



# UNIVERSITY OF CAMBRIDGE

## NATURAL SCIENCES TRIPOS Part IB

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**Friday 30th May 2014      13:30 to 16.30**

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### 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><b>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.</b></p>
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**A1**

Answer **all** parts of the question.

- (a) (i) Define the *commutator*  $[\hat{A}, \hat{B}]$  of two operators  $\hat{A}$  and  $\hat{B}$ .  
 (ii) Evaluate  $[\hat{p}, \hat{x}]$  (where  $\hat{p}$  is the momentum operator, and  $\hat{x}$  the position operator) and hence prove that  $\hat{p}$  and  $\hat{x}$  do not commute.
- (b) (i) The angular momentum operator,  $\hat{J}_x$ , in cartesian coordinates is given by:

$$\hat{J}_x = -i\hbar \left[ y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right]$$

Write down the angular momentum operators  $\hat{J}_y$  and  $\hat{J}_z$ , also in terms of cartesian coordinates.

- (ii) Derive an expression for  $[\hat{J}_x, \hat{J}_y]$ , and hence also (by cyclic permutation of  $(x, y, z)$ ) obtain expressions for  $[\hat{J}_y, \hat{J}_z]$  and  $[\hat{J}_z, \hat{J}_x]$ .
- (iii) Without derivation, state the value of the commutator  $[\hat{J}_z, \hat{J}^2]$ , where  $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$ .
- (iv) State very briefly what your answers to (ii) and (iii) predict about the ability of an experiment to measure precisely the angular-momentum vector of a quantum particle.
- (c) The angular part of a  $p_z$  orbital can be written in cartesian coordinates as

$$\Psi(x, y, z) = \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

Use your answers to (b)(i) to determine whether  $\Psi(x, y, z)$  is an eigenfunction of any of the operators  $\hat{J}_x, \hat{J}_y, \hat{J}_z$ . Check that your results are consistent with your answer to (b)(iv).

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

**A2**

Answer *all* parts of the question.

- (a) State the variation principle and give the mathematical steps that must be followed to find the value of a parameter  $\alpha$  for which a trial wave function  $\Psi_\alpha$  gives the closest energy to the exact ground state energy.
- (b) A hydrogen 1s orbital satisfies the Schrödinger equation

$$\hat{H}_{1s}\Psi(r) = E\Psi(r)$$

where

$$\hat{H}_{1s} = -\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{1}{r}$$

and atomic units have been used. A proposed approximate 1s orbital has the form

$$\Psi_\alpha(r) = e^{-(r/\alpha)^2}$$

- (i) By integrating over spherical-polar coordinates, show that

$$\langle \hat{H}_{1s} \rangle = \frac{\int_0^\infty \Psi_\alpha(r)^* \hat{H}_{1s} \Psi_\alpha(r) r^2 dr}{\int_0^\infty \Psi_\alpha(r)^* \Psi_\alpha(r) r^2 dr}$$

and hence that

$$\langle \hat{V} \rangle = -\frac{1}{\alpha} \sqrt{\frac{8}{\pi}}$$

and

$$\langle \hat{T} \rangle = \frac{3}{2\alpha^2}$$

where  $\hat{V}$  and  $\hat{T}$  are respectively the potential and kinetic energy parts of  $\hat{H}_{1s}$ .

- (ii) Use these results to obtain an estimate of the energy, in atomic units, of a hydrogen atom in its 1s state.

[You may use the standard integrals:  $\int_0^\infty r \exp[-2(r/\alpha)^2] = \alpha^2/4$ ,  
 $\int_0^\infty r^2 \exp[-2(r/\alpha)^2] = (\alpha^3/8)(\pi/2)^{\frac{1}{2}}$ ,  $\int_0^\infty r^4 \exp[-2(r/\alpha)^2] = (3\alpha^5/32)(\pi/2)^{\frac{1}{2}}$ .]

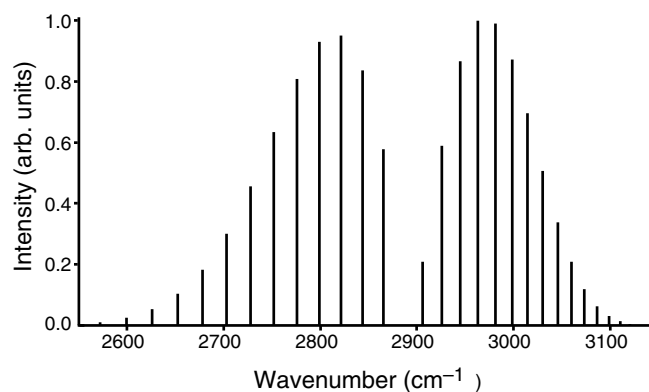
Approximate division of marks: (a) 15%, (b) 85%.

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**A3**

Answer *all* parts of the question.

The figure below shows schematically the infra-red spectrum of the fundamental vibration of  $^1\text{H}^{35}\text{Cl}$  in the gas phase.



- (a) Explain the pattern of frequencies and intensities that are observed.
- (b) Frequencies (in  $\text{cm}^{-1}$ ) and assignments of a number of transitions in the above spectrum are as shown in the table below.

$J''$	R branch	P branch
0	2905.92	
1	2925.59	2864.76
2	2944.64	2843.29
3	2963.06	2821.25
4	2980.85	2798.63
5	2997.97	2775.47
6	3014.43	2751.76

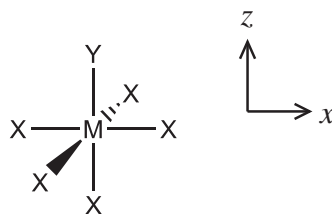
- (i) By graphical means, or otherwise, use this information to determine rotational constants,  $B_0$  and  $B_1$ , for the two vibrational levels.
- (ii) Derive the equilibrium rotational constant  $B_e$ , and calculate the equilibrium bond length  $r_e$ .
- (c) Derive an expression for the most populated rotational level, hence *estimate* the temperature of the HCl sample above.
- (d) Suggest how you might expect the bond length and hence the rotational constant to change with rotational quantum number  $J$ . Is there any evidence for this in the above spectrum?

Approximate division of marks: (a) 20%, (b) 40%, (c) 20%, (d) 20%.

## A4

Answer *all* parts of the question.

- (a) With the aid of a labelled molecular orbital diagram, describe the interaction between the metal, M, and the ligands, X, in an octahedral first row transition metal complex,  $\text{MX}_6$ . Assume that the ligands are purely  $\sigma$ -donors.
- (b) When put in equilibrium with a different  $\sigma$ -donor ligand, Y, the metal forms  $\text{MX}_5\text{Y}$ . The interaction between the metal orbitals with the ligand orbitals from Y is stronger than that with the ligand orbitals from X and the complex now has a different splitting pattern from the octahedral complex.



- (i) What is the point group of this molecule?
- (ii) By classifying the ligand and metal orbitals through symmetry, draw a qualitative MO diagram for this system, including the metal  $3d$ - and  $4s$ -orbitals, but ignoring the metal  $4p$ -orbitals. In this case, you should assume that any degenerate symmetry orbitals interact less strongly than the non-degenerate ones.
- (iii) Assuming the ligands X and Y are neutral, and that the exchange interaction is significantly smaller in magnitude than the splitting of orbitals, determine the first row transition metal, M, which would maximize the magnetic moment of the complex  $[\text{MX}_5\text{Y}]^{3+}$ . How does this compare to the octahedral case  $[\text{MX}_6]^{3+}$ ?

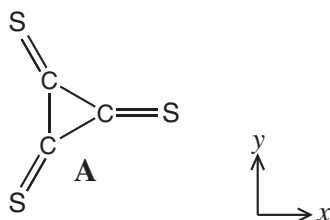
Approximate division of marks: (a) 35%, (b) (i) 5%, (b)(ii) 45%, (b)(iii) 15%.

[TURN OVER

**A5**

Answer *all* parts of the question.

Compound A is an unstable sulfide of carbon based on an equilateral triangle of carbons.



- (a) (i) What is the point group of the molecule?
- (ii) Considering only the  $p_z$ -orbitals on the carbons and sulfur atoms separately, determine what irreducible representations are spanned, and form the corresponding symmetry orbitals.
- (iii) Use your symmetry orbitals to calculate, through Hückel Theory, a quantitative molecular orbital diagram including the progression from atomic to symmetry to molecular orbitals, labelling each orbital with its symmetry and energy. You should assume that the carbon-carbon and carbon-sulfur resonance interactions,  $\beta$ , have the same magnitude and the difference in carbon and sulfur  $p$ -orbital energies is  $2\beta$ . State any further assumptions you have made. [You are not required to determine the molecular orbital coefficients.]
- (b) The molecule is to be investigated spectroscopically.
- (i) Determine the symmetries of the vibrational normal modes of this molecule.
- (ii) For each normal mode, state whether its fundamental is active in:
- (1) IR spectroscopy
  - (2) Raman spectroscopy.
- (iii) Sketch the displacements involved in the four non-degenerate normal mode vibrations.

Approximate division of marks: (a) 60%, (b) 40%.

END OF PAPER



# UNIVERSITY OF CAMBRIDGE

## NATURAL SCIENCES TRIPOS Part IB

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**Wednesday 4th June 2014      13.30 to 16.30**

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### CHEMISTRY A: PAPER 2

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**A6**

Answer **all** parts of the question.

- (a) Explain why and under what conditions the partition function,  $Q_N$ , for a system of  $N$  non-interacting indistinguishable particles (atoms or molecules) can be written as  $(q^N/N!)$ , where  $q$  is the partition function for an individual particle. Write down, giving your reasoning, the equivalent expression for identical atoms in a solid.
- (b) Starting from the bridge relationship linking the Helmholtz free energy,  $A$ , to the partition function  $Q_N$ , derive an expression for the translation entropy,  $S_{trans}$ , of a system of  $N$  non-interacting indistinguishable particles.
- (c) The expression for the translation partition function for one particle  $q_{trans}$  is:

$$q_{trans} = \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V$$

where the constants have their usual meanings. Evaluate the molar entropy of a gas consisting of  $^4\text{He}$  atoms at 298 K and 1 bar pressure.

- (d) Calculate the molar entropy for  $^3\text{He}$  at 600 K and 10 bar; do the same for  $^4\text{He}$ .  
[The nuclear spins for  $^3\text{He}$  and  $^4\text{He}$  are  $\frac{1}{2}$  and 0 respectively.]

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



**A7**

Answer *all* parts of the question.

The  $\text{Cr}^{3+}$  ion in chromium methylammonium alum  $\text{Cr}(\text{CH}_3\text{NH}_3)(\text{SO}_4)_2$  has an electronic ground state energy of  $E$  and a first excited state close to this ground state at an energy of  $E + \varepsilon$ . We assume that both these states are non-degenerate and the other excited states are significantly higher in energy and are not populated.

- (a) Compute the partition function for a single  $\text{Cr}^{3+}$  ion.
- (b) By making use of the identity

$$U = NkT^2 \left( \frac{\partial \ln q}{\partial T} \right)_V$$

find an expression for the (electronic) internal energy for one mole of chromium methylammonium alum.

- (c) Using your result in (b), show that the molar heat capacity follows the relationship

$$C_V = R \left( \frac{\varepsilon}{kT} \right)^2 \frac{\exp(\varepsilon/kT)}{[1 + \exp(\varepsilon/kT)]^2}$$

- (d) Show that the heat capacity for  $T \gg \varepsilon/k$  is of the form  $a \times 1/T^2$  where  $a$  is a constant related to  $\varepsilon$ .
- (e) The experimentally measured molar heat capacities for chromium methylammonium alum are given below for four temperatures:

Temperature / K	$C_V / \text{J K}^{-1} \text{mol}^{-1}$
0.208	2.66
0.257	2.00
0.329	1.39
0.396	0.97

By plotting an appropriate graph, find the value of the parameter  $a$  from part (d) and hence determine the energy of the first excited state of the  $\text{Cr}^{3+}$  ion relative to its ground state.

- (f) Based on the value of  $\varepsilon$  that you have determined in (e), explain why the measurements have been performed at such low temperatures.

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

[TURN OVER

## A8

Answer **all** parts of the question.

The Eyring equation provides a means for calculating absolute rate constants for reactions:

$$k_{1st} = \frac{kT}{h} \exp(-\Delta G^{\circ\ddagger}/RT)$$

where  $k_{1st}$  is a first-order rate constant and  $\Delta G^{\circ\ddagger}$  is the standard Gibbs energy of activation.

- Starting from the Eyring equation, show that the standard enthalpy of activation,  $\Delta H^{\circ\ddagger}$ , is given by  $\Delta H^{\circ\ddagger} = E_a - RT$ , where  $E_a$  is defined by the Arrhenius equation  $k_{1st} = A \exp(-E_a/RT)$ . You may assume that both the enthalpy and the entropy of activation are independent of temperature.
- By substituting the results from part (a) into the Eyring equation, find an expression for the Arrhenius pre-exponential factor  $A$  as a function of the standard entropy of activation,  $\Delta S^{\circ\ddagger}$ .
- The activation energy and pre-exponential factor were measured for the catalytic step of an enzyme, *3-chloroacrylate dehalogenase*, (*CaaD*).  
The values obtained at  $T = 300$  K were  $A = 9.7 \times 10^7 \text{ s}^{-1}$  and  $E_a = 41.5 \text{ kJ mol}^{-1}$ . Use these values to compute  $\Delta S^{\circ\ddagger}$ ,  $\Delta H^{\circ\ddagger}$ , and  $\Delta G^{\circ\ddagger}$ .
- In the absence of the enzyme, the parameters for the uncatalysed reaction were measured to be  $A = 3.36 \times 10^8 \text{ s}^{-1}$  and  $E_a = 113.5 \text{ kJ mol}^{-1}$ . Calculate by how much  $\Delta G^{\circ\ddagger}$  has been lowered by the effect of *CaaD*. State, giving your reasons, whether this lowering of the activation free energy is primarily driven by an entropic or an enthalpic effect.

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

**A9**

Answer *all* parts of the question.

Bulk Ag adopts the face-centred cubic crystal structure, with lattice vectors given by

$$\mathbf{a}_1 = \frac{a}{2}(1, 1, 0) \quad \mathbf{a}_2 = \frac{a}{2}(0, 1, 1) \quad \mathbf{a}_3 = \frac{a}{2}(1, 0, 1)$$

where the lattice constant,  $a$ , is 4.09 Å.

- (a) Calculate the volume of the primitive unit cell, and hence estimate the density of valence electrons (assuming *one* valence electron is contributed by each Ag atom).
- (b) Calculate the volume of the first Brillouin zone. How does this compare with the volume of the free-electron Fermi sphere for this material? You may use any relationship without derivation.
- (c) Derive an approximate expression for the electronic heat capacity (at constant volume) of bulk Ag within the free-electron model, and comment upon its temperature dependence at very low temperatures. How does this compare with that of the heat capacity arising from motion of the ions?
- (d) Atoms of Ag are deposited on an insulating surface, building up a uniform layer a few atoms thick. Assuming that valence electrons are confined within the Ag layer, describe qualitatively how its electronic structure is likely to differ from that of the bulk metal.

Approximate Division of Marks: (a) 20%, (b) 30%, (c) 30%, (d) 20%

[TURN OVER

**A10**

Answer *all* parts of the question.

- (a) A sheet of graphene is entirely defect-free, apart from a low concentration of boron atoms substituted in place of carbon at random locations. Assuming a carbon–carbon bond length of  $1.42 \text{ \AA}$ , estimate the percentage of carbon atoms that must be substituted to achieve a hole concentration of  $10^{13} \text{ cm}^{-2}$ .
- (b) The density of states (in units of  $\text{eV}^{-1} \text{ atom}^{-1}$ ) close to the Fermi level in *perfect* graphene may be approximated as  $D(\varepsilon) = |\varepsilon|/20$ , where  $\varepsilon$  is the energy (in eV) measured relative to the Fermi level. Estimate the energy of the Fermi level in the *p*-doped graphene sheet described above, relative to the point of zero density of states, assuming that the density of states profile remains unchanged from that of the perfect graphene sheet.
- (c) The *p*-doped graphene sheet is joined edge to edge (to form a single layer) to a sheet of *n*-doped graphene, obtained by substituting a similar percentage of nitrogen atoms, instead of boron atoms, in place of carbon. By outlining how a light-emitting diode works, explain why this junction would not function in this way if all the assumptions mentioned in previous parts of this question are strictly correct.
- (d) Another graphene sheet possesses neither nitrogen nor boron impurities, but instead features a non-negligible concentration of carbon vacancies (i.e. single carbon atoms missing from the structure). The remaining carbon atoms surrounding each vacancy are assumed not to move appreciably from their original positions. By considering the change in the number of bonds and the change in the number of valence electrons, how many charge carriers (and of what type) should each vacancy contribute to the graphene sheet?

Approximate Division of Marks: (a) 20%, (b) 30%, (c) 30%, (d) 20%

END OF PAPER