

NATURAL SCIENCES TRIPOS Part IB

Thursday 30th May 2002 1.30 to 4.30

CHEMISTRY A: PAPER 1

There are seven questions on this paper.

Candidates should attempt any 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.

A Periodic Table, the structures of the amino acids and nucleotide bases, the values of physical constants, character tables and selected mathematical formulae will be found in the data book provided.

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.

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| <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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[TURN OVER

A1

Answer *all* parts of the question

- (a) Show that e^{-Zr} is an un-normalized 1s orbital in atomic units for a one electron atom with nuclear charge Z .

$$\left[\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right]$$

- (b) Write down the energies of the 1s, 2s and 2p orbitals for this atom.
- (c) Write down an un-normalized form for the $2p_z$ orbital and suggest a form for the 2s orbital. Your answer should be expressed in Cartesian form but may also include r , the distance from the nucleus ($r = \sqrt{x^2 + y^2 + z^2}$).
- (d) Write down approximate forms for the 1s and $2p_z$ orbitals in nitrogen, giving reasons for your suggested exponents.
- (e) Hence give a form for the three bonding orbitals of N_2 , with their symmetry labels.
- (f) The three lowest electronic states of N_2 are denoted $^1\Sigma_g^+$, $^3\Sigma_u^+$, and $^3\Pi_g$ and are separated by 50203 cm^{-1} and 9416 cm^{-1} respectively. Suggest electronic configurations for these three states.

Approximate division of marks:

(a) 20%, (b) 10%, (c) 20%, (d) 10%, (e) 20% (f) 20%

A2

Answer *all* parts of the question

- (a) The classical kinetic energy of a vibrating diatomic molecule can be written $\frac{1}{2}\mu\dot{r}^2$, where μ is the reduced mass and \dot{r} is the time derivative of the bond length. An approximation for the potential energy is $\frac{1}{2}k(r-r_e)^2$ where r_e is the equilibrium bond length. Discuss briefly how these expressions are obtained.
- (b) Introducing $x = r - r_e$ and the momentum $p = \mu\dot{x}$, obtain the Schrödinger equation for the vibrational energy levels. Show that the ground state wavefunction has the form $e^{-\alpha x^2}$. Determine α and the energy of the ground state.
- (c) The fundamental frequency of vibration for $^{12}\text{C}^{16}\text{O}$ is 2170 cm^{-1} . Obtain the constant k in N m^{-1} .
- (d) Discuss the principal deficiency in the above model and how the Morse oscillator model overcomes it.

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

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A3

Answer *all* parts of the question

- (a) (i) Classical angular momentum, L , is written in terms of a particle's position r and momentum p as $L = r \times p$. Write down the quantum mechanical expressions for the angular momentum operators \hat{L}_x , \hat{L}_y and \hat{L}_z .

(ii) The total angular momentum operator is $\hat{L}^2 \equiv \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$. The spherical harmonics $Y_{lm}(\theta, \phi)$ are eigenfunctions of \hat{L}^2 and \hat{L}_z . Write down identities for $\hat{L}^2 Y_{lm}$ and $\hat{L}_z Y_{lm}$.

- (b) A diatomic molecule AB is rotating about its centre of mass with angular velocity ω . Obtain the classical expression for the kinetic energy, T :

$$T = \frac{1}{2} \frac{L^2}{I}$$

where $L = I\omega$, $I = m_A r_A^2 + m_B r_B^2$ and r_A and r_B being the distances of atoms A and B from the centre of mass. Hence write down the quantum mechanical energies of the rotating molecule. Give the formula for the transitions between neighbouring levels.

- (c) The absorption lines in the rotational spectrum of $^1\text{H}^{35}\text{Cl}$ that lie between 100 and 200 cm^{-1} have been measured at 104.13, 124.73, 145.37, 165.89 and 186.23 cm^{-1} . Assign the transitions giving rise to these absorptions and determine the equilibrium internuclear distance in $^1\text{H}^{35}\text{Cl}$.

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

A4

Answer *all* parts of the question

- (a) Show that the value of J for the rotational energy level of a diatomic molecule with the maximum population, denoted J_{\max} , is given by:

$$J_{\max} \approx \sqrt{\frac{kT}{2hc\tilde{B}}} - \frac{1}{2}$$

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

- (b) In the vibrational Raman spectroscopy of a linear triatomic molecule, a vibration-rotation spectrum is seen either side of the incident laser line. The spectrum is composed of O , Q and S branches which correspond to transitions where the vibrational energy change is accompanied by changes in the rotational energy level with $\Delta J = J' - J'' = -2, 0$ and $+2$ respectively.

(J' and J'' refer to the quantum numbers for the rotational energy levels in the upper and lower vibrational states respectively.)

- (i) Show that for the anti-Stokes lines, the frequency of a peak in the O -branch is given by:

$$\tilde{O}(J'') = \tilde{\omega}_i + \tilde{\omega}_0 + \tilde{B}_1(J''-2)(J''-1) - \tilde{B}_0 J''(J''+1)$$

where $\tilde{\omega}_i$ is the frequency of the incident laser, $\tilde{\omega}_0$ is the frequency of the pure vibrational transition, and \tilde{B}_0 and \tilde{B}_1 are the rotational constants for the molecule when in the lower and upper vibrational states respectively.

- (ii) Find a similar expression for the frequency of a peak in the S -branch of the anti-Stokes spectrum, $\tilde{S}(J'')$, and hence an expression for the difference between any peak in the S -branch and the O -branch which share the same lower rotational energy level, $\tilde{S}(J'') - \tilde{O}(J'')$.

[Question A4 continues on the next page]

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[Continuation of Question A4]

- (c) Whilst the separate rotational lines in the *O* and *S* branches often cannot be distinguished, the position of the maximum in each branch can be measured. Using your answers from parts (a) and (b) show that the separation between the maxima in the *S* and *O* branches in cm^{-1} is given by:

$$\tilde{S}(J''_{\text{max}}) - \tilde{O}(J''_{\text{max}}) = \sqrt{\frac{32\tilde{B}_1 kT}{hc}}.$$

- (d) The separation between the maxima in the *S* and *O*-branches in the vibrational Raman spectrum of the linear molecule $^{127}\text{I}-^{202}\text{Hg}-^{127}\text{I}$ at 292°C is 11.4 cm^{-1} . Find \tilde{B}_1 and use it to calculate a value for the Hg–I bond length.

Approximate division of marks: (a) 20%, (b) 30%, (c) 10%, (d) 40%.

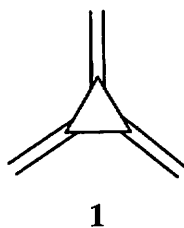
A5

Answer *all* parts of the question

(a) Define the following terms:

- Hückel theory
- Linear combination of atomic orbitals
- Symmetry orbital
- Molecular orbital
- Representation of a point group

(b) What is the point group for molecule 1, C_6H_6 , shown below? Derive symmetry orbitals for the six p^π atomic orbitals and hence find the Hückel molecular orbital energies and draw an energy level diagram for the π system. Does this molecule have a favourable delocalization energy?



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

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A6

Answer *all* parts of the question

- (a) What is the point group of the ammonia molecule? Draw diagrams to show the effect of each symmetry operation on a suitable reference geometry with labelled atoms.
- (b) Find the characters of and reduce the representations of the point group of the ammonia molecule using (i) the valence atomic orbitals, and (ii) sp^3 hybrids on the nitrogen. Why are these representations equivalent? Sketch a qualitative molecular orbital energy level diagram for ammonia and describe the bonding characteristics of each orbital.
- (c) Predict the appearance of the photoelectron spectrum of ammonia in as much detail as you can.

Approximate division of marks: (a) 25%, (b) 40%, (c) 35%.

A7

Answer *all* parts of the question

- (a) What is meant by the term *spectrochemical series*? Describe the factors that determine the position of a given ligand in this series.
- (b) State Wade's rule and show how it can be used to predict the structures of (i) $\text{B}_6\text{H}_6^{2-}$, (ii) $\text{C}_2\text{B}_5\text{H}_7$ and (iii) B_5H_{11} .
- (c) What is the point group of the structure you proposed for $\text{B}_6\text{H}_6^{2-}$ in (b)(i)? Predict the symmetries of the six B–H stretching vibrations in this molecule and deduce their infra-red and Raman activities.

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

[END OF PAPER]

NATURAL SCIENCES TRIPOS Part IB

Wednesday 5th June 2002 1.30 to 4.30

CHEMISTRY A: PAPER 2

There are seven questions on this paper.

Candidates should attempt any FIVE questions.

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A8

Answer *all* parts of the question

- (a) In the rotation-vibration spectrum of $^{12}\text{C}^{16}\text{O}$ gas peaks were observed at the following frequencies in the IR spectrum:

$$2149.30, 2153.15, 2160.85, 2164.70 \text{ cm}^{-1}$$

Determine the value of the rotational constant, B , and the vibrational frequency, ν_0 , in cm^{-1} . Any relationships you need can be quoted without proof.

- (b) Starting from the "bridge" relationship

$$A = -kT \ln Q_N$$

which gives the value of the Helmholtz energy, A , in terms of the partition function for the system, Q_N , derive an expression for the entropy in terms of Q_N . Show that in the case of a system of N non-interacting indistinguishable particles the entropy is given by

$$S = Nk \ln q - Nk \ln N + Nk + \frac{U}{T}$$

where q is the molecular partition function and U is the internal energy. State any approximations that you use.

- (c) Using your answers to part (a) compute the rotational and vibrational contributions to the molar entropy of $^{12}\text{C}^{16}\text{O}$ gas at 298 K. Comment on their relative sizes.
- (d) Using your answers to part (c) and including any other relevant contributions, compute the standard molar entropy of $^{12}\text{C}^{16}\text{O}$ gas at 298 K.

[Atomic masses: $^{12}\text{C} = 12$, $^{16}\text{O} = 16$ amu]

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

A9

Answer *all* parts of the question

- (a) Derive an expression for the Helmholtz energy of a gas consisting of N indistinguishable non-interacting particles in terms of the molecular partition function, q . You may assume the "bridge" relationship

$$A = -kT \ln Q_N$$

where Q_N is the partition function for the system.

Go on to show that for a non-interacting mixture, the chemical potential of species i , μ_i , is given by

$$\mu_i = -kT \ln \frac{q_i}{N_i}$$

where q_i is the molecular partition function for species i , N_i is the number of particles of i . State any approximations that you use.

- (b) For the equilibrium



show that the equilibrium constant in terms of concentrations, K_c , is given by an expression of the form

$$K_c = \frac{f_C^2}{f_A f_B} \exp\left(\frac{-\Delta\epsilon_0}{kT}\right).$$

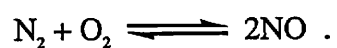
You should explain precisely what the f_i are and how $\Delta\epsilon_0$ is defined.

[Question A9 continues on the next page]

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[Continuation of Question A9]

- (c) Use the data below to compute the equilibrium constant, K_c , for the following gas phase reaction at 1500 K



| molecule | $\theta_{\text{rot}} / \text{K}$ | $\theta_{\text{vib}} / \text{K}$ | electronic ground state |
|--------------|----------------------------------|----------------------------------|-------------------------|
| N_2 | 2.88 | 3374 | $^1\Sigma_g^+$ |
| O_2 | 2.07 | 2256 | $^3\Sigma_g^-$ |
| NO | 2.44 | 2719 | $^2\Pi$ |

$\Delta\epsilon_0$ for this reaction is 180 kJ mol^{-1} .

[Any formulae you need can be quoted without proof]

[Atomic masses: $^{14}\text{N} = 14$, $^{16}\text{O} = 16 \text{ amu}$]

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

A10

Answer *all* parts of the question

- (a) What are the key assumptions of transition state theory? Explain what you understand by the terms *potential energy surface*, a *transition state* and the *reaction coordinate*.

For a reaction between an atom A and a diatomic BC, transition state theory gives the following expression for the second-order rate constant, k_{2nd} :

$$k_{2nd} = \frac{kT}{h} \frac{f'_{TS}}{f_A f_{BC}} \exp\left(\frac{-\Delta\epsilon_0^\ddagger}{kT}\right).$$

Explain carefully what f_A , f_{BC} , f'_{TS} and $\Delta\epsilon_0^\ddagger$ represent.

- (b) Starting from the Eyring equation

$$k_{2nd} = \left(\frac{1}{c_0}\right) \frac{kT}{h} K^\ddagger$$

where K^\ddagger is the equilibrium constant for the formation of the transition state and c_0 is the standard concentration, show how the concept of a *volume of activation* can be introduced. Also show how measurements of the rate constant as a function of pressure can be used to determine a value for this volume of activation.

- (c) The alkaline hydrolysis of chloroform (CHCl_3) in aqueous solution follows second order kinetics. The following values for this second order rate constant, k_{2nd} , were obtained at 298 K as a function of pressure, p :

| | | | | | |
|---|------|------|------|------|------|
| p / bar | 1000 | 2000 | 3000 | 4000 | 5000 |
| $10^5 \times k_{2nd} / \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ | 6.47 | 4.10 | 2.59 | 1.64 | 1.04 |

Use a *graphical method* to determine the volume of activation.

Is your value consistent with the proposal that the rate determining step involves the dissociation of the ion CCl_3^- to the carbene CCl_2 plus Cl^- ?

$$[1 \text{ bar} = 10^5 \text{ N m}^{-2}]$$

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

[TURN OVER

A11

Answer *all* parts of the question

The quantum free electron theory for a three dimensional solid yields energy levels

$$E_{\mathbf{k}} = \hbar^2 \mathbf{k}^2 / 2m_e.$$

- (a) Explain the assumptions that underlie the theory, and derive an expression for the Fermi energy in terms of the electron concentration.
- (b) Derive an expression for the density of states of a free electron gas. Outline a spectroscopic technique which might be used to test the form of the density of states predicted by the free electron theory.
- (c) Copper has a face-centred cubic lattice with unit cell parameter $a = 3.615 \text{ \AA}$. Calculate the Fermi energy and the electron velocity at the Fermi level for copper at 0K.

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

A12

Answer *all* parts of the question

- (a) Show how Bloch functions can be used to describe bonding in a one-dimensional solid, including a demonstration of how orbital topology determines the dependence of energy states E on the electron wave vector k .
- (b) How does this theory provide a basis for a qualitative explanation of the bonding in (i) graphite; and (ii) polyacetylene?
- (c) Polyacetylene is an insulator – why is this surprising and how do you account for this behaviour?
- (d) When polyacetylene is reacted with iodine, a highly conductive polymer is produced. Use band theory to account for this observation.

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

A13

Answer *all* parts of the question

- (a) The sublimation energies of sodium and diamond are 108 kJ mol^{-1} and 717 kJ mol^{-1} respectively. The lattice energy of NaCl is 771 kJ mol^{-1} . Outline the most appropriate model for the electronic structure and show how it contributes to our understanding of cohesion for each of these materials. Indicate the strengths and limitations of the theory in each case.
- (b) Using the data given below, estimate (i) the lattice energy and (ii) the atomisation energy for NaF, indicating any assumptions that you use. What would be the practical consequences that would arise from the difference between these two values?

Madelung potential $A = 1.7475$; minimum interionic distance = 2.317 \AA .

Electron Affinity of fluorine = 333 kJ mol^{-1} .

Ionisation energy of sodium = $495.8 \text{ kJ mol}^{-1}$; $\rho = 3.5 \times 10^{-11} \text{ m}$.

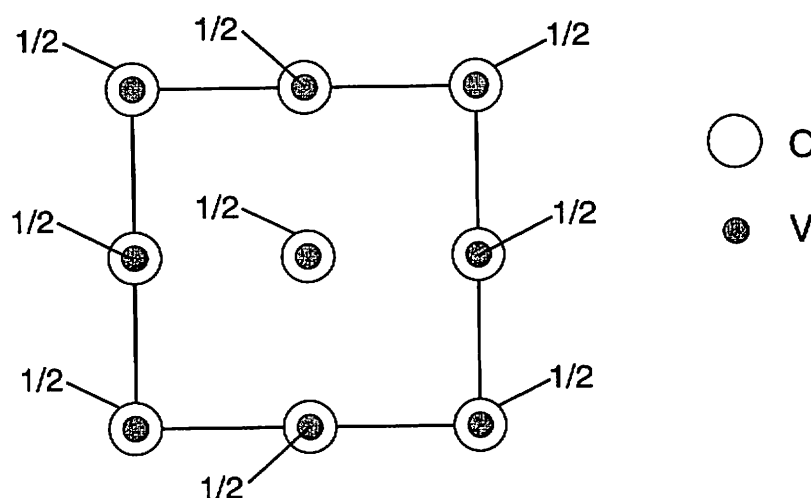
Approximate division of marks: (a) 55%, (b) 45%.

A14

Answer *all* parts of the question

- (a) Why do defects occur in solids? Describe the defects commonly found in ionic materials and show how defects can lead to non-stoichiometry in transition metal compounds.

Vanadium(II) oxide, VO has a cubic structure with lattice parameter $a = 4.092 \text{ \AA}$. The unit cell contents are shown below in projection.



- (b) How many formula units are present in the unit cell?
- (c) What is the coordination around the V and O sites?
- (d) After treatment at high temperature the density of VO is found to be 5.92 g cm^{-3} . Comment as fully as possible upon the possible reasons for this value.

Approximate division of marks (a) 40%, (b) 10%, (c) 10%, (d) 40%.

[END OF PAPER]