

NOT TO BE
TAKEN AWAY

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

Wednesday 26th May 1999 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.

[TURN OVER

SECTION A

Introduction to Quantum Chemistry

A1

Answer *all* parts of this question:

- (a) Write down the Schrödinger equation for the hydrogen atom in atomic units. Verify that $\phi_1 = e^{-r}$, $\phi_2 = ze^{-r/2}$ are hydrogen orbitals and determine their energies. Sketch these orbitals. Give the exact form of two other real hydrogen orbitals, ϕ_3, ϕ_4 .
- (b) Evaluate $\hat{L}_x\phi_2$, $\hat{L}_y\phi_2$, $\hat{L}_z\phi_2$. Hence show that ϕ_2 is an eigenfunction of \hat{L}_z and \hat{L}^2 . How are the eigenvalues of these operators interpreted?
- (c) Explain how orbitals of this nature may be used to describe the ground state of the N atom.

$$\left[\nabla^2 f(r) = \frac{d^2 f}{dr^2} + \frac{2}{r} \frac{df}{dr}; \quad \nabla^2 z f(r) = z \frac{d^2 f}{dr^2} + \frac{4z}{r} \frac{df}{dr}; \quad \frac{\partial f(r)}{\partial z} = \frac{z}{r} \frac{df}{dr}; \right.$$

$$\left. \hat{L}_x = -i \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \text{ etc}; \quad \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \right]$$

Approximate division of marks: (a) 40%, (b) 50%, (c) 10%.

A2

Answer *all* parts of this question:

- (a) Consider a two electron system, with space orbitals ϕ_a, ϕ_b .

Write down the triplet and singlet spin wavefunctions. What are the values of S and M_s for these functions?

Write down also two electron symmetric and antisymmetric orbital wavefunctions involving ϕ_a and ϕ_b .

Use the Pauli principle to construct wavefunctions which involve both space and spin functions, identifying them as singlet or triplet. Are these wavefunctions zero when two electrons are in the same place? Hence give a simple explanation of Hund's first rule.

- (b) What are Hund's second and third rules?
- (c) Give the ground state term symbols for all atoms in the first row H – Ne.
- (d) The first four excited states of the C atom are: 16.4, 43.5, 10193.7 and 21648.4 cm^{-1} above the ground state. Give term symbols for these states.

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

[TURN OVER

SECTION B*Symmetry and Bonding***A3**

Answer *all* parts of this question:

Consider the trigonal planar complex ML_3 where M is a first-row transition metal and L is a ligand that you may regard as being structureless and supporting a single s orbital.

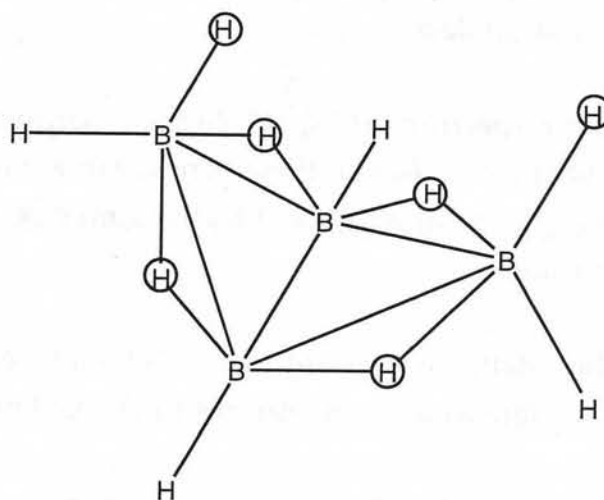
- (a) What is the point group of the complex?
- (b) Find the representation matrix for the C_3 operation applied to the metal $4p$ orbitals.
- (c) Which irreducible representations (IRs) are spanned by the $3d$, $4s$ and $4p$ orbitals of the metal ion?
- (d) Which IRs are spanned by the s orbitals of the ligands?
- (e) Generate the ligand symmetry orbitals.
- (f) Construct a qualitative energy level diagram for the ML_3 complex.

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

A4

Answer *all* parts of this question:

- (a) What are Wade's rules?
- (b) Use Wade's rules to show that the structure of B_4H_{10} is derived from an octahedron.
- (c) Assign the point-group symmetry of B_4H_{10} , shown below:



- (d) How do the 1s orbitals of the encircled H atoms transform in this symmetry?
- (e) B_4H_{10} is derived from an octahedron with two missing vertices. Draw a diagram to identify these missing vertices.
- (f) If there were B-H units at each missing vertex, what orbitals would they contribute to the bonding in the molecule? How would these orbitals transform under the symmetry of the B_4H_{10} molecule?
- (g) Use your answers to (c)-(f) to justify Wade's rules.

Approximate division of marks: (a) 10%, (b) 15%, (c) 5%, (d) 20%, (e) 10%, (f) 25%, (g) 15%.

[TURN OVER]

SECTION C*Molecular Energy Levels and Thermodynamics***A5**Answer *all* parts of this question:

- (a) State the selection rules for rotational and vibrational transitions of a diatomic molecule. Outline the general features of the microwave and infrared spectra of a diatomic molecule which result, indicating in your answer how the spectra provide details of the fundamental properties of that molecule.
- (b) A low-resolution spectrum of $^{12}\text{C}^{16}\text{O}$ shows absorptions at 2143.3, 4259.7 and 6349.1 cm^{-1} . Assign these bands, explaining your reasoning. Suggest what additional features may be seen at higher spectral resolution.
- (c) Given that the rotational constant for $^{12}\text{C}^{16}\text{O}$ is 1.93 cm^{-1} , compute the rotational and vibrational temperatures of the CO molecule.
- Evaluate the rotational and vibrational partition functions of the molecule at 300K. You need not derive formulae used, but you should indicate any approximations or assumptions associated with them.
- (d) Compute the rotational and vibrational contributions to the entropy of the $^{12}\text{C}^{16}\text{O}$ molecule at 300K. You may quote any formulae you use without proof.
- (e) Taking $^{12}\text{C}^{16}\text{O}$ at 300K as an example, indicate how the partition function relates to intensities of the various spectral features.

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

A6

Answer *all* parts of this question:

- (a) The vibrational partition function of a diatomic molecule can be written as:

$$q_{\text{vib}} = \frac{e^{-\Delta\epsilon/kT}}{1 - e^{-h\nu_0/kT}}$$

where ν_0 is the fundamental vibration frequency and $\Delta\epsilon$ is the energy difference between a reference energy level and the vibrational ground state (i.e. $\frac{1}{2}h\nu_0 - \epsilon_{\text{ref}}$). What are the important underlying principles leading to this expression?

Using the above relation write down expressions for the vibrational partition function for ϵ_{ref} equal (i) to the ground vibrational state and (ii) the bottom of the potential energy curve.

For both cases derive expressions for the vibrational contribution to the internal energy (U) and the heat capacity (C_v). Comment on the expressions you have obtained.

- (b) Outline, without excessive mathematical detail, how the above arguments can be extended to calculate the heat capacities of crystals.
- (c) The fundamental vibration frequency of HF is 3958 cm^{-1} . Estimate the total heat capacity of the molecule at 1000K and 30K, justifying any approximations or assumptions used.

[Atomic masses: $^1\text{H} = 1$, $^{19}\text{F} = 19$ a.m.u., the equilibrium bond length of HF is 0.09 nm]

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

[TURN OVER

SECTION D

Solids, Surfaces and Heterogeneous Catalysis

A7

Answer *all* parts of this question:

- (a) Give a concise definition of:
 - (i) a metal;
 - (ii) an insulator.

- (b) Explain the origin of the bandgap in silicon in terms of the interaction between sp^3 hybrid orbitals. If the energy difference between bonding and antibonding combinations of hybrid orbitals on two atoms making up a bond is denoted as 2β , and the valence - (or conduction-) band width is denoted as ΔE , what is the condition for there to be a band gap? Does this model depend on the existence of translational periodicity? Would you expect the bandgap of amorphous Si to be bigger or smaller than, or the same as, that of crystalline Si?

- (c) Give a brief account of the effect on the electrical characteristics of crystalline Si of the substitutional incorporation of Ga or As. What would you expect the effect to be if *equal* concentrations of Ga *and* As were incorporated? What would be the effect on the electrical characteristics of crystalline GaAs of the substitutional incorporation of Si?

- (d) The temperature dependence of the electrical conductivity of a semiconductor is found to be activated, with an activation energy of 0.35eV at high temperatures, but an activation energy of only 0.01eV at low temperatures. Account for this behaviour. What would you expect the threshold energy for optical absorption of the semiconductor to be in the same two temperature regions?

Approximate division of marks: (a) 10%, (b) 35%, (c) 25%, (d) 30%.

A8

Answer *all* parts of this question:

- (a) Derive, making clear your assumptions, an expression for the Langmuir isotherm for non-dissociative adsorption of a gas on a surface, written in terms of V_m , the volume of gas corresponding to monolayer coverage. Sketch the expected behaviour of the volume of gas adsorbed as a function of pressure at a given temperature.
- (b) The BET isotherm is:

$$\frac{p}{V(p_o - p)} = \frac{1}{cV_m} + \frac{(c-1)p}{cV_m p_o}$$

State clearly the assumptions made in deriving this expression and how they differ from those underlying the Langmuir isotherm. Sketch the expected behaviour of the volume of gas adsorbed as a function of pressure at a given temperature for the BET isotherm for two cases, viz large and small values of the difference between the energy of adsorption of the first monolayer, q_1 , and the latent heat of vaporization, q_v .

- (c) The volume of butadiene adsorbed per kilogram of adsorbant varies with pressure as follows at 300K:

$10^3 V \text{ (m}^3/\text{kg)}$	19.5	35.4	50.1	64.3	79.3	95.7
$10^{-4} p \text{ (Pa)}$	1.33	2.66	4.00	5.33	6.67	8.00

Test whether the Langmuir or the BET isotherm best accounts for the data by plotting appropriate functions of pressure and volume versus pressure. Hence obtain values for V_m and $(q_1 - q_v)$. (The saturated vapour pressure of liquid butadiene at the same temperature is $p_o = 0.2 \text{ MPa}$.)

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

[TURN OVER

SECTION E

Reactivity and Solutions

A9

Answer *both* parts of this question:

- (a) Explain the underlying principles for the application of transition state theory to the derivation of a reaction rate constant of the form

$$k = k_{\text{B}}TK^{\ddagger}/h$$

where k_{B} , T , and h have their usual meanings.

- (b) Calculate the Arrhenius parameters (E_{a} and A) as well as $\Delta H_{\text{o}}^{\ddagger}$ and $\Delta S_{\text{o}}^{\ddagger}$ for the hydrolysis of *t*-butyl chloride from the following results:

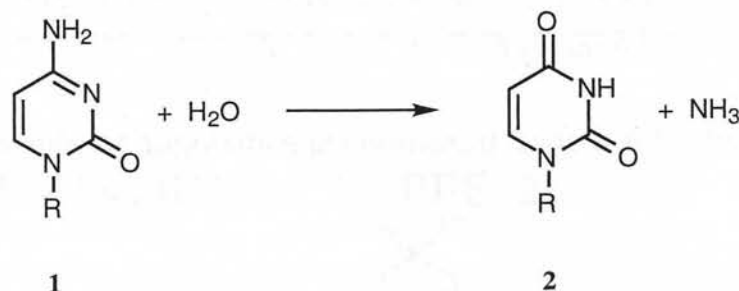
T/K	274	278	283	288	293
$10^3 k/\text{s}^{-1}$	0.84	1.62	3.57	7.49	15.19

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

A10

Answer *all* parts of this question:

The nucleotide cytidine **1** undergoes a deamination reaction to give the nucleotide uridine **2**.



This reaction can occur either by an uncatalysed or a base-catalysed mechanism. At 85 °C, the rate constants of the uncatalysed and base-catalysed deaminations are:

$$k_{\text{H}_2\text{O}} = 8.8 \times 10^{-8} \text{ s}^{-1}$$

$$k_{\text{OH}^-} = 4.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

- (a) Sketch how the logarithm of the rate of this reaction varies with pH.
- (b)
 - (i) Suggest a mechanism for the base-catalysed deamination.
 - (ii) Draw a free-energy diagram to illustrate this mechanism and include possible high-energy intermediates and transition states.

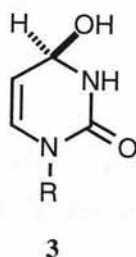
[question continued over page]

[TURN OVER

A10 continued

- (c) The same reaction is also catalysed by the enzyme cytidine deaminase. Zebularine hydrate **3** is a tight binding inhibitor of cytidine deaminase ($K_i = 10^{-12} \text{ mol dm}^{-3}$) and is thought to act as a transition state analogue.

Explain why **3** is a good transition state analogue for this reaction.



- (d) It is known that Zn^{2+} plays an important role in the enzymic catalysis. Suggest a mechanism for the enzyme-catalysed reaction.

Approximate division of marks: (a) 10%, (b) 40% (approximately equally divided amongst the parts), (c) 30%, (d) 20%.

END OF PAPER

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

Monday 31st May 1999 9 to 12

CHEMISTRY A: PAPER 2

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 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.

[TURN OVER

A11

Answer *all* parts of this question:

- (a) Write down the Schrödinger equation for the harmonic oscillator, for a particle of mass m which moves in the potential $\frac{1}{2}m\omega^2x^2$. Verify by substitution that the form of the ground state wavefunction is $e^{-\alpha x^2}$; determine α and the energy. Show also that $xe^{-\alpha x^2}$ is a wavefunction for the same α , and determine its energy. Sketch these wavefunctions. Sketch also the form of some higher energy wavefunctions, and write down their energy.
- (b) On a new diagram, sketch the harmonic oscillator potential and the Morse potential, for a diatomic molecule. Indicate the pattern of the energy levels for the two potentials. Give brief reasons why the hydrogen atom has an infinite number of bound states but a diatomic molecule has only a finite number of vibrational levels.
- (c) Write down an approximate formula for the rotational energy levels of a diatomic molecule. On a new diagram, indicate the rovibrational energy levels ($J \leq 4$) for the two lowest vibrational states of a diatomic molecule. Show the allowed transitions between the energy levels.

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

A12

Answer *all* parts of this question:

- (a) Determine the normalised stationary state wavefunctions and energies of a particle of unit mass in a one dimensional box, $0 \leq x \leq 1$.
- (b) At a particular instant, the wavefunction for a particle in $0 \leq x \leq 1$ is $Ax(1-x)$. Determine the normalisation constant A. What is the probability that a measurement of the energy gives $\hbar^2 \pi^2/2$? Comment on the value of this probability.

$$\left[x(1-x) = \sum_n^{\text{odd}} \frac{8}{n^3 \pi^3} \sin n\pi x \right]$$

- (c) Explain the terminology 'expectation value'. What is the expectation value of x for the wavefunction given in part (b).

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

[TURN OVER

A13

Answer *all* parts of this question:

- (a) Construct the group multiplication table for the C_{2h} point group.
- (b) What are the two non-trivial subgroups of the C_{2h} point group?
- (c) What are the key approximations leading to the Hückel model?
- (d) Write down the secular determinant for the π system in the *trans*-configuration of butadiene.
- (e) Use group theory to reduce this determinant to two simpler determinants.
- (f) Which butadiene conformer is predicted by Hückel theory to be the lower in energy, the *cis* or the *trans*? Explain your answer.

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

A14

Answer *all* parts of this question:

In the solid state, PF_5 comprises a mixture of the tetrahedral ions $[\text{PF}_4]^+$ and the octahedral ions $[\text{PF}_6]^-$ in equal proportion.

- (a) How do P valence atomic orbitals ($3s$, $3p$, $3d$) transform in T_d and O_h symmetry?
- (b) How do the groups of F σ valence orbitals in $[\text{PF}_4]^+$ and $[\text{PF}_6]^-$ transform?
- (c) Construct molecular orbital diagrams for the σ bonding in each ion. Discuss how these diagrams will change as functions of the charge of the central P atoms.
- (d) Comment upon the relative involvement of the P $3d$ orbitals in the bonding in $[\text{PF}_4]^+$ and $[\text{PF}_6]^-$.

Approximate division of marks: (a) 15%, (b) 25%, (c) 30%, (d) 30%.

[TURN OVER

A15

Answer *both* parts of this question:

- (a) Show, without excessive mathematical detail, how knowledge of the partition functions of the reactants and products can be related to the equilibrium constant for that reaction.
- (b) Using the information given below, calculate the equilibrium constant at 500K for the gas phase reaction



stating any assumptions you make.

Vibrational frequencies (cm^{-1}):

HDO:	2726.7, 1402.2, 3707.5
H ₂ O:	3656.7, 1594.8, 3755.8
HCl:	2991
DCl:	2145

Rotational constants (cm^{-1}):

HDO:	23.38, 9.10, 6.42
H ₂ O:	27.88, 14.51, 9.29
HCl:	10.59
DCl:	5.449

The rotational partition function of a non-linear molecule at temperature T rotating about its three principal axes a , b , and c is:

$$q_{\text{rot}} = (\pi^{1/2} / \sigma) [(T / \Theta_a)(T / \Theta_b)(T / \Theta_c)]^{1/2}$$

where Θ are the corresponding rotational temperatures. Other formulae may be quoted without proof.

[Atomic masses: H = 1, D = 2, O = 16, Cl = 35 a.m.u.]

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

A16

Answer *all* parts of this question:

- (a) Show how the factorisation of the total partition function of a molecule into components arising from its various dynamical degrees of freedom leads to simplifications in the representation of the thermodynamic properties of the molecule. Your answer should consider the free energy (A), the internal energy (U), the heat capacity (C_v) and the entropy (S).
- (b) The low-resolution infra-red spectrum of gaseous SO_2 shows absorptions at 519, 1151 and 1361 cm^{-1} . Use this information to calculate the total internal energy of the molecule at 300K and 3000K, providing an explanation for any assumptions or approximations you make. Comment on the results you have obtained.

Any formulae used may be quoted without proof.

$$\text{S} = 32 \text{ a.m.u.}; \quad \text{O} = 16 \text{ a.m.u.}$$

- (c) Without giving numerical details, indicate how the calculations performed in (b) would be expected to differ for the N_2O molecule.

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

[TURN OVER

A17

Answer *both* parts of this question:

- (a) Derive an expression for the electron velocity at the Fermi surface, v_F , using the free-electron model. Obtain estimates for v_F for Na and Al metals, given that the respective atomic densities are $2.652 \times 10^{28} \text{ m}^{-3}$ and $6.02 \times 10^{28} \text{ m}^{-3}$. What is the value of the electrical conductivity of a free-electron gas?
- (b) Discuss what factors control the electrical conductivity of real metals. Derive an expression for the electrical conductivity, σ , in this case. If the mean-free path of electrons in Na metal is 2000 \AA at a particular temperature, what is the value of σ at this temperature?

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

A18

Answer *all* parts of this question:

- (a) Nickel crystallizes in the f.c.c. structure. If the atomic radius of Ni is 1.245 \AA , what is the value of the conventional cubic unit-cell parameter, a ? Determine the surface atomic density for the ideal {100} surface.
- (b) The cohesive energy (latent heat of vaporization) of solid Ni is 428 kJ mol^{-1} . What is the value of the surface energy for the Ni {100} surface?
- (c) Explain how short-range lateral repulsive interactions between adsorbate atoms can lead to well-ordered structures in the adsorbate layer. What is the effect of *attractive* lateral interactions at low values of adsorbate coverage? In the limit of very strong nearest-neighbour repulsive lateral interactions, determine the closest distance between adsorbate atoms on the Ni{100} surface of saturation coverage. Give a sketch of this monolayer adsorbate structure relative to the underlying unreconstructed metal surface, and give the Wood's notation for the structure.
- (d) The repulsive interaction energy between oxygen atoms on a Ni{100} surface is 48 kJ/mol . If the limiting heat of adsorption of O atoms on this surface at zero coverage is $q = 570 \text{ kJ/mol}$, what is the value of q at saturation coverage?

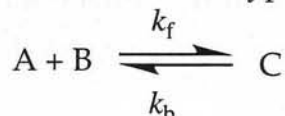
Approximate division of marks: (a) 10%, (b) 30%, (c) 30%, (d) 30%.

[TURN OVER

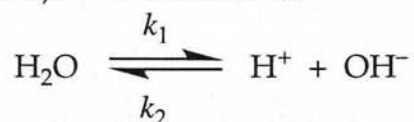
A19

Answer *both* parts of this question:

- (a) Describe how chemical relaxation methods may be used to determine the rate constants for reactions of the type



- (b) When pure water is subjected to a sudden temperature rise, the conductivity increases with a relaxation time of $\tau = 3.7 \times 10^{-5}$ s (final temperature = 296 K). The reaction is:



Given that the forward reaction is first-order and the reverse is second-order, calculate the rate constants k_1 and k_2 for the forward and reverse reactions. (Use $K_w = 1.0 \times 10^{-14}$).

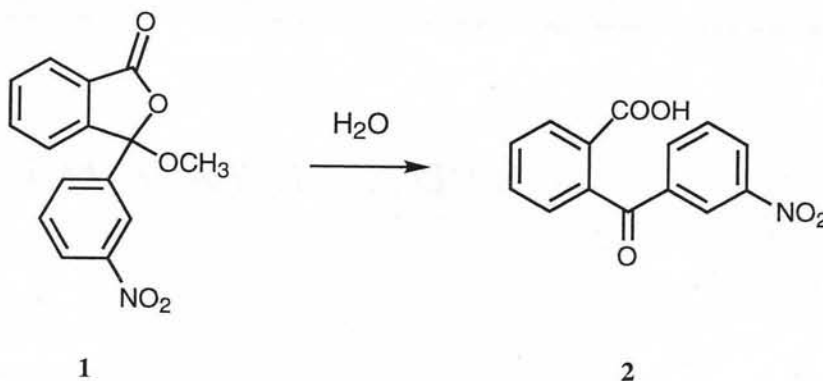
Approximate division of marks: (a) 50%, (b) 50%.

A20

Answer *all* parts of this question:

The hydrolysis of **1** to **2** follows the rate expression:

$$k_{\text{obs}} = 1.6 \times 10^{-6} + 6.38 \times 10^{-4} [\text{H}^+] + 49 [\text{OH}^-]$$



- (a) Sketch how the logarithm of the rate of hydrolysis varies with pH.
- (b) Propose possible mechanisms for the hydrolysis reaction at acidic pH and basic pH and explain how these mechanisms are consistent with the entropies of activation being -108 and $-21 \text{ J mol}^{-1} \text{ K}^{-1}$ at pH 1.3 and 7.7, respectively.
- (c) The reaction can also be catalysed by acetate ions (CH_3CO_2^-). The solvent isotope effect ($k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$) for the acetate-catalysed reaction is 2.65. Suggest a mechanism.

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

END OF PAPER