



UNIVERSITY OF CAMBRIDGE

NATURAL SCIENCES TRIPOS Part IB

Thursday 3rd June 2021

11:00 to 14:00

CHEMISTRY A: PAPER 1

Candidates should attempt all five questions; where a question is divided into parts, candidates should answer all parts.

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*]**

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>
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A1

- (a) The angular momentum operators are defined to be

$$\begin{aligned}\hat{j}_x &= -i\hbar \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right] \\ \hat{j}_y &= -i\hbar \left[z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right] \\ \hat{j}_z &= -i\hbar \left[x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right]\end{aligned}$$

and

$$\hat{j}^2 = \hat{j}_x^2 + \hat{j}_y^2 + \hat{j}_z^2$$

- (i) Prove that $[\hat{j}_x, \hat{j}_y] = i\hbar \hat{j}_z$, where the commutator $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$. **[4]**
- (ii) State the analogous relations for $[\hat{j}_y, \hat{j}_z]$ and $[\hat{j}_z, \hat{j}_x]$. **[1]**
- (iii) Using your results from (i) and (ii), prove that $[\hat{j}_z, \hat{j}^2] = 0$. **[5]**
- (iv) What do your answers to (i)-(iii) imply about the eigenfunctions of the operators $\hat{j}_x, \hat{j}_y, \hat{j}_z$ and \hat{j}^2 ? **[1]**
- (v) What does your answer to (iv) allow you to predict about possible experimental measurements of the components of the angular momentum of a particle such as an electron? **[1]**

[Qu. **A1** continued on next page]

[Continuation of Qu. A1]

- (b) The hamiltonian operator for the hydrogen atom can be written in atomic units as

$$\hat{H} = -\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\hat{l}^2}{2r^2} - \frac{1}{r}$$

The eigenfunctions $Y_{lm}(\theta, \phi)$ of the operator \hat{l}^2 are defined by the equation

$$\hat{l}^2 Y_{lm}(\theta, \phi) = l(l+1) Y_{lm}(\theta, \phi)$$

- (i) To which physical observable does the operator \hat{l}^2 correspond? [1]
- (ii) Write down another eigenfunction equation satisfied by $Y_{lm}(\theta, \phi)$. [1]
- (iii) Prove that the functions

$$\Psi_{lm}(r, \theta, \phi) = R(r) Y_{lm}(\theta, \phi)$$

are eigenfunctions of \hat{H} , and obtain the differential equation satisfied by $R(r)$.

[3]

- (iv) Calculate the energy of an electron in a hydrogen 2p orbital, given that $R(r) = N r e^{-r/2}$ where N is a normalisation constant that you need not evaluate. [3]

[TURN OVER]

A2

- (a) (i) State the *variation principle* relating the approximate ground-state energy \tilde{E} obtained from a trial function $\tilde{\Psi}$ to the exact ground state energy. [2]
- (ii) Prove the variation principle by expanding $\tilde{\Psi}$ in the following way:

$$\tilde{\Psi} = \sum_n c_n \phi_n$$

where ϕ_n are the exact normalised eigenfunctions of the hamiltonian operator. [4]

- (b) (i) Write down the hamiltonian \hat{H} of a particle confined to a one-dimensional box with boundaries at $x = 0$ and $x = a$. [1]
- (ii) Show that the functions

$$\phi_n(x) = \sin\left(\frac{n\pi x}{a}\right)$$

are eigenfunctions of \hat{H} , specifying any conditions on n , and determine the associated eigenvalues E_n . [2]

- (c) Now pretend that you do not know $\phi_n(x)$ and that you plan to approximate the ground state eigenfunction $\phi_1(x)$ by the trial function

$$\tilde{\Psi}(x) = x(x - c)$$

- (i) What is the appropriate choice of the constant c and why? [1]
- (ii) What other properties of $\tilde{\Psi}(x)$ suggest that this function is a reasonable guess for $\phi_1(x)$? [1]
- (iii) Normalise $\tilde{\Psi}(x)$. [1]
- (iv) Use $\tilde{\Psi}(x)$ to obtain an estimate \tilde{E} of the ground state energy E_1 . [4]
- (v) Show numerically that the relation between \tilde{E} and E_1 is consistent with the variation principle. [1]
- (vi) Show that,

$$\frac{|c_3|^2}{|c_1|^2} \simeq \frac{\tilde{E} - E_1}{E_3 - \tilde{E}},$$

stating any assumptions you have made about the relative magnitude of the coefficients $|c_i|^2$. [Hints: Start with your answer to (a)(ii); consider the symmetry of any integrals but do not evaluate them explicitly.] [3]

A3

- (a) Carbon monosulfide (CS) is a diatomic gas, and is the first compound of sulphur to be discovered in the interstellar medium.

- (i) Sketch a diagram of CS labelling the masses m_C and m_S , and the bond length r_{CS} . [1]
- (ii) Derive an expression (in terms of m_C , m_S and r_{CS}) for the distance r_1 between the carbon atom and the centre of mass of the molecule. [2]
- (iii) Show that the moment of inertia of the rotor about an axis passing through the centre of mass and perpendicular to the internuclear axis is given by

$$I_{CS} = \frac{m_C m_S}{m_C + m_S} r_{CS}^2 \quad [4]$$

- (iv) Given that the equilibrium bond length (r_{CS}) of CS is 1.53 \AA , calculate the rotational constant (in cm^{-1}) for the isotopomer $^{12}\text{C}^{32}\text{S}$. Use integer masses. [3]

- (b) The population of molecules with rotational quantum number J , relative to the molecules in the rotational ground state, is

$$\frac{N_J}{N_0} = (2J + 1) \exp \left[-\tilde{B}J(J + 1)h\tilde{c}/kT \right]$$

where k is Boltzmann's constant, T is the temperature and h is Planck's constant (all in SI units); \tilde{B} is the rotational constant in cm^{-1} and \tilde{c} is the speed of light in cm s^{-1} .

- (i) Sketch the graph of N_J/N_0 versus J to show the approximate shape of the above expression. [1]
- (ii) Using differentiation, obtain an expression for the most populated rotational state J_{max} . [4]
- (iii) Compute J_{max} at room temperature and at 8.7 K . [3]
- (iv) Comment on why rotational spectra are well suited to molecular discovery in the interstellar medium. [2]

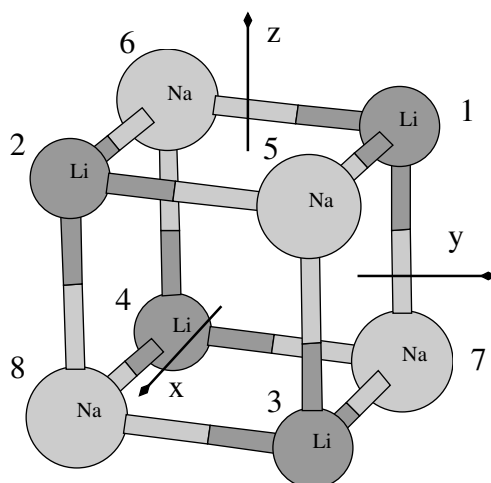
[TURN OVER]

A4

- (a) The ammonia molecule (NH_3) has a trigonal pyramidal geometry.
- (i) State the point group of the ammonia molecule. [1]
 - (ii) State the symmetries of the valence orbitals of the nitrogen atom. [2]
 - (iii) For the three $1s$ hydrogen atomic orbitals (AOs) determine the characters of the representation and then reduce it. [2]
 - (iv) Denoting the three hydrogen AO wavefunctions as s_A , s_B and s_C , write down the form of the normalized symmetry orbitals and sketch them. [3]
 - (v) Construct a molecular orbital (MO) diagram, labelling each MO with an appropriate symmetry label, and indicating which orbitals are occupied. Comment on the bonding orbitals. [3]
- (b) Ammonia is able to invert its structure by passing through a planar transition state in which the hydrogen atoms lie at the vertices of an equilateral triangle.
- (i) Assign a point group to the planar transition state. [1]
 - (ii) Construct a labelled MO diagram of the transition state, commenting on any bonding differences with the MO diagram of trigonal pyramidal NH_3 . Sketches of the MOs are not required. [5]
 - (iii) By comparing the two diagrams, speculate on what is required for NH_3 (a Lewis base) and BH_3 (a Lewis acid) to react together to form the 1:1 adduct $\text{NH}_3\text{-BH}_3$. Your answer should explain the role played by the HOMO and LUMO. [3]

A5

- (a) (i) Define the terms *symmetry orbital* and *molecular orbital*. [1]
 (ii) When is a symmetry orbital a molecular orbital? [1]



- (b) In the nano-alloy cluster Li_4Na_4 shown in the figure the atoms lie at the vertices of a cube, and the cluster belongs to the T_d point group.
- (i) Identify one C_2 axis and one C_3 axis. [1]
 (ii) Find the characters of the representations spanned by the Li $2s$ orbitals and the Na $3s$ orbitals, and reduce them. [3]
 (iii) Construct the corresponding symmetry orbitals using the axis system and numbering scheme in the figure. [3]
 (iv) Using the simplest Hückel approximation, and assuming that the α parameter is the same for the Li $2s$ orbitals and the Na $3s$ orbitals, calculate the molecular orbital energies (the molecular orbital coefficients are not required). Hence sketch a molecular orbital energy level diagram for Li_4Na_4 . [11]

END OF PAPER



UNIVERSITY OF
CAMBRIDGE

NATURAL SCIENCES TRIPOS Part IB

Thursday 17th June 2021

11:00 to 14:00

CHEMISTRY A: PAPER 2

Candidates should attempt all five questions; where a question is divided into parts, candidates should answer all parts.

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A6

Consider a system of N homonuclear diatomic molecules which can adsorb on a surface. Assume that all the surface adsorption sites are occupied and that the molecules do not interact with each other.

When adsorbed, the molecules can be in one of three states: (1) with the internuclear axis oriented in the z -direction perpendicular to the surface; (2) lying flat on the surface parallel to the x axis; or (3) lying flat on the surface parallel to the y axis. The energies of these states are $-\epsilon + \delta, -\epsilon, -\epsilon$ respectively. The parameters ϵ and δ are both positive.

- (a) What is the lowest energy of the system and how many microstates have this energy? [2]
- (b) Compute the partition function and the internal energy of the system. [5]
- (c) Compute the energy of the system in the limits $T \rightarrow 0$ and $T \rightarrow \infty$, and comment on your answer. [3]
- (d) Without computing the expression for the entropy, explain why at high temperatures the entropy approaches the value $Nk_B \ln(3)$. Above which temperature is this value reached? [3]
- (e) Calculate the heat capacity of the system, compute both the high and low temperature limits and sketch the approximate form of the heat capacity as a function of temperature. [5]
- (f) Without detailed calculations comment on what you expect the entropy to tend to in the low temperature limit. [2]

A7

- (a) Consider helium atoms weakly adsorbed onto a surface and assume that they behave like a two-dimensional monatomic gas. By assuming that the atoms can move freely on the surface of area σ , find an expression for the translational partition function.

[5]

- (b) How does this situation compare with the free helium gas? Compute the loss of molar Helmholtz free energy upon adsorption on the surface.

[6]

- (c) Now consider molecular hydrogen adsorbed on a flat surface where the molecules behave as a non-interacting two-dimensional gas. In addition to the translational partition function calculated above, the molecules have a rotational contribution to the partition function.

For molecules rotating in a plane the energy states are given by $E_J = J^2 \hbar^2 / (2I)$ where I is the moment of inertia. What are the possible values for J and what is the degeneracy for each state? How does this situation compare for the free hydrogen gas?

[3]

- (d) Find an expression for the rotational partition function at high temperatures for the molecules adsorbed onto the surface.

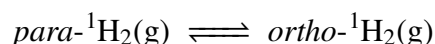
[6]**[TURN OVER]**

A8

$^1\text{H}_2$ exists in two forms: *para*, in which only the even rotational states are occupied; and *ortho*, in which only the odd states are occupied. In the presence of a suitable catalyst the two forms interconvert freely, but without the catalyst they do not.

Throughout this question, unless specifically requested, formulae may be quoted without proof.

- (a) (i) Explain briefly and concisely why the equilibrium constant for



is given by

$$K = \frac{3 \sum_{\text{odd } J} (2J+1) e^{-J(J+1)\theta_{\text{rot}}/T}}{\sum_{\text{even } J} (2J+1) e^{-J(J+1)\theta_{\text{rot}}/T}}$$

where J runs from 0 to infinity and θ_{rot} is the rotational temperature. [3]

- (ii) Calculate the value of K in the low temperature limit, $T \ll \theta_{\text{rot}}$, and in the high temperature limit, $T \gg \theta_{\text{rot}}$, justifying any approximations you make. Comment on your answers. [2]

- (b) (i) Derive an expression for the molar heat capacity at constant volume of a gas consisting of non-interacting molecules with molecular partition function q . [3]

[There are a number of ways of expressing this result, one of which is

$$\frac{C_{V,m}}{R} = \frac{T^2}{q} \frac{d^2 q}{dT^2} - \frac{T^2}{q^2} \left(\frac{dq}{dT} \right)^2 + \frac{2T}{q} \frac{dq}{dT}$$

where all of the derivatives are at constant volume. You do not have to derive the expression in this form.]

- (ii) For a rigid rotor the partition function in the high-temperature limit, $T \gg \theta_{\text{rot}}$, is given by T/θ_{rot} . Show that, in this limit, the expression you have derived in (b)(i) gives the expected result for the heat capacity of the rigid rotor. [2]

[Qu. A8 continued on next page]

[Continuation of Qu. A8]

- (c) For $^1\text{H}_2$ $\theta_{\text{rot}} = 85.3$ K. At 150 K the following sums have been evaluated

$$q_{\text{even}} = \sum_{\text{even } J} (2J + 1) e^{-J(J+1)\theta_{\text{rot}}/T} = 1.165$$

$$\frac{dq_{\text{even}}}{dT} = 3.76 \times 10^{-3} \text{ K}^{-1} \quad \frac{d^2q_{\text{even}}}{dT^2} = 3.58 \times 10^{-5} \text{ K}^{-2}$$

$$q_{\text{odd}} = \sum_{\text{odd } J} (2J + 1) e^{-J(J+1)\theta_{\text{rot}}/T} = 0.970$$

$$\frac{dq_{\text{odd}}}{dT} = 7.64 \times 10^{-3} \text{ K}^{-1} \quad \frac{d^2q_{\text{odd}}}{dT^2} = -3.08 \times 10^{-5} \text{ K}^{-2}$$

For (i) and (ii) you should express your answers as multiples of R .

- (i) Evaluate $C_{V,m}$ for *para*- $^1\text{H}_2$ at 150 K, and for *ortho*- $^1\text{H}_2$ at 150 K.
 Comment on these values. [5]
- (ii) Evaluate $C_{V,m}$ for a mixture of *ortho*- $^1\text{H}_2$ and *para*- $^1\text{H}_2$ at 150 K where the ratio of *ortho* to *para* is that expected at high temperatures.
 Evaluate $C_{V,m}$ for a mixture of *ortho*- $^1\text{H}_2$ and *para*- $^1\text{H}_2$ at 150 K where the ratio of *ortho* to *para* is that expected at this temperature.
 Comment on these values. [5]

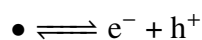
[TURN OVER]

A9

- (a) (i) In the context of the free-electron gas model what do you understand by the terms *Fermi energy* and *Fermi wavevector*? [2]
- (ii) For a simple monovalent metal (e.g. sodium) why is the Fermi energy very much greater than $k_B T$ at room temperature? [1]
- (iii) Derive an expression for the Fermi energy and the Fermi wavevector for a two-dimensional free-electron gas for which the electrons have an number density n_e (expressed in number of electrons per unit area). [4]
 [You may assume that the density of Born von Karman states in two dimensions is $\mathcal{A}/(2\pi)^2$, where \mathcal{A} is the Born von Karman area.]
- (b) A researcher deposits a mono-layer of gold on a substrate. Careful measurements indicated that $1.56 \mu\text{g}$ of gold are deposited on 1.00 cm^2 of surface. It is thought that on the surface the gold atoms are arranged according to a square lattice, and that each atom contributes one electron to the electron gas.
- (i) Estimate the spacing of the atoms. [2]
- (ii) Estimate the electron density in (number of electrons) m^{-2} . [1]
- (iii) Hence determine the Fermi energy in eV and the Fermi wavevector in m^{-1} according to the two-dimensional free-electron gas model. [2]
- (c) Now consider the reciprocal lattice corresponding to this arrangement of atoms on the surface.
- (i) Assuming that the real-space lattice spacing is a , make a labelled sketch of the reciprocal-space lattice. On your sketch identify the first Brillouin zone. [2]
- (ii) Using your results from (b) confirm that the Fermi circle falls within the first zone. Explain carefully why this is the expected result. [4]
- (iii) The researcher believes that the substrate is contributing additional electrons to the system, and finds that for one particular substrate the gold monolayer ceases to be a metallic conductor.
 A possible explanation for this behaviour is that there is a substantial band gap present at the edges of the first zone. Assuming this to be the case, estimate how many additional electrons per atom need to be added to the system in order for it to cease being a metallic conductor. [2]

A10

- (a) Electrical conductivity in an intrinsic semiconductor arises due to the presence of electrons (e^-) and holes (h^+) which are formed by thermal excitation from the ground state (\bullet). This process can be described by an equilibrium



The electrical conductivity σ of such a material can be written

$$\sigma = n_e e \mu_e + n_h e \mu_h$$

where n_e is the number density of the electrons and μ_e is their mobility; e is the charge on the electron. n_h and μ_h are the corresponding quantities for the holes.

- (i) Derive an expression for the equilibrium constant for the equilibrium given above at temperature T and in terms of the effective mass of an electron m_e^* , the effective mass of a hole m_h^* , and the band gap E_g .

Briefly note the assumptions you make in your derivation. [5]

- (ii) For pure germanium the band gap is found to be 0.67 eV, and a reasonable estimate of the effective masses is $m_e^* = m_h^* = 0.3 m_e$. At 400 K the electrical conductivity of this material is measured as 48 S m^{-1} .

Assuming that $\mu_e = \mu_h$, use these data to estimate a value for μ_e , in units of $\text{m}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Be sure to show how the units of your result are consistent with those used in the calculation. [4]

[1 A = 1 C s⁻¹; 1 S = 1 A V⁻¹]

- (iii) Explain briefly why doping the solid germanium with arsenic can be expected to increase the conductivity significantly. [2]
- (iv) Estimate the level of doping needed to increase the conductivity by a factor of 1000. [4]

[The density of solid germanium is 5.32 g cm^{-3} .]

[Qu. A10 continued on next page]

[TURN OVER]

[Continuation of Qu. A10]

- (b) The effective mass of an electron, m_e^* , is defined in terms of the curvature of the dispersion curve, E_k

$$\frac{1}{m_e^*} = \frac{1}{\hbar^2} \frac{d^2 E_k}{dk^2}$$

- (i) For a free-electron gas $E_k = k^2 \hbar^2 / 2m_e$. Derive an expression for m_e^* and comment on your result. [1]
- (ii) For one-dimensional band modelled using the simplest Hückel theory $E_k = \alpha + 2\beta \cos(ka)$. Derive an expression for m_e^* . [2]
- (iii) What does your result in (ii) predict about the likely effective mass for the electrons responsible for conduction in an n-type semiconductor? [2]

END OF PAPER