



UNIVERSITY OF CAMBRIDGE

NATURAL SCIENCES TRIPOS Part IB

Friday 27th May 2016

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>
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A1

Answer *all* parts of the question.

- (a) (i) Define the terms in the commutator

$$[\hat{J}_x, \hat{J}_y] = i\hbar \hat{J}_z$$

and give the related expressions for $[\hat{J}_y, \hat{J}_z]$, $[\hat{J}_z, \hat{J}_x]$, $[\hat{J}_x, \hat{J}^2]$, $[\hat{J}_y, \hat{J}^2]$ and $[\hat{J}_z, \hat{J}^2]$ (where \hat{J}_x , \hat{J}_y , \hat{J}_z are angular momentum operators, and $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$).

- (ii) By giving the relevant eigenvalue equations, explain which properties of the angular momentum of a quantum particle can and cannot be measured simultaneously and precisely.

- (b) The *raising* and *lowering* operators are defined by

$$\begin{aligned}\hat{J}^+ &= \hat{J}_x + i\hat{J}_y \\ \hat{J}^- &= \hat{J}_x - i\hat{J}_y\end{aligned}$$

- (i) Use your answer to (a) to show that

$$\begin{aligned}[\hat{J}^+, \hat{J}_z] &= -\hbar \hat{J}^+ & [\hat{J}^-, \hat{J}_z] &= \hbar \hat{J}^- \\ [\hat{J}^+, \hat{J}^2] &= [\hat{J}^-, \hat{J}^2] &= 0\end{aligned}$$

- (ii) Hence, by considering the eigenfunctions of \hat{J}_z and \hat{J}^2 , show that

$$\hat{J}^\pm Y_{JM}(\theta, \phi) = c_{JM}^\pm Y_{JM\pm 1}(\theta, \phi)$$

where c_{JM}^\pm is a proportionality constant which you need not determine.

- (c) By representing the operators \hat{J}_x , \hat{J}_y , \hat{J}_z in cartesian coordinates or otherwise, use your answer to (b) to generate the angular dependencies of $Y_{1\pm 1}(\theta, \phi)$, given that the angular dependence of $Y_{10}(\theta, \phi)$ is $\cos \theta$.

Approximate division of marks: (a) 15%, (b) 50%, (c) 35%.

A2

Answer *all* parts of the question.

- (a) (i) State the variation principle.
 (ii) Starting with a hamiltonian \hat{H} , and a trial wave function of the form

$$\widetilde{\Psi} = c_1\phi_1 + c_2\phi_2,$$

use the variation principle to eliminate the coefficients c_1, c_2 , to give an approximate expression for the ground-state energy in terms of the matrix elements

$$H_{ij} = \int \phi_i^* \hat{H} \phi_j d\tau$$

where $\int \dots d\tau$ denotes integration over the system coordinates. You may assume that the basis functions ϕ_1, ϕ_2 are orthonormal, and that the coefficients c_1, c_2 are real.

- (b) The orthonormal basis functions

$$\begin{aligned}\phi_1(q) &= \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha q^2/2} \\ \phi_2(q) &= (2\alpha)^{1/2} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha q^2/2} q\end{aligned}$$

are eigenfunctions of the hamiltonian

$$\hat{H}_0 = -\frac{1}{2} \frac{d^2}{dq^2} + \frac{q^2}{2}$$

when $\alpha = 1$.

- (i) Use these basis functions with $\alpha = 1$, and your answer to (a), to estimate the ground-state energy of the hamiltonian

$$\hat{H} = \hat{H}_0 + q$$

- (ii) Use the variation principle to estimate the ground-state energy of \hat{H} using just the basis function $\phi_1(q)$, with α free to take any value. Comment on your answer.
 (c) Obtain upper and lower bounds to the approximate ground-state energy that would result if (b)(i) were repeated, with α free to take any value (without calculating this approximate energy explicitly).

Approximate division of marks: (a) 45%, (b) 35%, (c) 20%.

[TURN OVER

A3

Answer *all* parts of the question.

- (a) Discuss the differences between the harmonic oscillator and the anharmonic oscillator as models for the vibrations of a diatomic molecule. Include qualitative labelled sketches of the vibrational spectra you expect to observe for both cases.
- (b) (i) Give an expression for the vibrational energy levels of a diatomic molecule assuming the Morse potential, defining all the terms used.
- (ii) Use the expression from above to derive an expression for the dissociation energy, D_e . Explain how the observed dissociation energy, D_0 , differs from D_e .

The table below lists a number of IR transitions in the spectrum of the ClO molecule in the ground ($X^2\Pi$) and first excited ($A^2\Pi$) electronic states:

	$v'' = 0 \rightarrow v' = 1$	$v'' = 1 \rightarrow v' = 2$
$X^2\Pi$ electronic state	842.6 cm^{-1}	831.6 cm^{-1}
$A^2\Pi$ electronic state	505.1 cm^{-1}	490.7 cm^{-1}

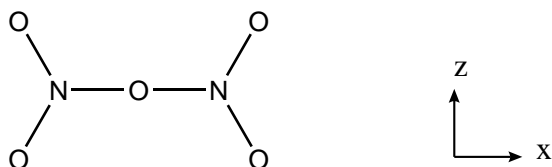
- (c) Use these data to calculate the fundamental vibrational frequencies, the anharmonicity constants, and the dissociation energies, D_e , for the X and A electronic states of the ClO molecule.
- (d) Sketch an MO energy-level diagram for ClO. Suggest electronic configurations for the X and A states, explaining how they are consistent with the term symbols, and the results of your calculations in (c).

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

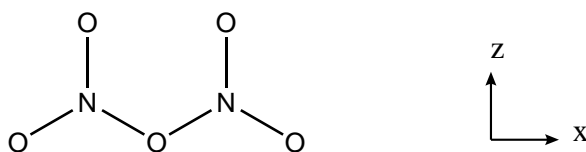
A4

Answer *all* parts of the question.

- (a) In the solid state, a metastable phase of N_2O_5 contains molecules with the planar geometry given below.



- (i) Determine the point group of the molecule.
 - (ii) Considering only the out-of-plane p-orbitals, determine and sketch the symmetry orbitals of this system.
 - (iii) Using Hückel theory, and by approximating the energies of the p-orbitals to be $\epsilon_{\text{O}} = \alpha$ and $\epsilon_{\text{N}} = \alpha - \beta$, and each resonance integral between adjacent oxygen and nitrogen atoms to be β , determine the energies of all the molecular orbitals. State any further approximations you have made.
 - (iv) Draw a molecular-orbital energy diagram, labelling each state with its energy and symmetry, and comment on the likely reactivity of the molecule in this geometry.
- (b) The stable form of N_2O_5 in its gaseous state retains its planarity but adopts instead the geometry below.



- (i) Using the approximations in part (a)(iii), the molecular-orbital energies of the gaseous molecule are identical to those of the solid-state molecule. Briefly explain why this is the case.
- (ii) Suggest how the approximations in part (a)(iii) might be relaxed, and, by considering the shapes of the highest occupied molecular orbitals, draw a qualitative molecular-orbital energy diagram indicating how the energies of the orbitals might change.

Approximate division of marks: (a) i) 5%, ii) 15%, iii) 45%, iv) 10%, (b) i) 10%, ii) 15%.

[TURN OVER

A5

Answer *all* parts of the question.

- (a) Gaseous ScCl_3 can be formed from the solid at high temperatures and its structure could be either trigonal planar or pyramidal. Given the vibrational infrared spectrum shows three distinct absorbances, determine its geometry.
- (b) The scandium dimer, Sc_2 , when studied computationally was found to have the ground state term symbol $^5\Sigma_u^-$. When this state dissociates, it produces two scandium atoms, each with a different term symbol: ^2D and ^4F . The electronic structure of both the dimer and each of the separated atoms was found to involve only the 4s and 3d orbitals.
- (i) For each of the term symbols of the dissociated atoms, write down a possible configuration of occupied **atomic** orbitals.

The molecular orbitals of the dimer can be formed from the 4s and 3d atomic orbitals of the atoms. Whilst the full point group of the molecule is $\mathcal{D}_{\infty h}$, a subgroup of operations whose character table is given below is sufficient to treat this system.

		E	$2C_4$	C_4^2	$2\sigma_v$	$2\sigma_d$	i	$2S_4$	σ_h	$2C_2$	$2C_2'$
Σ_g^+	(A_{1g})	1	1	1	1	1	1	1	1	1	1
Σ_g^-	(A_{2g})	1	1	1	-1	-1	1	1	1	-1	-1
Π_g	(E_{1g})	2	0	-2	0	0	2	0	-2	0	0
Δ_g	(E_{2g})	1	-1	1	1	-1	1	-1	1	1	-1
		1	-1	1	-1	1	1	-1	1	-1	1
Σ_u^+	(A_{1u})	1	1	1	1	1	-1	-1	-1	-1	-1
Σ_u^-	(A_{2u})	1	1	1	-1	-1	-1	-1	-1	1	1
Π_u	(E_{1u})	2	0	-2	0	0	-2	0	2	0	0
Δ_u	(E_{2u})	1	-1	1	1	-1	-1	1	-1	-1	1
		1	-1	1	-1	1	-1	1	-1	1	-1

The C_2 axes coincide with the x and y axes, and the σ_v operations with the xz and yz planes. In this character table, the Δ representations each contain two different irreducible components which together make up the doubly-degenerate Δ representation.

- (ii) Using this table, or otherwise, determine the symmetry orbitals of the dimer, and give sketches of them.

[Qu. 5 continued on next page]

[Continuation of Qu. 5]

- (iii) In this molecule, the 4s orbitals are well below the 3d in energy. By considering the magnitude of overlaps, draw a molecular-orbital energy-level diagram for this system, labelling each orbital with its symmetry.
- (iv) By considering how the sets of orbitals occupied in the atoms combine to form molecular orbitals, propose an occupancy for the **molecular** orbitals of Sc_2 and explain how the term symbol $^5\Sigma_u^-$ arises.

Approximate division of marks: (a) 25%, (b)(i) 10%, (ii) 25%, (iii) 20%, (iv) 20%.

END OF PAPER



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Wednesday 1st June 2016

13.30 to 16.30

CHEMISTRY A: PAPER 2

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A6

Answer *all* parts of the question.

- (a) Define the variables in the bridge relationship $A = -k_B T \ln Q_N$. Use this relationship to derive an expression for the molar entropy of N non-interacting, indistinguishable particles in terms of the internal energy, U , and molecular partition function, q . Be sure to explain each step of your derivation.
- (b) Explain why the expression for the contribution of translational entropy to the total entropy takes a different form to the expressions for the other contributions.
- (c) Using the following data, calculate the standard molar entropy of $^{35}\text{Cl}^{16}\text{O}(\text{g})$ at 298 K, explaining any assumptions you make.

Rotational temperature: $\theta_{\text{rot}} = 0.8972 \text{ K}$

Vibrational temperature: $\theta_{\text{vib}} = 1228 \text{ K}$.

Approximate division of marks: (a) 35%, (b) 15%, (c) 50%.

A7

Answer *all* parts of the question.

Consider the equilibrium between a neutral atom M and its ionised (plasma) state consisting of a positively charged ion M^+ and a free electron e^- . The chemical potential of a species i is given as:

$$\mu_i = -k_B T \ln \frac{f_i}{c_i} + \varepsilon_i.$$

In this expression, c_i is the concentration [particles per volume, $c_i = \frac{N_i}{V}$], and ε_i is the energy of the electronic ground state with respect to a common origin.

The volume-independent partition function, f_i , is given by

$$f_i = (2\pi m_i k_B T / h^2)^{\frac{3}{2}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}.$$

- (a) At equilibrium, the sum of the chemical potentials of the products is equal to that of the reactants. Show that the equilibrium constant for the ionisation of M is

$$K_c = \frac{f_{e^-} f_{M^+}}{f_M} \frac{1}{c^\circ} \exp\left(\frac{-E_I}{k_B T}\right)$$

and give an expression for E_I , the ionization energy of M. [c° is the standard concentration: $c^\circ = 1 \text{ m}^{-3}$.]

- (b) Show that this equation can be simplified further to:

$$K_c = (2\pi m_e k_B T / h^2)^{\frac{3}{2}} \frac{1}{c^\circ} \frac{2g_{M^+}}{g_M} \exp\left(\frac{-E_I}{k_B T}\right)$$

where g_{M^+} and g_M are the electronic ground-state degeneracies of M^+ and M. State clearly the assumptions that you have made to arrive at this equation.

- (c) Does K_c , as given in (b), increase or decrease with temperature? Reason in terms of entropy and enthalpy to explain whether plasmas are expected to be more common at high or low temperatures.
- (d) The outer shell of the sun, the photosphere, is at a temperature of approximately 6400 K. The concentration of the hydrogen is $10^{23} \text{ (atoms) m}^{-3}$. Calculate the value of K_c . Would you expect hydrogen in the photosphere to occur mostly as a neutral atomic species or in its ionised form? (The ionization energy of hydrogen is 1312 kJ mol^{-1} .)

Approximate division of marks: (a) 25%, (b) 20%, (c) 20%, (d) 35%.

A8

Answer *all* parts of the question.

The rate constant k describing many simple reactions $A \longrightarrow B$ is given by the Eyring equation:

$$k = \frac{k_B T}{h} \exp \frac{-\Delta_r G^{\ddagger}}{k_B T}.$$

where $d[A]/dt = -k[A]$

- (a) Starting with the appropriate master equation, show that the standard molar volume of activation at constant temperature is given by:

$$\Delta_r V^{\ddagger} = (\partial \Delta_r G^{\ddagger} / \partial p)_T.$$

- (b) The substitution reaction

$[\text{Fe}(\text{CN})_5(3,5\text{-dimethylpyridine})]^{3-} + \text{CN}^- \longrightarrow [\text{Fe}(\text{CN})_6]^{4-} + 3,5\text{-dimethylpyridine}$
 was carried out with a large excess of CN^- giving effective first-order rate constants, which were determined as a function of pressure at 298 K.

Pressure (bar)	1	450	690	1034	1379
$k \text{ (s}^{-1}\text{)}$	1.33	0.85	0.71	0.515	0.41

By plotting an appropriate graph, determine the standard molar volume of activation for this reaction.

- (c) Based on the value for the molar activation volume that you have obtained in (b), discuss whether the mechanism of the reaction is likely to be associative or dissociative.
- (d) The compressibility coefficient of activation is defined as:

$$\beta^{\ddagger} = -(\partial \Delta_r V^{\ddagger} / \partial p)_T$$

Referring to your graph in part (b), comment on whether the data support a compressibility coefficient that is different from zero. Large values of β^{\ddagger} usually arise due to electrostriction from newly generated ions. Comment on the role (or lack thereof) of electrostriction in determining the volume of activation for this reaction.

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

A9

Answer *all* parts of the question.

- (a) Bulk potassium crystallises in a cubic structure for which the primitive lattice vectors are: $\frac{1}{2}a(1, 1, -1)$; $\frac{1}{2}a(-1, 1, 1)$; $\frac{1}{2}a(1, -1, 1)$. Draw a perspective sketch of this crystal structure, showing the atomic positions, and identify the Bravais lattice.
- (b) The value of the unit-cell parameter is $a = 5.3\text{\AA}$. Calculate the volumes of the Wigner-Seitz unit cell in both real and reciprocal space.
- (c) Assuming that the valence electrons in crystalline potassium obey the free-electron-gas model, calculate the value of the Fermi wavevector, k_F , at $T = 0\text{ K}$. Determine how many Brillouin zones are filled by the Fermi sphere in reciprocal space, and hence rationalise the electrical-conductivity behaviour expected for crystalline potassium.
- (d) Calculate the corresponding Fermi energy of the valence electrons in potassium at $T = 0\text{ K}$. Explain why this is a non-zero value.
- (e) The atomic density of lithium (with the same crystal structure as potassium) is approximately three times the value of that for potassium. Estimate the value for the Fermi energy for Li. Would you expect valence electrons in Li and K equally well to obey the free-electron-gas model? Give your reasons.

(You may use any relevant formulae without derivation.)

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

A10

Answer *all* parts of the question.

- (a) Explain, in terms of the electronic bonding and their band structures, why the carbon allotropes, diamond and graphene, are electrically insulating and semi-metallic, respectively. Sketch the corresponding electronic densities of states to illustrate the answer.
- (b) Describe how, by doping with nitrogen, diamond can be made semiconducting or metallic. What are the dominant charge carriers in N-doped diamond?
- (c) Describe how, by doping with bromine, graphite can be made metallic. What are the dominant charge carriers in this case?
- (d) Assuming that a periodic one-dimensional chain of atoms, with interatomic spacing a , has a single s orbital at each lattice site, obtain an expression for the electronic-structure energy, E_k , as a function of electron wavevector, k , in the tight-binding approximation (TBA) of the linear combination of atomic orbitals (LCAO) model.
- (e) Hence, obtain a general expression for the effective electron mass, $m^*(k)$, for this system. Sketch the k -dependence of m^* . What is the value of m^* at $k = 0$ and π/a ? Comment on these values.
- (f) Explain why the one-dimensional carbon-based material, *poly*-acetylene (*poly*-ethyne), is semiconducting, rather than metallic, under certain conditions.

(You may use any relevant formulae without proof in the course of deriving the final expressions in (d) and (e).)

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

END OF PAPER