



UNIVERSITY OF CAMBRIDGE

NATURAL SCIENCES TRIPOS Part IB

Friday 31st May 2019

13:30 to 16:30

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*]**

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

- (a) Write down (i) the hamiltonian operator \hat{H}_b and (ii) the boundary conditions, for a particle of mass m trapped in a one-dimensional box along a coordinate x of length a . [2]

- (b) The eigenfunctions of \hat{H}_b have the general form

$$\Psi(x) = A \sin \frac{px}{\hbar} + B \cos \frac{px}{\hbar}$$

Use your answer to (a) to obtain a set of allowed values for A , B and p , ensuring that $\Psi(x)$ is normalized. [4]

- (c) Evaluate the associated eigenvalues and thus demonstrate that the confinement in the box has quantized the energy. [2]
- (d) Prove that any pair of $\Psi(x)$ that correspond to different energies are *orthogonal*, and rationalise this finding by choosing two particular $\Psi(x)$ (with different energies) and sketching them. [3]
- (e) Derive expressions for the expectation values of the position operator \hat{x} and the momentum operator \hat{p} as a function of quantum number. Comment on your answers. [5]
- (f) Without evaluating additional integrals, obtain the uncertainty Δp_x as a function of quantum number. [2]
- (g) Use your answer to (f) to estimate a lower bound for the corresponding uncertainty Δx in position. [2]

A2

- (a) Starting with the form of the hydrogen-atom wave function

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

where $R_{nl}(r)$ and $Y_{lm}(\theta, \phi)$ are the (normalised) radial and angular parts of the wavefunction and n, l, m have the usual definitions, show that the probability of finding the electron in a spherical shell of radius r and thickness dr is

$$P_{nl}(r) dr = r^2 R_{nl}^2(r) dr$$

[3]

- (b) The 2s and 2p radial wave functions are (in atomic units)

$$R_{20}(r) = \frac{1}{\sqrt{8}} (2 - r) e^{-r/2}$$

$$R_{21}(r) = \frac{1}{\sqrt{24}} r e^{-r/2}$$

- (i) Write down the expressions for $P_{20}(r)$ and $P_{21}(r)$. **[1]**
- (ii) By integrating $P_{20}(r)$ and $P_{21}(r)$, confirm that $R_{20}(r)$ and $R_{21}(r)$ are normalised. **[3]**
- (iii) By evaluating the values of r at which $P_{20}(r)$ and $P_{21}(r)$ are stationary, give an annotated plot of these functions, labelling the key features. **[6]**
- (iv) Calculate the expectation values of $\langle \hat{V} \rangle$ in atomic units for the 2s and 2p states, where \hat{V} is the potential energy operator. **[4]**
- (v) Comment on your answer to (iv). Use your answer to (iii) to predict how $\langle \hat{V} \rangle$ would change for the 2s and 2p orbitals in a multi-electron atom. **[3]**

[Note that $x^3 - 8x^2 + 16x - 8 = 0$ has a root at $x = 2$.]

[TURN OVER]

A3

- (a) The term symbol for the ground electronic state of $^{12}\text{C}^{16}\text{O}$ is $X\ ^1\Sigma^+$.

Explain the meaning of the different components of this term symbol.

Draw a molecular orbital diagram for CO and give the electronic configuration which is consistent with this term symbol. **[5]**

- (b) The following table shows the wavenumbers (in units of cm^{-1}) of some transitions seen in an electronic spectrum of CO involving a transition from the $^1\Sigma^+$ ground state to a higher electronic state. The lines are labelled with the vibrational quantum numbers of the upper (v') and lower states (v'').

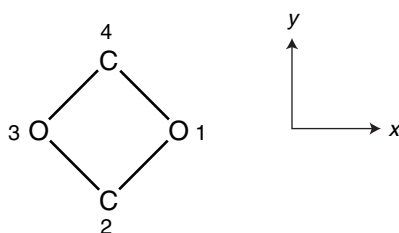
	v''	0	1	2
v'				
0		64747	62603	60487
1		66228	64084	61968
2		67674	65531	

From these data calculate for both states:

- (i) $\tilde{\omega}_e$, the wavenumber of the harmonic vibrational frequency (in cm^{-1}); **[2]**
 - (ii) $\tilde{\omega}_e x_e$, the product of the harmonic vibrational frequency and the anharmonicity constant (in cm^{-1}); **[2]**
 - (iii) Giving your reasoning, the number of vibrational levels. **[3]**
 - (iv) \tilde{D}_e , the dissociation energy (in cm^{-1}); **[2]**
- (c) On the basis of your results, suggest, with reasoning:
- (i) the relative bond lengths of the two states. **[1]**
 - (ii) how you expect the intensities of the vibrational features in the spectrum to change with the vibrational quantum number v' for $v'' = 0$. **[2]**
- (d) (i) On the basis of your results from (a) and (b), suggest, with reasoning, a suitable electronic excited state giving both its electronic configuration and its term symbol. **[2]**
- (ii) What form would you expect any rotational fine structure to have (although they cannot be observed at the low spectral resolution here)? **[1]**

A4

- (a) (i) State the point group of the H_2O molecule. [1]
- (ii) Write down the symmetries and sketch the symmetry orbitals for the two hydrogen 1s atomic orbitals (AOs) and the oxygen 2s and 2p AOs. (Assume the molecule lies in the yz -plane.) [2]
- (iii) Qualitatively sketch, with reasoning, a MO diagram for H_2O . [3]
- (iv) Suggest a suitable (ground state) electronic arrangement, and explain how this results in two equivalent O–H bonds. [3]
- (b) Consider the hypothetical planar small ring system:

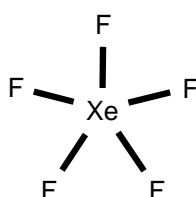


- (i) State the point group of this molecule. [1]
- (ii) *Using the numbering and axis system indicated* write down the symmetry orbitals which arise from a basis set consisting of an out-of-plane 2p AO on each atom. [3]
- (iii) Using the Hückel approximations, construct the secular equations and determine the orbital energies. (Take $\alpha_{\text{O}} = \alpha_{\text{C}} + \beta$, $\beta_{\text{CO}} = \beta$, $\beta_{\text{OO}} = \beta_{\text{CC}} = 0$.) [4]
- (iv) Now consider an additional interaction between the two carbon atoms (i.e. $\beta_{\text{CC}} = \beta$ but still with $\beta_{\text{OO}} = 0$). Solve the secular equations for this case and find the new orbital energies. If there are four π electrons, would such an interaction make the system more, or less, stable? [3]

[TURN OVER]

A5

- (a) (i) In the context of the vibrational spectroscopy of polyatomic molecules explain what is meant by a *fundamental transition*. [1]
- (ii) Show that the fundamental of a normal mode which transforms as Γ_{pq} , where Γ_{pq} is one of the irreducible representations spanned by the functions pq (p and q are any of x , y , and z), is symmetry allowed for vibrational Raman scattering. [3]
- (b) The anion $[\text{XeF}_5]^-$ is planar with the fluorine ligands arranged as a regular pentagon around the centrally placed xenon atom; the point group is D_{5h} .



- (i) Determine the symmetries (irreducible representations) of *all* of the normal modes of this molecule. [6]
- (ii) Assume that the fundamental of each normal mode gives rise to a feature in the spectrum provided the transition is symmetry allowed. Identify the symmetries of the normal modes which will give rise to such features in: (1) the infra-red spectrum; and (2) the vibrational Raman spectrum. Hence determine the number of such features that will be observed in: (1) the infra-red spectrum; and (2) the vibrational Raman spectrum. How many are common to both types of spectra? [4]
- (c) An alternative geometry for this molecule is for the fluorine atoms to remain in a planar regular pentagon but for the xenon atom to be displaced vertically out of the plane the ring; the resulting arrangement can be described as a pentagonal pyramid.
- (i) State the point group of a molecule with this alternative geometry. [1]
- (ii) Determine the symmetries (irreducible representations) of *all* of the normal modes of this molecule. [3]
- (iii) On the basis of the infra-red and vibrational Raman spectra, is it possible to distinguish between these two possible geometries? Explain your reasoning carefully. [2]

END OF PAPER



UNIVERSITY OF
CAMBRIDGE

NATURAL SCIENCES TRIPOS Part IB

Wednesday 5th June 2019

13:30 to 16:30

CHEMISTRY A: PAPER 2

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*]**

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

- (a) Consider a two-level system in which the ground level has energy 0 and degeneracy g_0 , and in which the upper level has energy ε and degeneracy g_1 .

- (i) Show that the internal energy of N such non-interacting two-level systems is given by (you may quote any relationships you need, without proof) [3]

$$U = \frac{N g_1 \varepsilon}{g_0 e^{\varepsilon/kT} + g_1}$$

- (ii) Hence derive an expression for the molar constant-volume heat capacity $C_{V,m}$. [3]

- (iii) Suppose that the energy zero of the system is altered such that the energy of *both* levels is changed by an amount δ . Write down expressions for U and $C_{V,m}$, giving brief reasons for your answers. [3]

- (b) NO_2 is a paramagnetic molecule with one unpaired electron. When a magnetic field \mathcal{B}_0 is applied the interaction with the electron spin gives rise to two (non-degenerate) energy levels with energies

$$\varepsilon_m = g_e \mu_B \mathcal{B}_0 m \quad \text{where } m = +\frac{1}{2}, -\frac{1}{2}$$

and where g_e is the g -value of the electron, which may be taken as having the value 2, and μ_B is the Bohr magneton, which has the value $9.27 \times 10^{-24} \text{ J T}^{-1}$ (T denotes tesla, the unit of magnetic field).

- (i) Evaluate (in J) the energy separation between the two levels for an applied magnetic field of 10.0 T. Hence evaluate the contribution that the unpaired electron spin makes to $C_{V,m}$ at a temperature of 50.0 K (assume that the molecule remains in the gas phase). [3]
- (ii) *Estimate* $C_{V,m}$ for $\text{NO}_2(\text{g})$ at this temperature, and hence find the contribution, expressed as a percentage, that the unpaired electron spin makes to the *total* heat capacity. [2]
- (iii) Giving your reasons, describe how you would expect the contribution from the electron spin to the heat capacity to change as the temperature is steadily increased *from* 50 K *to* room temperature (298 K). [3]
- (iv) Giving your reasons, describe how would you expect the contribution from the electron spin to the heat capacity to change as the magnetic field is steadily increased from zero, at a fixed temperature of 50 K. [3]

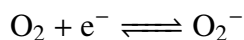
A7

- (a) For the gas-phase equilibrium $A + B \rightleftharpoons C$ the equilibrium constant may be computed using the expression

$$K_c = \frac{f_C}{f_A f_B} \left(\frac{1}{c^\circ} \right)^{-1} e^{-\Delta \varepsilon_0 / kT}$$

Explain what the following symbols represent

- (i) f_A , f_B , and f_C [1]
 - (ii) c° [1]
 - (iii) $\Delta \varepsilon_0$. [1]
- (b) Consider the gas-phase equilibrium in which an electron is attached to O_2 to give the anion



At a temperature of 298 K, taking the mass of an oxygen atom as $16.0 m_u$, and using the data below:

- (i) Compute the translational contribution to the ratio $f(O_2^-)/f(O_2)f(e^-)$. [3]
- (ii) Compute the rotational contribution to the above ratio. [3]
- (iii) Compute the vibrational contribution to the above ratio. [3]
- (iv) Compute the electronic contribution to the above ratio. [4]
- (v) Hence compute the value of the equilibrium constant; comment on your numerical answer. [4]

Bond lengths: O_2 121 pm; O_2^- 135 pm

Vibrational frequencies: O_2 1580 cm^{-1} ; O_2^- 1098 cm^{-1}

$\Delta \varepsilon_0 = -141 \text{ kJ mol}^{-1}$

[TURN OVER

A8

- (a) The rate constant $k_{2\text{nd}}$ for a second-order reaction in solution may be expressed in terms of transition state theory as

$$k_{2\text{nd}} = \frac{1}{[\]^\circ} \frac{kT}{h} K^\ddagger$$

where $[\]^\circ$ is the standard concentration (1 mol dm^{-3}). By definition the activation energy E_a is given by

$$\left(\frac{d \ln k_{2\text{nd}}}{dT} \right)_V = \frac{E_a}{RT^2}$$

and, for a reaction in solution, it is the case that

$$\left(\frac{d \ln K^\ddagger}{dT} \right)_V = \frac{\Delta H^{\circ,\ddagger}}{RT^2}$$

where $\Delta H^{\circ,\ddagger}$ is the enthalpy of activation.

Consider a reaction in which the rate constant is found to obey the Arrhenius law $k_{2\text{nd}} = A e^{-E_a/RT}$

- (i) Use the above to derive the relationship between E_a and $\Delta H^{\circ,\ddagger}$. [3]
- (ii) Derive an expression for the entropy of activation, $\Delta S^{\circ,\ddagger}$, in terms of A . [4]
- (iii) The second-order rate constant for a certain reaction in solution is found to obey the following empirical relationship at temperatures close to 30°C

$$k_{2\text{nd}} = A e^{(-8681 \text{ K})/T}, \text{ with } A = 2.05 \times 10^{13} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Find values for $\Delta H^{\circ,\ddagger}$ and $\Delta S^{\circ,\ddagger}$ at around this temperature. [4]

- (b)
 - (i) Explain how the *volume of activation* is defined and describe how a value for this parameter is measured. [Note that $(\partial G/\partial p)_T = V$.] [5]
 - (ii) An apparatus can apply a pressure of between 1 bar and 500 bar to a solution-phase reaction vessel, and it is suspected that the smallest change in the rate constant that can be measured reliably is an increase or decrease by 3%. Estimate the magnitude of the smallest volume of activation that can be measured using this apparatus at 298 K. [4]

A9

- (a) (i) Restricting your discussion to one-dimension explain concisely what you understand by the terms *commensurate wave* and *reciprocal lattice*. [3]
- (ii) In a one-dimensional case, if the real-space lattice spacing is a , what is the spacing of the points in the reciprocal lattice? [1]
- (b) (i) Consider a two-dimensional real-space lattice, defined by lattice vectors \mathbf{a}_1 and \mathbf{a}_2 . The reciprocal-space lattice vectors \mathbf{b}_1 and \mathbf{b}_2 satisfy

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij} \quad \text{where } \delta_{ij} = 1 \text{ if } i = j \text{ and } = 0 \text{ otherwise}$$

Suppose that the real-space lattice vectors are $\mathbf{a}_1 = a[1, 0]$ and $\mathbf{a}_2 = \frac{1}{2}a[0, 1]$. Find the corresponding reciprocal-lattice vectors \mathbf{b}_1 and \mathbf{b}_2 , and hence make a labelled sketch of the reciprocal lattice. [4]

- (ii) Calculate the area of the real-space and reciprocal-space unit cells. What is the relationship between these two quantities? [2]
- (c) (i) On a piece of graph paper make a careful sketch to scale of the two-dimensional reciprocal lattice described in (b) (i); then use a geometric construction to find the first and second Brillouin zones. On your diagram, be sure to indicate clearly which zone is which. [4]
- (ii) Calculate the lowest value of the wavevector k for which the Fermi circle just touches an edge of the first Brillouin zone, and the value of k which results in the Fermi circle just enclosing the first Brillouin zone. [3]
- (iii) The density of Born von Karman allowed states in two dimensions is $L_1 L_2 A_c / (2\pi)^2$, where there are L_1 and L_2 units cells along the \mathbf{a}_1 and \mathbf{a}_2 directions, respectively, and A_c is the area of the real-space unit cell. Use your result from (c) (ii) to compute how many electrons per lattice point will result in a Fermi circle which just touches an edge of the first Brillouin zone. [3]

[TURN OVER

A10

- (a) In the tight-binding approximation a band in one dimension arises from the overlap of N identical atomic orbitals. The resulting crystal orbitals can be expressed as

$$\psi_k = \sum_{r=1}^N c_k^{(r)} \phi_r \quad \text{where} \quad c_k^{(r)} = e^{ikra}$$

In this expression ϕ_r is the atomic orbital at position r and a is the lattice spacing. If the Hückel approximations are made, the energies of the crystal orbitals which comprise the band can be expressed as a function of k as

$$E_k = \alpha + 2\beta \cos(ka)$$

- (i) explain concisely what range the wavevector k takes. [4]
 - (ii) Make a labelled plot of the dispersion curve for this band. [1]
 - (iii) In the context of a band, describe what you understand by the *density of states*. Sketch a graph of the density of states of this one-dimensional band as a function of k , briefly explaining how you deduced the form of the plot and pointing out any key features. [3]
- (b) In two dimensions and using the Hückel approximations, the energies of the crystal orbitals arising from a square lattice with spacing a are

$$E_{k_x, k_y} = \alpha + 2\beta \cos(k_x a) + 2\beta \cos(k_y a)$$

In reciprocal space the point $(k_x, k_y) = (0, 0)$ is labelled Γ , the point $(k_x, k_y) = (\pi/a, 0)$ is labelled X, and the point $(k_x, k_y) = (\pi/a, \pi/a)$ is labelled M

- (i) Make separate labelled plots of the dispersion curve for this band when moving: (1) from Γ to X; (2) from X to M; (3) from M to Γ . [3]
- (ii) Near to Γ show that the energy may be approximated by

$$E_k = \alpha + 4\beta - \beta a^2 k^2$$

where $k^2 = k_x^2 + k_y^2$; you may wish to use the approximation $\cos \theta \approx 1 - \frac{1}{2}\theta^2$, which is valid for $|\theta|$ close to zero. [1]

[Qu. 10 continued on next page]

[Continuation of Qu. 10]

- (iii) Within this approximation, describe where in k -space states with a given energy E_k lie.

Hence derive an expression for $W(k)$, the number of k states with energies between E_0 and E_k ; note that each k state occupies an 'area' of $(2\pi/Na)^2$ in k -space. [3]

- (iv) Hence derive an expression for the density of states, $D(E)$, also within this approximation. You will find it convenient to compute this using

$$D(E) = \frac{dW(E)}{dE} = \frac{dW(k)}{dk} \times \frac{dk}{dE}$$

Compare your result to that for the one-dimensional case close to $k = 0$. [2]

- (c) Consider a sample of pure solid Si, whose electronic structure can be thought of in terms of a valence band and a conduction band, which is doped with a small amount of As.

Measurements on such a doped sample indicate the presence of dopant levels, the lowest of which is at about 30 meV below the conduction band. Using a simple hydrogenic model for the dopant atom, estimate the apparent relative permittivity of the solid and the effective Bohr radius (in nm) of the dopant atom. [Take the effective mass of the electron as 0.3 times the electron mass.] [3]

[The Rydberg constant is given by $R_H = e^4 m_e / 32\pi^2 \hbar^2 \epsilon_0^2$ and has the value 13.6 eV; the Bohr radius is given by $a_0 = 4\pi\hbar^2 \epsilon_0 / e^2 m_e$ and has the value 53 pm.]

END OF PAPER