{ for } {}^2\text{H}-{}^{12}\text{C} \equiv {}^{12}\text{C}-{}^2\text{H}$$

- (i) Give a general expression for the calculation of the moment of inertia of a molecule about a particular axis, clearly defining your terms. [2]
- (ii) Give an expression for the (non-zero) moment of inertia for ethyne in terms of the distances to the centre of the C–C bond shown below and the masses m_{C} and m_{H} . [1]



- (iii) Briefly explaining your method, use the data given to determine values for a and b (give your answers in pm). Hence determine values for the C–C and C–H bond lengths in ethyne.

Use integer masses for the isotopes.

[5]

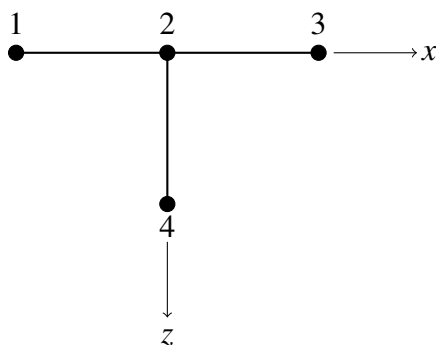
You will find it easier first to determine a^2 and b^2 .

[TURN OVER]

A4

Answer *all* parts of the question.

- (a) Consider the hypothetical cation H_4^{2+} in the T-shaped geometry shown below, along with a numbering system and an axis system. All the bond lengths are equal.



- (i) List the symmetry elements possessed by this molecule and hence identify its point group. [1]
- (ii) Consider a basis consisting of the single 1s atomic orbital on each atom. These orbitals are denoted ϕ_i and can be assumed to be normalized. Construct the symmetry orbitals that are formed from these atomic orbitals, expressing each in its normalized form in terms of the ϕ_i , and giving the relevant symmetry label. [4]
- (iii) For the symmetry orbitals which transform as the totally symmetric irreducible representation, and using the simplest Hückel approximations, set up the secular equations using [4]

$$\int \phi_i \phi_j d\tau = \delta_{ij}$$

$$\int \phi_i \hat{H} \phi_i d\tau = \alpha$$

$$\int \phi_i \hat{H} \phi_j d\tau = \beta \text{ if } i \text{ and } j \text{ are adjacent, and } = 0 \text{ otherwise}$$

- (iv) Solve these secular equations to obtain the energies of the molecular orbitals. Express each molecular orbital as $\psi = \sum_{i=1,4} c_i \phi_i$ and find the coefficients c_i of the normalized orbital. [6]

[Qu. 4 continued on next page]

[Continuation of Qu. 4]

- (v) Find the energy or energies of any remaining molecular orbitals. [1]
 - (vi) Sketch a diagram showing the relative energies of the molecular orbitals, giving each the appropriate symmetry label and indicating which are occupied. Sketch the form of any occupied orbitals. [2]
- (b) Aside from T-shaped, other possible geometries for H_4^{2+} are a tetrahedral arrangement or a square planar arrangement. Without making any further calculations, and giving brief reasons, suggest which of the three possible geometries is likely to have the lowest energy. [2]

[TURN OVER

A5

Answer *all* parts of the question.

- (a) ClF_3 is a planar T-shaped molecule, belonging to the point group C_{2v} ; assume that the molecule lies in the xz -plane.

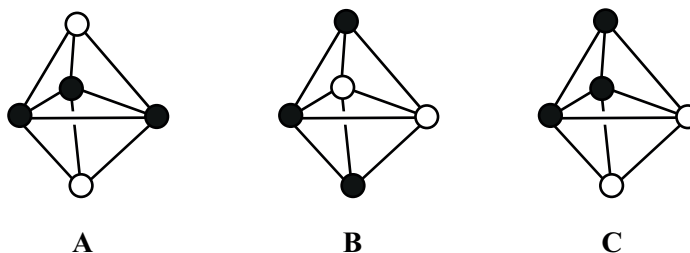
- (i) Show that the normal modes have symmetries $3A_1 \oplus 2B_1 \oplus B_2$. [4]
- (ii) The approximate vibrational frequencies (expressed as wavenumbers) of the normal modes are given in the table below

mode	1	2	3	4	5	6
symmetry	A_1	A_1	A_1	B_1	B_1	B_2
vibrational wavenumber / cm^{-1}	752	528	326	703	434	364

The infra-red spectrum shows features at approximately 1504 cm^{-1} , 1231 cm^{-1} , and 1454 cm^{-1} . One of these is a first overtone, and the other two are combination lines involving one or other of the B_1 normal modes.

Identify which energy levels are involved in each of these transitions and show that the transitions you propose are symmetry allowed in the infra-red. [4]

- (b) Shown below are three possible structural isomers for the complex $\text{M}(\text{CO})_3\text{L}_2$, where M is a metal and L is a ligand which, for the purposes of this question, can be considered to be structureless. In all three the arrangement of ligands is based on a trigonal bipyramid, with the metal at the centre. In the diagrams the position of the CO ligand is indicated by a filled circle ●, and the position of the ligand L by an open circle ○.



[Qu. 5 continued on next page]

[Continuation of Qu. 5]

Considering only vibrations involving C–O stretches, for each of the isomers **A–C**:

- (i) state the point group;
- (ii) determine the irreducible representations of the C–O vibrations;
- (iii) determine the irreducible representations of those vibrations which are expected to be active in the infra-red;
- (iv) determine the number of features (bands) you would expect to see in the infra-red.

[4 for each isomer]

END OF PAPER



UNIVERSITY OF CAMBRIDGE

NATURAL SCIENCES TRIPOS Part IB

Wednesday 6th June 2018

13:30 to 16:30

CHEMISTRY A: PAPER 2

Candidates should attempt all five questions

Each question is marked out of 20. Where a question is divided into parts, the *approximate* number of marks available for each part is indicated thus **[*n*]**

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.

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.

A6

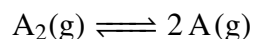
Answer *all* parts of the question.

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

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

Here q_i is the molecular partition function, and N_i is the number of particles of each species i .

- (i) Describe the meaning of the term $\varepsilon^{0,i}$. [1]
 (ii) By considering the change in the Gibbs free energy, show that the equilibrium constant K_p of the reaction



is given by

$$K_p = \frac{(q_A^\circ)^2}{q_{\text{A}_2}^\circ N_A} \exp\left(\frac{-\Delta\varepsilon_0}{kT}\right)$$

where q_i° denotes the partition function for one mole of species i in the standard state, and N_A is Avogadro's constant. [4]

- (iii) Describe the meaning of the term $\Delta\varepsilon_0$. [1]

- (b) Use the data given below to determine the equilibrium constant K_p at 298 K of the gas phase dissociation $\text{Li}_2(\text{g}) \rightleftharpoons 2 \text{Li}(\text{g})$. Explain any assumptions that you make.

Li: Molar mass 6.94 g mol⁻¹, atomic term symbol ²S_{1/2}.

Li₂: Bond length = 0.2673 nm, vibrational frequency = 353.59 cm⁻¹, $\sigma = 2$, electronic ground state ¹Σ_g⁺, $D_e = 99.38$ kJ mol⁻¹. [14]

A7

Answer *all* parts of the question.

- (a) (i) Explain the terms *partition function* of the system and *molecular partition function*, and describe how the two quantities are related. Write down an expression for the partition function Q_N of the system, explaining carefully the meaning of any symbols that you use. [3]
- (ii) Suppose that the system is in a state X , and that the number of microstates of this system is w_X . Write down a formula that you can use to calculate the entropy of this state. [1]
- (iii) Consider a general system that has an initial state X with w_X microstates, and a final state Y , with w_Y microstates.
What proportion of time, P_X/P_Y , will the system spend in microstates corresponding to state X ? Derive a relationship between P_X/P_Y and the change in entropy between the two states. [2]
- (b) Consider a one-dimensional lattice with $N + M$ different sites, where $N, M \gg 1$. The lattice contains n green particles and m red particles, where $n < N$, and $m < M$, and $n, m \gg 1$; only one particle may occupy any given site.
- (i) Consider a state X of the system in which the green particles *must* be placed in the first N sites, and in which the red particles *must* be placed in the next M sites; red particles cannot be placed in the first N sites. What is the total number of microstates available to the system? [3]
- (ii) Use the result from (i), together with Stirling's approximation, to derive an expression for the entropy of this state, S_X . [3]
- (c) Now consider a state Y of the system, in which all $N + M$ sites are available to both the green and the red particles. The particles remain distinguishable by colour. Derive an expression for the entropy of this state S_Y . [3]
- (d) For the case in which $N = M$, and $n = m$, determine $\Delta S = S_Y - S_X$. Comment on the value you find for ΔS . [3]
- (e) Next consider the case in which $N = M$, and $n \gg m$. Without detailed calculations, explain *qualitatively* whether you would expect $\Delta S = S_Y - S_X$ to be different from the value found in (d), being sure to make your reasoning clear. [2]

[TURN OVER

A8

Answer *all* parts of the question.

For a system with partition function Q_N the Helmholtz energy is given by $A = -kT \ln Q_N$ and the internal energy by $U = kT^2(\partial \ln Q_N / \partial T)_V$.

- (a) Derive expressions for (i) the entropy and (ii) the internal energy of N non-interacting distinguishable particles, being careful to define any new functions you introduce. [4]

The remainder of this question is concerned with a system consisting of N non-interacting nuclei with spin $I = 1$ in a magnetic field of strength B . Each spin has three states with energies $\varepsilon_m = -m\mu B$, where $m = -1, 0, +1$ and μ is the magnetic moment of the nucleus, which is a constant.

- (b) (i) Derive an expression for the internal energy of these N nuclei. [3]
(ii) Deduce the value of the internal energy in the limit that the temperature goes to zero; comment on your result. [2]
- (c) (i) Derive an expression for the entropy of these N nuclei. [2]
(ii) Show that in the high-temperature limit, that is $kT \gg \mu B$, the entropy becomes $S = Nk \ln 3$. Comment on this value. [3]
- (d) The component of the magnetic moment in the direction of the magnetic field, the z -direction, is given by $m\mu$, with $m = -1, 0, +1$ as above. The magnetization M of the sample is found by taking a weighted sum of these three contributions

$$M = \sum_{m=-1,0,+1} p_m \times (m\mu)$$

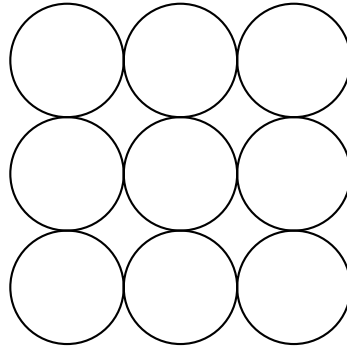
where p_m is the fractional population of state m .

- (i) Derive an expression for M . [4]
(ii) Use your expression to find the value of M in the high-temperature limit. [2]

A9

Answer *all* parts of the question.

- (a) Consider a two-dimensional lattice formed from circles of radius r , a fragment of which is shown below



- (i) Draw a diagram indicating a (two-dimensional) primitive unit cell for this lattice. Specify the length of the sides of the cell and any relevant angles. [1]
 - (ii) Calculate the packing fraction of this lattice, that is the fraction of the area of a unit cell which is occupied by the circles, assuming that the circles just touch. [2]
 - (iii) Calculate, in terms of r , the radius of the largest circle that will fit in the interstices in the lattice. [3]
- (b)
- (i) Sketch the arrangement of circles which has the greatest packing fraction. On your sketch identify a primitive unit cell; specify the length of the sides of the cell and any relevant angles. [2]
 - (ii) Calculate the packing fraction of this lattice, assuming that the circles just touch. [3]
 - (iii) Calculate, in terms of r , the radius of the largest circle that will fit in the interstices in the lattice. [3]
- (c) The density of Born von Karman allowed points in k -space is $LV_c/(2\pi)^3$, where L is the number of unit cells and V_c is the volume of the real-space unit cell.
- (i) Derive an expression for the Fermi energy and the Fermi wavevector for the free-electron gas in terms of the electron density n_e . [4]
 - (ii) Rb metal has a density of 1.53 g cm^{-3} ; estimate the Fermi wavevector (giving your answer in m^{-1}) and the Fermi energy (giving your answer in eV). Point out any assumptions you make. [2]

[TURN OVER

A10

Answer **all** parts of the question.

- (a) (i) Use a simple argument, based on the free-electron gas model, to explain the observation that at low temperatures the heat capacity of a metal has a contribution which is linear in the temperature T . [3]

- (ii) A more detailed treatment of the heat capacity shows that the linear term is $C_{V,m} = \pi^2 RT/2T_F$, where T_F is the Fermi temperature.

The data below give the heat capacity of potassium metal as a function of temperature. *By plotting a suitable graph*, show that these data fit the expression $C_{V,m} = aT + bT^3$, and hence obtain an estimate for the Fermi energy of potassium, giving your answer in eV. [5]

T/K	0.316	0.447	0.548
$C_{V,m}/\text{mJ K}^{-1} \text{mol}^{-1}$	0.738	1.16	1.56

- (b) (i) Sketch the band structure expected for an intrinsic semiconductor (such as pure Si), indicating on your sketch the band gap E_g and the approximate position of the Fermi energy E_F for a finite temperature. [1]

- (ii) Explain how measurements of the conductivity of such a semiconductor as a function of temperature can be used to determine the band gap. [3]

[The Fermi–Dirac distribution is

$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1} \quad]$$

- (iii) Making the simplest approximations, and using statistical thermodynamics, derive an expression for the equilibrium constant which describes the formation of electrons and holes in a semiconductor. [4]

[For the equilibrium $A \rightleftharpoons B + C$ the equilibrium constant is given by

$$K_c = \frac{f_B f_C}{f_A c^\circ} e^{-\Delta \varepsilon_0 / k_B T}$$

where f_i is the volume-independent partition function.]

- (iv) Use the expression derived in (iii) to predict the form of the temperature-dependence of the conductivity of the material. Compare your prediction with that in (ii). [4]

END OF PAPER