



# UNIVERSITY OF CAMBRIDGE

## NATURAL SCIENCES TRIPOS Part IB

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**Friday 29th May 2015**

**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) Show that the set of wavefunctions  $\psi_n \propto \sin\left(\frac{n\pi x}{a}\right)$  are eigenfunctions of the Hamiltonian for a particle inside a one-dimensional box of length  $a$ , where the potential is given by:

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < a \\ \infty & \text{otherwise} \end{cases}$$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

- (ii) What is the energy for the  $n$ th excited state,  $E_n$ ?
- (iii) Sketch the three lowest energy eigenfunctions.
- (iv) What is the expectation value of the momentum squared,  $\langle \hat{p}_x^2 \rangle$ , for the ground-state wavefunction, where  $\hat{p}_x = -i\hbar \frac{d}{dx}$ .
- (b) (i) For a Hamiltonian  $\hat{H}(x, y) = \hat{H}_1(x) + \hat{H}_2(y)$ , show that the eigenfunctions can take a product form  $\Psi_j(x)\Phi_k(y)$ , where  $\Psi_j(x)$  are eigenfunctions of  $\hat{H}_1(x)$  and  $\Phi_k(y)$  are eigenfunctions of  $\hat{H}_2(y)$ .
- (ii) For a particle in a two-dimensional rectangular box of dimensions  $(a \times \sqrt{2}a)$ , the Hamiltonian is written using the potentials:

$$V_1(x) = \begin{cases} 0 & \text{for } 0 < x < a \\ \infty & \text{otherwise} \end{cases} \quad \text{and} \quad V_2(y) = \begin{cases} 0 & \text{for } 0 < y < \sqrt{2}a \\ \infty & \text{otherwise} \end{cases}$$

$$\hat{H}(x, y) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_1(x) - \frac{\hbar^2}{2m} \frac{d^2}{dy^2} + V_2(y)$$

Using the answers to the previous parts of the question, give the eigenfunctions and energies.

- (iii) What are the three lowest energy eigenfunctions?
- (iv) Assuming the particle to be an electron, what is the difference in energy between the first and second excited states for  $a = 1 \times 10^{-9}$  m?

Approximate distribution of marks: (a) i) 15%, ii) 10%, (iii) 5%, (iv) 10%,  
(b) (i) 20%, (ii) 20%, (iii) 10%, (iv) 10%.

## A2

Answer *all* parts of the question.

- (a) (i) State Hund's three rules and use them to give the ground-state term symbol for the carbon atom including values for  $S$  and  $L$ . Give the possible values for  $J$  and state which is the lowest energy level.
- (ii) Two excited states of the carbon atom are denoted  $^1D_J$  and  $^1S_J$ . Give the values for  $J$  in these cases.
- (b) (i) The one-electron spin eigenfunctions are  $\alpha$  with  $m_s = +\frac{1}{2}$  and  $\beta$  with  $m_s = -\frac{1}{2}$ .

Show that  $\alpha_1\alpha_2$ ,  $\beta_1\beta_2$ ,  $\alpha_1\beta_2$  and  $\beta_1\alpha_2$  are eigenfunctions of the two-electron operator  $\hat{S}_z = \hat{s}_{1z} + \hat{s}_{2z}$  and give the value of  $M_S$  for each of them.

What is the singlet two-electron spin function which is a normalised combination of the two  $M_S = 0$  eigenfunctions that is antisymmetric under exchange of electrons?

- (ii) Show that

$$\Psi^{\text{angular}}(\theta_1, \phi_1, \theta_2, \phi_2) = \sin \theta_1 e^{i\phi_1} \sin \theta_2 e^{i\phi_2}$$

is an eigenfunction of the two-electron operator,

$$\hat{L}_z = \hat{l}_{1z} + \hat{l}_{2z},$$

where the angular momentum operator for electron  $k$  is given by

$$\hat{l}_{kz} = -i\hbar \frac{\partial}{\partial \phi_k}.$$

What is the value of  $M_L$ ?

- (iii) If  $\Psi^{\text{angular}}$  is combined with the symmetric radial wavefunction

$$\Psi^{\text{radial}}(r_1, r_2) = R(r_1)R(r_2),$$

what is the total wavefunction including spin that obeys the Pauli principle? Give the term symbol that it corresponds to.

Approximate distribution of marks: (a) (i) 30%, (ii) 10%, (b) (i) 20%, (ii) 20%, (iii) 20%.

**A3**

Answer *all* parts of the question.

- (a) Contrast, giving your reasons, the appearance of the vibrational spectra you would expect for a diatomic molecule assuming harmonic and anharmonic oscillators.
- (b) Explain what additional considerations are required to explain the vibrational structure of electronic transitions.
- (c) Draw a molecular orbital diagram for the diatomic molecule CO, given that the HOMO is singly degenerate. Use this to show the electronic configurations of the ground state and of the first electronic excited state, and determine the term symbol for each of these states.
- (d) Frequencies (in  $\text{cm}^{-1}$ ) and assignments of a number of vibrational transitions between the ground and first excited electronic states of carbon monoxide (CO) are shown in the table below.

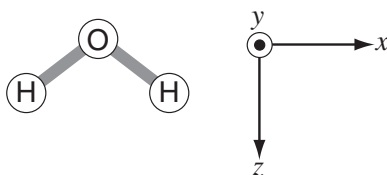
	$\nu' = 4$	$\nu' = 5$	$\nu' = 6$	$\nu' = 7$
$\nu'' = 0$	70464.0	71807.1	73115.7	74389.8
$\nu'' = 1$	68320.7	69663.8	70972.4	72246.5
$\nu'' = 2$	66204.3	67547.4	68856.0	70130.1

- (i) Draw a schematic of the transitions shown in the table.
- (ii) By graphical means or otherwise, and assuming a Morse potential, use the information in the table to determine frequencies and anharmonicity constants for the two electronic states.
- (iii) Derive an expression for the dissociation energy of a Morse potential, and evaluate it for the two electronic states. What is the energy separation (in  $\text{cm}^{-1}$ ) of the bottom of the PE curves of the two electronic states?
- (iv) How might you expect the bond lengths for the two electronic states to differ, and explain how you might determine them experimentally.

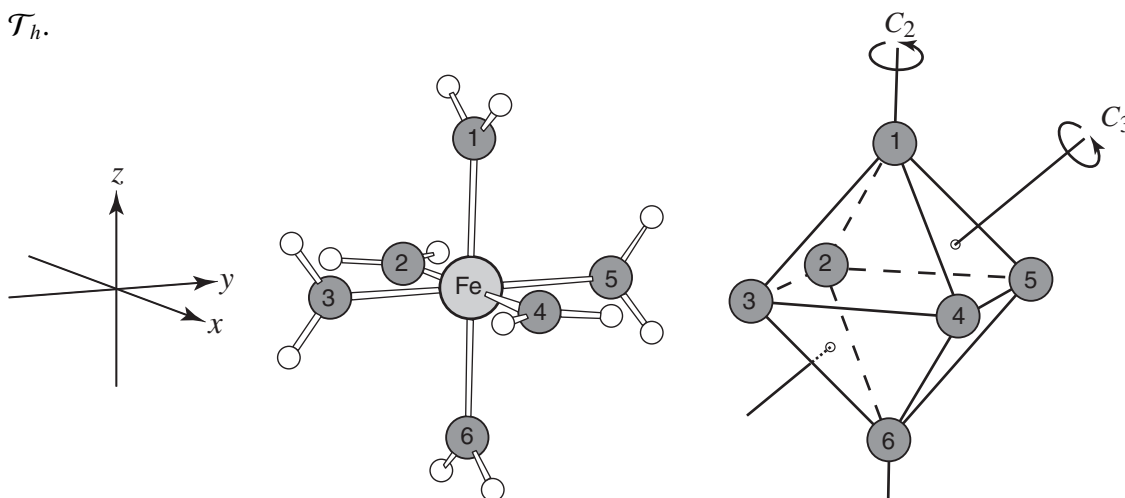
Approximate division of marks: (a) 15%, (b) 15%, (c) 20%, (d) 50%.

## A4

Answer *all* parts of the question.



- (a) (i) For the geometry of the water molecule above, determine the point group and symmetry orbitals of the valence orbitals, and use this to determine and sketch the approximate forms of the molecular orbitals.
- (ii) Briefly explain why the  $2p_y$  orbital is the highest occupied molecular orbital and indicate the position of all the orbitals on an MO energy diagram, marking the HOMO and the LUMO. Detailed calculations of the coefficients are not required.
- (b) With  $\text{Fe}^{3+}$ , water forms the octahedral coordination complex  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  with the geometry shown below. Note how the water molecules are aligned within the complex. Whilst the coordination is octahedral, the point group of this complex is  $\mathcal{T}_h$ .



The character table for the  $\mathcal{T}_h$  point group is given below

$\mathcal{T}_h$	$E$	$8C_3$	$3C_2$	$i$	$8S_6$	$3\sigma_h$
$A_g$	1	1	1	1	1	1
$E_g$	2	-1	2	2	-1	2
$T_g$	3	0	-1	3	0	-1
$A_u$	1	1	1	-1	-1	-1
$E_u$	2	-1	2	-2	1	-2
$T_u$	3	0	-1	-3	0	1

[Qu. 4 continued on next page]

[Continuation of Qu. 4]

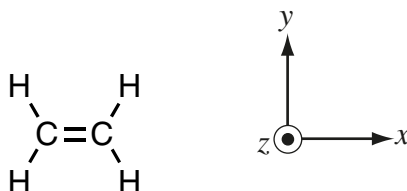
- (i) Using the axes shown, and by considering the effect of the  $C_2$  and  $C_3$  operations depicted, determine which of the 3d orbitals on the metal are mapped onto each other by the symmetry operations of the group.  
[Hint: The  $C_3$  rotations permute the Cartesian axes.]
  - (ii) For each of the interconverting groups of orbitals, construct the representation matrix of the  $C_2$  operation depicted.
  - (iii) By considering the characters of the representation matrices of the  $C_2$  and the remaining symmetry operations, show that the set of 3d orbitals transforms as  $E_g \oplus T_g$ , stating which orbitals transform according to each irreducible representation.
- (c)
- (i) The HOMO of each water molecule contributes to the electronic structure of this complex. Determine the irreducible representations spanned by considering the HOMOs from all the water molecules together.
  - (ii) By considering the interaction of these ligand orbitals with the metal d-orbitals, produce a qualitative MO energy diagram for the complex, with each set of orbitals labelled according to symmetry. Indicate which sets of orbitals are primarily metal- or ligand-based.
  - (iii) Given the orbital interactions in this complex, do you expect  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  to be high or low spin?

Approximate distribution of marks: (a) 30%, (b) 40%, (c) 30%.

**A5**

Answer *all* parts of the question.

This question considers the ethene molecule below:



In this question, you should ignore any non-valence orbitals, and consider the carbon atoms to be  $sp^2$  hybridized with all C–H bonds having the same length.

- (a) Determine the point group of the molecule.
- (b) Considering the 1s orbitals on hydrogen and the valence p and  $sp^2$  hybrid orbitals on carbon, determine what irreducible representations are spanned, and form and sketch the corresponding symmetry orbitals.
- (c) The molecular orbitals and their energies may be determined by Hückel Theory. Denoting the Hamiltonian  $\hat{h}$ , the required energies and resonance integrals have been determined and are given in the table at the end of the question. [Note: you will only need to use some of these integrals, not all of them. ]
  - (i) Determine the energies of the MOs formed from the p-orbital on each carbon.
  - (ii) From the symmetry orbitals with  $B_{2u}$  symmetry, form the Hückel Hamiltonian matrix and determine the energies and coefficients of the normalized molecular orbitals of this symmetry.
  - (iii) Without further detailed calculation, sketch the form of the lowest energy molecular orbital.

[Qu. 5 continued on next page]

[Continuation of Qu. 5]

$\phi_a$	$\phi_b$	$\langle \phi_a   \hat{h}   \phi_b \rangle$
		$\alpha + 5\beta$
		$4\beta$
		$\alpha + \beta$
		$2\beta$
		$2\beta$
		$4\beta$
		$\alpha + \beta$
		$\alpha$
		$\beta$

Atoms have been omitted for clarity. Integrals which are the equivalent through symmetry will have the same values as those in the table.

Approximate distribution of marks: (a) 10%, (b) 35%, (c) (i) 10%, (ii) 40%, (iii) 5%.

END OF PAPER





UNIVERSITY OF  
CAMBRIDGE

**NATURAL SCIENCES TRIPOS Part IB**

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**Wednesday 3rd June 2015**

**13.30 to 16.30**

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**CHEMISTRY A: PAPER 2**

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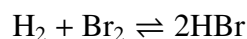
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**A6**

Answer *all* parts of the question.

The equilibrium constant for the gas-phase reaction:



is given by:

$$K_c = \frac{f_{\text{HBr}}^2}{f_{\text{H}_2} f_{\text{Br}_2}} \exp\left(\frac{-\Delta\varepsilon^0}{kT}\right)$$

[In this question, assume all molecules are in their electronic ground states. Use the isotopes  $^1\text{H}$  and  $^{79}\text{Br}$  and assume integer atomic masses.]

- (a) Calculate the translational partition function contributions to the molecular partition functions for  $K_c$  at 400 K.
- (b) Rotational constants (in  $\text{cm}^{-1}$ ) are given by:

$$\tilde{B} = \frac{h}{8\pi^2 c I}$$

Given that the equilibrium bond lengths for  $\text{H}_2$ ,  $\text{Br}_2$  and  $\text{HBr}$  are 74 pm, 228 pm, and 145 pm respectively, calculate the rotational partition functions at 400 K, assuming the high-temperature limit applies.

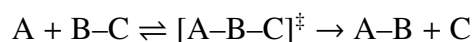
- (c) The fundamental vibrational frequencies of  $\text{H}_2$ ,  $\text{Br}_2$  and  $\text{HBr}$  are 4401, 325 and 2649  $\text{cm}^{-1}$  respectively, and  $\varepsilon^0$  for these molecules are 0, 2.51 and 0.73 eV respectively (relative to  $\text{H}_2$ ). Using these data, and your values for the translational and rotational contributions to the molecular partition function, calculate the value of  $K_c$  at 400 K, stating any assumptions made.

Approximate division of marks: (a) 20%, (b) 30%, (c) 50%.

**A7**

Answer *all* parts of the question.

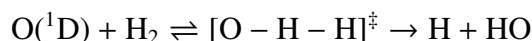
- (a) For the reaction:



use transition-state theory to derive an expression for the bimolecular (second-order) rate constant, making clear any assumptions made.

[The transition structure  $[A-B-C]^{\ddagger}$  is linear.]

- (b) Singlet oxygen reacts with  $H_2$  in the upper atmosphere to form hydrogen atoms and hydroxyl radicals according to the reaction:



Using the expression you derived in (a) and the following information, calculate a value for the rate constant for the reaction between  $O(^1D)$  and  $H_2$  at 350 K.

Data:  $H_2$  bond length 74 pm, fundamental vibrational frequency  $4401\text{ cm}^{-1}$ . Transition-state bond lengths O-H 102 pm, H-H 91 pm, vibrational frequencies  $1200\text{ cm}^{-1}$  (symmetric stretch) and  $670\text{ cm}^{-1}$  (bend, doubly degenerate).

$\Delta\epsilon^{\ddagger} = 23\text{ kJ mol}^{-1}$ , referenced to the bottom of the potential well.

You may assume the high-temperature limit applies. Use integer atomic masses.

- (c) Assuming the partition function of the transition state remains unchanged, without detailed calculations, indicate how the reaction rate constant would be changed on substituting  $H_2$  for (i) H-D and (ii)  $D_2$ .

Approximate division of marks: (a) 25%, (b) 50%, (c) 25%.

**A8**

Answer *all* parts of the question.

- (a) Assuming that the energy levels of a molecule can be represented as a rigid rotor, show that the rotational partition function of a hetero-nuclear diatomic molecule in the high-temperature limit can be written as:

$$q_{\text{rot}} = \frac{T}{\theta_{\text{rot}}}$$

giving your expression for  $\theta_{\text{rot}}$  and stating any assumptions made. Indicate how, in reality,  $q_{\text{rot}}$  differs from this expression at low temperatures.

- (b) A more general expression for the rotational partition function at high temperatures is:

$$q_{\text{rot}} = \frac{T}{\sigma \theta_{\text{rot}}}$$

Explain the significance of the symmetry parameter  $\sigma$ , and why it differs for hetero- and homo-nuclear diatomic molecules.

- (c) Show how the symmetry parameter influences the rotational contributions to the molar energy, heat capacity and entropy of a diatomic molecule.
- (d) Making clear any assumptions, sketch, as quantitatively as you can, how you might expect the total molar energy and heat capacity of  $\text{CO}_2$  gas to vary with temperature.

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

**A9**

Answer *all* parts of the question.

- (a) (i) Derive an expression for the density of states,  $D(E)$ , for a two-dimensional (2D) free-electron gas (FEG) by generalizing the corresponding derivation for the three-dimensional (3D) case. Compare this result with that for the 3D FEG.
- (ii) Hence obtain an expression for the average energy per electron at zero Kelvin of a 2D FEG in terms of the Fermi energy,  $E_F$ .
- (b) Derive an expression for the Fermi energy of a 2D FEG in terms of the area electron density,  $n_A = N/A$ , where  $N$  is the number of free electrons in the 2D system with (Born–von Karman) area,  $A$ . What is the physical significance of the Fermi energy?
- (c) The bulk modulus,  $B$ , represents the resistance of a substance to isotropic compression. For a 3D system, this is defined as

$$B = -V \left( \frac{\partial p}{\partial V} \right)_{T,N}$$

where  $V$  is the (Born–von Karman) volume, and the pressure,  $p$ , is given by the equation

$$p = - \left( \frac{\partial U}{\partial V} \right)_N,$$

where  $U$  is the total internal energy of the FEG at  $T = 0$  K.

Generalize the expression for  $B$  to the 2D case, where an inward force,  $F$ , is applied to each of the four sides, of length  $L$ , of a square FEG system ( $A = L^2$ ) containing  $N$  electrons, i.e. the system is subject to an isotropic line stress,  $\sigma = F/L$ .

- (d) Hence obtain an expression for  $B$  for a 2D FEG in terms of  $n_A$  and  $E_F$ .
- (e) Explain the physical origin of  $B$ , i.e. of the resistance to isotropic compression of a 2D FEG.

Approximate division of marks: (a)(i) 30%, (ii) 10%, (b) 20%, (c) 15%, (d) 15%, (e) 10%.

**A10**

Answer *all* parts of the question.

- (a) Explain briefly how the substitutional doping of crystalline Ge with either P or B changes the electrical characteristics of the host semiconductor.
- (b) Estimate the dopant concentration in Ge for which the hydrogenic-like dopant electronic orbitals begin to overlap. What happens to the electronic behaviour of the semiconductor when this occurs?  
[The Bohr radius of hydrogen atoms is 53 pm, the relative permittivity of Ge is 16, and the effective mass of electrons and holes in Ge may be taken to be  $0.2 m_e$ .]
- (c) By considering the change in the number of bonds, and hence the change in the number of valence electrons, determine how many charge carriers (and of what type) does the creation of an atomic vacancy in Ge (by the removal of a Ge atom) introduce into the material? It may be assumed that the Ge atoms surrounding the vacancy do not move appreciably from their original positions in the perfect crystal.
- (d) Crystalline GaAs is a III–V material with the zinc-blende structure (i.e. the two crystallographically distinct lattice sites in the diamond-cubic structure are occupied either by Ga or by As atoms in a chemically-ordered tetrahedral arrangement). By considering, in turn, an As atom surrounded by Ga atoms, and a Ga atom surrounded by As atoms, in this structure, calculate the effective number of valence electrons associated with the bonding to the central atom in each case. Hence explain why this material is a semiconductor.
- (e) Now consider a pair of nearest-neighbour ‘anti-site’ defects in GaAs, i.e. a Ga atom occupying an As site and vice versa. Repeat the calculation in (d) for these anti-site defects, commenting on your answers.
- (f) What is the effect on the electrical behaviour of GaAs of substitutionally doping it with Ge, on: (i) only the Ga sites; (ii) only the As sites; (iii) or an equal number of both sites?

Approximate Division of Marks: (a) 10%, (b) 25%, (c) 15%, (d) 15%, (e) 20%, (f) 15%.

END OF PAPER