

NOT TO BE
TAKEN AWAY

NATURAL SCIENCES TRIPOS Part IB
NATURAL SCIENCES TRIPOS Part II (General)



Wednesday 27th May 1998 1.30 to 4.30

CHEMISTRY A: PAPER 1

Candidates should attempt FIVE questions, ONE from each section.

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 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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SECTION A

Introduction to Quantum Chemistry

A1

Answer *all* parts of this question:

- (a) What are *configurations*, *terms* and *levels* in many-electron atoms? Explain, *briefly*, the main cause of the energy difference between different configurations, and between different terms within the same configuration.
- (b) Give Hund's rules for predicting the lowest energy term in a given configuration. Explain which terms are allowed with a $2p^2$ configuration. Which is the lowest energy term?
- (c) What is the relationship between the total angular momentum $\hat{\mathbf{J}}$, the orbital angular momentum $\hat{\mathbf{L}}$ and the spin angular momentum $\hat{\mathbf{S}}$? What values can $\hat{\mathbf{J}}$ take for given values of $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$? Show that

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2}(\hat{\mathbf{J}}^2 - \hat{\mathbf{S}}^2 - \hat{\mathbf{L}}^2)$$

and use this relationship to prove the Landé interval rule for the splitting of levels in a given term.

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

A2

Answer *all* parts of this question:

- (a) What is the variation principle and why is it useful in quantum mechanics?
- (b) The hamiltonian for a one-electron atom with nuclear charge Z is, in atomic units,

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$$

Show that the wavefunction $\Psi = e^{-\alpha r}$ is an eigenfunction of this hamiltonian only for a specific value of α .

- (c) Show that the wavefunction $\Psi = e^{-\alpha r^2}$ cannot be an eigenfunction of this hamiltonian for any value of α .
- (d) For the trial wavefunction $\Psi = e^{-\alpha r^2}$ use the variation principle to find the optimum value of α and the corresponding energy. How does this energy compare with the exact answer?

Use the integrals:

$$\int_0^\infty r e^{-ar^2} dr = \frac{1}{2a} \quad \int_0^\infty r^2 e^{-ar^2} dr = \frac{1}{4a} \sqrt{\frac{\pi}{a}} \quad \int_0^\infty r^4 e^{-ar^2} dr = \frac{3}{8a^2} \sqrt{\frac{\pi}{a}}$$

The expression for ∇^2 is in the data book under spherical polar coordinates.

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

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SECTION B

Symmetry and Bonding

A3

Answer *all* parts of this question:

Consider the hypothetical small ring system



Assume the structure is planar and consider a basis set of one p-function from each atom perpendicular to the plane.

- (a) Construct the appropriate symmetry orbitals.
- (b) Using the Hückel approximation, construct the secular equations and find the orbital energies. Take $\alpha_o = \alpha_c + \beta$, $\beta_{co} = \beta$, $\beta_{cc} = \beta_{oo} = 0$.
- (c) Now consider that there is an interaction between the two carbon atoms, i.e. take $\beta_{cc} = \beta$. Solve the secular equations for this case to find new orbital energies. If there are four π electrons, would such an interaction make the system more, or less, stable?

Approximate division of marks: (a) 30%, (b) 35%, (c) 35%.

A4

Answer *all* parts of this question:

- (a) From VSEPR theory, predict the shape of the PF_5 molecule.
- (b) Assign its point group symmetry and illustrate, with sketches, the operation of each class of symmetry element.
- (c) Assuming that each fluorine only offers a 2s atomic orbital for bonding with the phosphorus, deduce, assign and illustrate the fluorine symmetry group orbitals spanned by that point group.
- (d) With which phosphorus atomic orbitals may these group orbitals form bonding and anti-bonding molecular orbitals?
- (e) Construct a qualitative molecular orbital diagram for PF_5 ; explain your estimates of all appropriate relative atomic and molecular orbital energies.

Approximate division of marks: (a) 5% (b) 15% (c) 40% (d) 10% (e) 30%.

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SECTION C*Molecular Energy Levels and Thermodynamics***A5**

Answer *all* parts of this question:

- (a) Derive an expression for the rotational partition function of a diatomic molecule at high temperature. Contrast with the low-temperature case.
- (b) The pure rotational spectrum of HBr consists of a series of lines having a separation of 16.94 cm^{-1} . Calculate the rotational partition function at (i) 300K and (ii) 10K. At 10K calculate the relative populations of the three lowest energy rotational levels.
- (c) For HBr calculate the rotational contributions to the Helmholtz free energy (A_{rot}), the internal energy (U_{rot}) and the entropy (S_{rot}) at 300K.
- (d) Repeat the calculation in part (c) for a temperature of 10K.

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

A6

Answer *all* parts of this question:

- (a) Calculate the molar entropies of He and Ar at 1 atmosphere and 298K.

$$\text{He} = 4 \text{ a.m.u.}; \quad \text{Ar} = 40 \text{ a.m.u.}$$

- (b) Calculate the contribution to the molar entropy of Ni gas at 2000K from its three lowest energy electronic states.

State	Energy above ground electronic state ϵ_i/kT
3F_4	0
3D_3	0.147
3D_2	0.633

Assume no other states are occupied at this temperature.

- (c) For some molecules, differences are found between the entropy calculated using statistical mechanics (S_{stat}) and the value determined calorimetrically (S_{cal}).

$$\text{For CO, } S_{\text{stat}} - S_{\text{cal}} = 5.76 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{For NO, } S_{\text{stat}} - S_{\text{cal}} = 2.88 \text{ J K}^{-1} \text{ mol}^{-1}$$

Account for these differences.

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

[TURN OVER

SECTION D*Solids and Surfaces***A7**

Answer *all* parts of this question:

- (a) Explain how the electrical characteristics of a semiconductor can be changed by the incorporation of impurities, illustrating your discussion with reference to the cases of P and Ga in Si.
- (b) Sketch a representative Arrhenius plot of the electrical conductivity for a doped semiconductor, identifying the origins of any differing temperature-dependent behaviour in various regions of the plot. Make clear any assumptions made. Hence indicate how the bandgap of an extrinsic semiconductor may be determined experimentally.
- (c) Explain why the conduction and valence bands bend in the vicinity of a p-n junction between p-type and n-type regions of a given semiconductor. What is the maximum possible value of band bending? Show, by means of sketches, the effects on the degree of band bending of the imposition of an external d.c. electrical voltage of one polarity or the opposite with respect to the p-n junction.
- (d) Explain qualitatively how you think a solar cell made from a p-n junction might work when illuminated with light having a photon energy equal to the bandgap of the semiconductor.

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

A8

Answer *all* parts of this question:

- (a) Explain what is meant by the term "work function", making reference to a diagram showing the electrostatic potential of a solid in the vicinity of a free surface.
- (b) The thermionic current density emanating from a surface of a tungsten crystal is $44.4 \mu\text{A}/\text{m}^2$ at 1500K and $1.24 \text{A}/\text{m}^2$ at 2000K. What is the value of the work function, ϕ ?
- (c) The W crystal is now coated with a monolayer of Th, causing the thermionic current density at 1500K to become $24.9 \text{MA}/\text{m}^2$. What is the work function for the W:Th surface? Show, by means of a suitable sketch, the origin of the change in work function. What would be the maximum wavelength of light which would cause photoelectrons to be emitted from the W:Th surface?
- (d) Explain briefly how the work function of the Pt {111} surface changes with coverage of CO adsorbate.

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

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SECTION E

Reactivity and Solutions

A9

Answer *both* parts of this question:

- (a) Explain why the rate constant for the reaction between two ions in solution is affected by the ionic strength. Use the Debye-Hückel limiting law to derive an expression relating the rate constant to ionic strength.
- (b) Competitive reactions of X with Y and Z were studied as a function of ionic strength. The ratio of the rate constants for the two reactions varied with ionic strength as follows:

I/mol dm ⁻³	0	0.2	0.4	0.6
k(X+Y)/k(X+Z)	832	271	170	119

What deductions can you make about the ionic charges on X, Y and Z?

If X is a solvated electron and Y is Ag⁺, what is the charge on Z?

[The Debye-Hückel parameter is $A_r = 0.509 \text{ mol}^{-1/2} \text{ dm}^{3/2}$]

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

A10

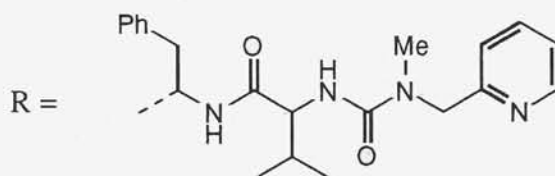
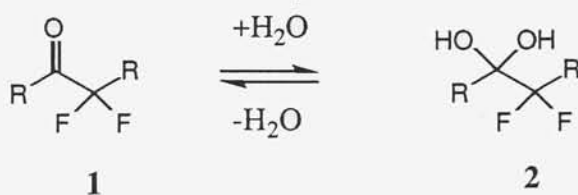
Answer *both* parts of this question:

- (a) Summarise the types of information can one obtain about a transition state for a reaction. Outline two examples of experimental techniques for obtaining this information.
- (b) The difluoroketone **1** shown below is a potent inhibitor of HIV protease (an enzyme which hydrolyses peptide bonds). The reaction catalysed by HIV protease is shown below



Suggest a detailed mechanism for the hydrolysis from the following information

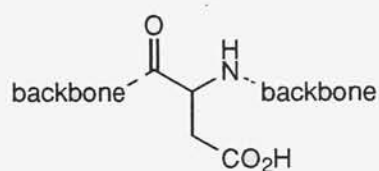
- (i) In water the ketone exists as a hydrate **2** which mimics the transition state for the hydrolysis reaction catalysed by HIV protease.



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- (ii) There are two amino acids in the enzyme essential for catalysis. They are both aspartic acid. It has been established that one aspartate acts as a base whilst the other acts as an acid.



aspartic acid in enzyme

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

NATURAL SCIENCES TRIPOS Part IB
NATURAL SCIENCES TRIPOS Part II (General)

Monday 1st June 1998 9 to 12

CHEMISTRY A: PAPER 2

Candidates should attempt ANY FIVE questions,

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[TURN OVER

A11

Answer *all* parts of this question:

- (a) If the hamiltonian for a system can be written as the sum of two simpler hamiltonians,

$$\hat{H} = \hat{H}_a + \hat{H}_b$$

and eigenfunctions of the simpler hamiltonians are known,

$$\hat{H}_a \Psi_a = E_a \Psi_a \text{ and } \hat{H}_b \Psi_b = E_b \Psi_b$$

show that $\Psi = \Psi_a \Psi_b$ is an eigenfunction of \hat{H} . What is the corresponding energy?

- (b) The hamiltonian for a one-dimensional harmonic oscillator is

$$\hat{H} = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} \omega^2 x^2$$

show that $\Psi_0 = e^{-\frac{1}{2}\omega x^2}$, $\Psi_1 = \sqrt{\omega} x e^{-\frac{1}{2}\omega x^2}$ and $\Psi_2 = (2\omega x^2 - 1)e^{-\frac{1}{2}\omega x^2}$ are eigenfunctions of this hamiltonian.

- (c) Consider the hamiltonian for a two dimensional harmonic oscillator:

$$\hat{H} = -\frac{1}{2} \frac{d^2}{dx^2} - \frac{1}{2} \frac{d^2}{dy^2} + \frac{1}{2} \omega_1^2 x^2 + \frac{1}{2} \omega_2^2 y^2$$

Show that $\Psi = e^{-\frac{1}{2}(\omega_1 x^2 + \omega_2 y^2)}$ is an eigenfunction of this hamiltonian. Suggest some other wavefunctions which are eigenfunctions for the two-dimensional case, and give their energies. Under what circumstances might two different eigenfunctions of this hamiltonian have the same energy?

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

A12

Answer *all* parts of this question:

- (a) Define the commutator $[\hat{A}, \hat{B}]$ of two operators \hat{A} and \hat{B} . For three operators, show that $[\hat{A}\hat{B}, \hat{C}] = [\hat{A}, \hat{C}]\hat{B} + \hat{A}[\hat{B}, \hat{C}]$
- (b) The angular momentum operators are,

$$\hat{l}_x = -i\hbar(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}), \hat{l}_y = -i\hbar(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z}) \text{ and } \hat{l}_z = -i\hbar(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x})$$

They obey the commutator equations,

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

Prove any *one* of the above commutator equations.

- (c) Evaluate the commutators $[\hat{L}^2, \hat{l}_z]$, $[\hat{l}_z, \hat{l}_+]$ and $[\hat{l}_z, \hat{l}_-]$ where

$$\hat{L}^2 = \hat{l}_x \hat{l}_x + \hat{l}_y \hat{l}_y + \hat{l}_z \hat{l}_z, \text{ and}$$

$$\hat{l}_+ = \hat{l}_x + i\hat{l}_y \text{ and } \hat{l}_- = \hat{l}_x - i\hat{l}_y.$$

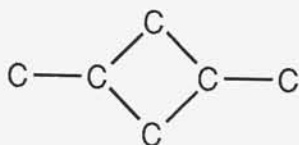
If ψ is an eigenfunction of \hat{l}_z use the commutator equations to find the effect of \hat{l}_+ and \hat{l}_- on the wavefunction ψ . What is the name for this type of operator?

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

A13

Answer *all* parts of this question:

- a) Briefly explain why symmetry orbitals are useful in molecular orbital theory.
- b) A possible geometry for the C_6 cluster is



The structure is planar, with the molecule in the xy plane. What is the point group of this molecule?

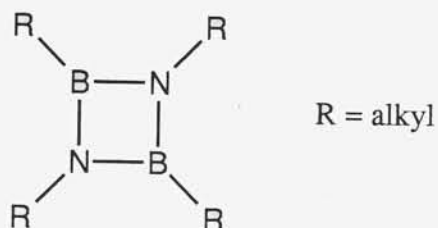
- c) What representations are spanned by a basis consisting of a p -orbital perpendicular to the molecular plane from each atom? Construct the symmetry orbitals.
- d) Construct the secular equations within the Hückel approximation and find the orbital energies. If there are 6 π -electrons, is the molecule likely to be a singlet or a triplet?

Approximate division of marks: (a) 15%, (b) 15%, (c) 30%, (d) 40%.

A14

Answer *all* parts of this question:

Diazaboretanes have the structure below; the (BN)₂ ring is planar.



- (a) Denoting Coulomb integrals for B and N in the ring p system as α_B and α_N and resonance integrals as β , write down, in an atomic orbital basis, the Hückel secular equation for the π electron system in the (BN)₂ ring. Why is it not convenient to solve this directly?
- (b) Assign the point group symmetry of the (BN)₂ ring.
- (c) Considering only the $2p_\pi$ orbitals on B and N, form all possible symmetry orbitals. Sketch their forms and assign their symmetry labels.
- (d) Construct a qualitative π molecular orbital diagram and sketch the molecular orbitals.
- (e) Predict qualitative changes to overall bond energies,
 - (i) as a square (BN)₂ ring distorts to a diamond shape, and
 - (ii) as a square (BN)₂ ring distorts to a rectangle.

Approximate division of marks: (a) 15%, (b) 5%, (c) 40%, (d) 20%, (e) 20%.

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A15

Answer *both* parts of this question:

- (a) Obtain an expression for μ_A , the chemical potential per molecule for the gaseous species A, in terms of the molecular partition function of A. Show how this may be used to obtain an expression for the equilibrium constant (K_C) for the gas phase reaction:



where ν_A , ν_B , ν_C , and ν_D are the stoichiometric coefficients for A, B, C, and D respectively.

- (b) Given that the fundamental vibrational frequency of H_2 is 12.95×10^{13} Hz, estimate the value of K_p at 800K for the reaction:



Indicate clearly any approximations or assumptions used in your calculations. You may assume integral masses.

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

A16

Answer *all* parts of this question:

- (a) Starting from the relation $A = -kT \ln Q_N$ obtain expressions in terms of the molecular partition function q for the Helmholtz free energy (A) and entropy (S) of a gas and hence show that the internal energy (U) is given by

$$U = \frac{NkT^2}{q} \frac{dq}{dT}$$

The vibrational partition function of a diatomic molecule treated as a harmonic oscillator is given by

$$q_{\text{vib}} = \frac{1}{1 - e^{-h\nu/kT}}$$

where ν is the fundamental frequency.

- (b) Obtain an expression for the vibrational contributions to the molar heat capacity and show that the vibrational contribution to the internal energy is equal to NkT at high temperatures.
- (c) For N_2 and I_2 , the fundamental vibrational frequencies are 2395 and 215 cm^{-1} respectively. For these gases, obtain values for the vibrational contributions to their respective heat capacities, C_v , at 298K. Comment on the values you obtain.

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

[TURN OVER

A17

Answer *all* parts of this question:

- (a) Derive the Langmuir expression for the pressure of a gas in equilibrium with a monolayer adsorbate for the case of non-dissociative adsorption, making clear the conditions for which it is valid. Indicate on a potential-energy diagram the activation energies for adsorption and desorption. How are these activation energies related to the heat of adsorption?
- (b) Obtain an expression for the half-life, $t_{\frac{1}{2}}$, of a non-dissociative adsorbate on a surface.
- (c) Calculate the activation energy for the non-dissociative adsorption of a gas on a solid for which, at a temperature of 250K, $t_{\frac{1}{2}} = 3.6 \times 10^{-11}$ s and the equilibrium gas pressure with the adsorbed film at a given fractional coverage θ is $p^\theta = 34$ atm, while at 200K $p^\theta = 5$ atm. You may take the desorption attempt frequency to be $\nu = 10^{13}$ Hz.
- (d) By considering the potential-energy curves of a molecule in its undissociated and dissociated states interacting with a surface, illustrate how an activation energy of adsorption arises.

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

A18

Answer *all* parts of this question:

- (a) Consider an electron moving in a 1D box, and treat the electron first as a standing wave and then as a running wave. What are the appropriate boundary conditions in both cases? Solve the Schrödinger equation in each case, and obtain expressions for the allowed energy states of the electron. How are the allowed values of the wavevector in each case related to each other?
- (b) A quantum well is an artificial structure comprising a thin layer of a narrow-gap semiconductor (e.g. GaAs) of thickness d sandwiched between two semi-infinite-thickness wide-gap semiconductors. Assume for simplicity that the two wide-gap semiconducting regions are made from the same material, (e.g. $\text{Al}_{1-x}\text{Ga}_x\text{As}$) and that there is no discontinuity in the positions of the valence-band maxima of GaAs and $\text{Al}_{1-x}\text{Ga}_x\text{As}$. Sketch the spatial profile of the energy-band extrema in the vicinity of the well. Mark on it the allowed electron energy states in the GaAs conduction band, assuming that the well can be regarded as having infinitely high barriers.
- (c) Give an estimate for the threshold energy for optical absorption in a GaAs quantum well with $d = 20\text{\AA}$, making clear your assumptions. The bandgap of bulk crystalline GaAs is 1.5 eV.

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

[TURN OVER

A19

Answer *all* parts of this question:

- (a) Use Fick's diffusion law (flux is proportional to concentration gradient multiplied by the diffusion coefficient) to derive an expression for the reaction rate constant of a diffusion-controlled reaction, k_{diff} , in terms of the diffusion coefficient and the radii of the reactants.
- (b) The Stokes-Einstein equation for the diffusion coefficient, D , of a sphere of radius, r , is $D = k_{\text{B}}T/6\pi\eta r$

where k_{B} = Boltzmann's constant

T = temperature

and η = viscosity

Use this equation to derive an expression relating k_{diff} to the viscosity.

- (c) Give examples of diffusion controlled reactions. Indicate how you might test whether a reaction is diffusion controlled.
- (d) The data given below refer to the rate constant k_{obs} of the reaction



in water. Use a graphical method to assess the claim that this is a diffusion-controlled reaction.

$T/^{\circ}\text{C}$	$k_{\text{obs}}/10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$\eta/10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$
10	2.11	1.31
20	2.80	1.00
30	3.64	0.80
40	4.67	0.65

Approximate division of marks: (a) 30%, (b) 10%, (c) 10%, (d) 50%.

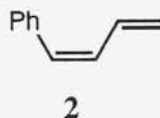
A20

Answer *both* parts of this question:

The following observations have been made concerning the reaction of cis-1 in strong acid:



- i) The reaction is acid catalysed
- ii) The rate of isomerisation is faster in $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$ than in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ by a factor of 2.5.
- iii) When ^{18}O -labelled cis-1 is used then the loss of ^{18}O to the solvent is equal to the rate of isomerisation.
- iv) No characteristic ultraviolet absorption due to 2 is observed.



- (a) Suggest a mechanism for this isomerisation reaction which is consistent with the information given. Describe a plausible alternative mechanism that is *not* consistent with the evidence.
- (b) Draw a free-energy profile for your mechanism indicating the structures of all states (intermediates and transition states).

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