NATURAL SCIENCES TRIPOS Part IB

Thursday 31st May 2001   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 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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SECTION A

Introduction to Quantum Mechanics

A1

Answer *all* parts of the question

(a) By 1924, in the development of the new quantum mechanics, it was realised that all particles could be wave-like or particle-like, with the important relation:

$$p(\equiv mv) = h/\lambda \qquad [1]$$

Give the names of three scientists associated with this work.

What do the symbols in equation 1 denote?

(b) Show that the total energy, E, can be written as:

$$E = \frac{p^2}{2m} + V \qquad [2]$$

What do the symbols in equation 2 denote?

Hence express $\frac{1}{\lambda^2}$ in terms of $E - V$.

(c) A wave can be described by:

$$\psi = \sin \frac{2\pi}{\lambda} x$$

Evaluate $\frac{d^2\psi}{dx^2}$ and express it in terms of ψ.

Then use your expression for $\frac{1}{\lambda^2}$ to 'derive' the Schrödinger equation.

[Continuation of Question A1]

(d) For the Schrödinger equation for a particle of mass m moving along the x-axis under a potential $V(x)$:

    (i)   Write down the Hamiltonian.

    (ii)   What is the interpretation attached to the wavefunction?

    (iii)   For a bound-state problem with $a \le x \le b$, and $V = \infty$ outside, what are the boundary conditions obeyed by the wavefunction?

    (iv)   Define the expectation value of a quantity represented by $\hat{Q}$.

    (v)   Define the uncertainty ΔQ in the expectation value.

    (vi)   Wavefunctions $\psi_i(x)$, $\psi_j(x)$ which correspond to different energies are orthogonal. What does this mean?

    (vii)   For a particle of mass m in a box, of side a, a wavefunction is
$$\psi_n(x) = \sin\frac{n\pi x}{a}.$$
What is the energy of this wavefunction?

Approximate division of marks: (a) 5%, (b) 10%, (c) 15%, (d) 70%.

[TURN OVER

A2

Answer *all* parts of the question

(a) Write down the Schrödinger equation for a one-electron hydrogen-like atom with central charge $+Ze$, describing all the symbols you introduce. Show by substitution that the ground-state 1s orbital has the form e^{-Zr/a_0}.

[Use $\nabla^2 = \dfrac{\partial^2}{\partial r^2} + \dfrac{2}{r}\dfrac{\partial}{\partial r}$].

Determine the energy, E, and a_0. Give numerical values for a_0 in:

(i) SI units

and

(ii) atomic units.

What is the energy expression, in atomic units, for any orbital of this atom (use the quantum number n).

(b) For $Z = 1$: Write down the probability that the electron is at a distance r from the proton; where is this probability a maximum?

Sketch the 1s orbital.

Sketch also the 2s orbital (its precise mathematical form is not required), emphasising how it differs from the 1s wavefunction.

Sketch the 2p orbital.

(c) Consider the atom oxygen. Suggest appropriate values of Z, with reasons, to model:

(i) the 1s orbital

(ii) the 2p orbital

Hence explain, in terms of both their energy and their electron density, why the 1s electrons of oxygen are chemically unreactive.

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

SECTION B

Symmetry and Bonding

A3

Answer *all* parts of the question

(a) What are the symmetry groups of the following molecules:
H_2O, NH_3, C_2H_4, SiH_4 and C_6H_6?

(b) The molecule HN=NH exists in cis and trans isomers. Both isomers are planar.
What are the point groups of the two isomers?
Sketch the symmetry operations for the cis isomer.

(c) Using the 1s orbitals on each H atom and the 2s, $2p_x$ and $2p_y$ orbitals from each N atom, find the symmetry orbitals for the trans isomer of HN=NH (the molecule lies in the xy plane).
Without detailed calculation, give approximate sketches of the lowest molecular orbital of each symmetry.

Approximate division of marks: (a) 20%, (b) 20%, (c) 60%.

A4

Answer *both* parts of the question

(a) (i) Assuming O_h symmetry, devise a molecular orbital diagram for $[B_6H_6]^{2-}$.

(ii) Outline the reasons why the number of bonding molecular orbitals present in the nido-borane $[B_5H_9]$ should be the same as that found in $[B_6H_6]^{2-}$. What general relationships therefore exist for closo- and nido-boranes?

(b) (i) Use a molecular orbital approach to investigate the two extremes of possible bonding in SF_6, involving and not involving d orbitals.

(ii) Suggest why SF_6 is the only sulfur(VI) hexa-halide to exist.

Approximate division of marks: (a) 70%, (b) 30%.

SECTION C

Molecular Energy Levels and Thermodynamics

A5

Answer *all* parts of the question

(a) Describe, without mathematical detail, how the particle-in-a-box theory can be used to treat the energy distribution of valence electrons in a metal.

(b) Starting from the expression for the energy, E_n, of a particle of mass m in a one-dimensional box of length a:

$$E_n = \frac{n^2 h^2}{8ma^2}$$

derive an expression for the Fermi energy, ε_F, in a metal with N valence electrons.

(c) Evaluate your expression for Ca (density 1.54 g cm^{-3}). Comment on your result.

(d) Estimate the heat capacity of the valence electrons in part (b) at room temperature (298K), making clear any assumptions you make.

(e) Indicate qualitatively how statistical thermodynamic arguments might be used to treat the vibrational heat capacity of a solid.

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

A6

Answer *all* parts of the question

(a) Derive an expression for the internal energy of a system of N indistinguishable diatomic molecules. You may assume formulae for the various partition functions without proof, but you should make clear any assumptions or approximations implicit in their use.

(b) Starting from the statistical thermodynamic expressions for the Helmholtz free energy, or otherwise, derive an expression for the entropy of the above system.

(c) Given the following information, evaluate the molar energy and the molar entropy for $^{79}Br_2$ at 600K. Comment on your results.

Rotational constant /cm^{-1}	0.081
Fundamental vibration frequency /cm^{-1}	323.2

(d) Sketch, giving as much quantitative detail as you can, how you would expect the molar heat capacity C_v of $^{79}Br_2$ to change with temperature between 0K and 1000K.

(e) Indicate how you would expect the molar energy and the molar entropy to change if instead you were considering the diatomic molecule $^{79}Br\ ^{81}Br$.

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

SECTION D

Solids, Surfaces and Heterogeneous Catalysis

A7

Answer *all* parts of the question

(a) Sodium crystallizes in the body-centred cubic (b.c.c.) structure, with unit-cell parameter $a = 4.225$ Å. What is the nearest-neighbour interatomic spacing?

(b) Calculate the packing fraction (the ratio of the volume actually occupied by spherical atoms in contact to the total crystalline volume) of the b.c.c. structure. Is this structure close packed?

(c) Derive an expression for the radius, k_F, of the Fermi sphere of a free-electron gas, and hence obtain a value for k_F for Na, making clear your assumptions.

(d) Write down an expression for the electrical conductivity of a metal. If the electron mean-free path for Na (at 77K) is 2000 Å, what is the value of its electrical conductivity?

Approximate division of marks: (a) 5%, (b) 30%, (c) 45%, (d) 20%.

A8

Answer *all* parts of the question

$K_2Pt(CN)_4$ ('KCP') is a semiconductor, but partially oxidized KCP (*e.g.* $K_2Pt(CN)_4.Br_{0.3}$) is a one-dimensional (1D) metal.

(a) Give a schematic illustration of the molecular-orbital level diagram for the molecule $K_2Pt(CN)_4$, and show how these levels form electron energy bands in the solid. Why are the Pt $5p_z$ and $5d_{z^2}$ orbitals the most important to consider for band formation in this 1D crystal?

(b) On the basis of this band diagram, explain why KCP is a semiconductor but $KCP:Br_{0.3}$ is a 1D metal.

(c) Illustrate schematically how the energy bands associated with the Pt $5p_z$ and $5d_{z^2}$ electrons vary with electron wavevector, $E(k)$, for KCP. Give a rationalization of the behaviour in terms of appropriate combinations of these orbitals.

(d) What is the value of the Fermi wavevector, k_F, as a fraction of the first Brillouin-zone-boundary wavevector, for $KCP:Br_{0.3}$?

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

SECTION E

Reactivity and Solutions

A9

Answer *all* parts of the question

(a) Describe how the presence of solvent molecules can affect the rate of reactions in liquids.

(b) (i) What is meant by a diffusion-controlled reaction as compared to an activation-controlled reaction?

   (ii) Derive an expression for the rate constant of a diffusion-controlled reaction in terms of the radii of the reactants and their diffusivities. Show, by making suitable approximations, that the rate constant for a diffusion-controlled reaction can be expressed in terms of the viscosity of the solvent.

(c) For the dimerisation of benzoic acid:

$$2\ C_6H_5COOH \longrightarrow (C_6H_5COOH)_2$$
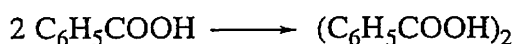
the rate constant at 300 K is $5 \times 10^6\ M^{-1}\ s^{-1}$ in water and $7 \times 10^{10}\ M^{-1}\ s^{-1}$ in hexane. The viscosity of water is $1 \times 10^{-3}\ kg\ m^{-1}\ s^{-1}$ and the viscosity of hexane is 3.3×10^{-4} $kg\ m^{-1}\ s^{-1}$ at 300 K.

   (i) Calculate the rate constant for a diffusion-controlled reaction in both solvent, and hence determine if this reaction is diffusion controlled in water or hexane. Give an explanation for the difference in reaction rates in the two solvents.

   (ii) Suggest an experiment that could be performed to confirm your conclusion.

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

A10

Answer *all* parts of the question

Consider the following data which have been determined to elucidate the mechanism of reduction of ketones using lithium aluminium hydride.

A large molar excess of $LiAlH_4$ to the ketone was used when studying the kinetics, to ensure that only one of the hydride ions from $LiAlH_4$ was transferred. The reaction was found to be first order with respect to the concentration of the ketone:

$$-\frac{d[\text{ketone}]}{dt} = k_{obs}[\text{ketone}] \quad \text{where} \quad k_{obs} = k[LiAlH_4]^x$$

A graph of how k_{obs} varies with $[LiAlH_4]$ is shown in **Fig. 1**.

Fig. 1

Fig. 2
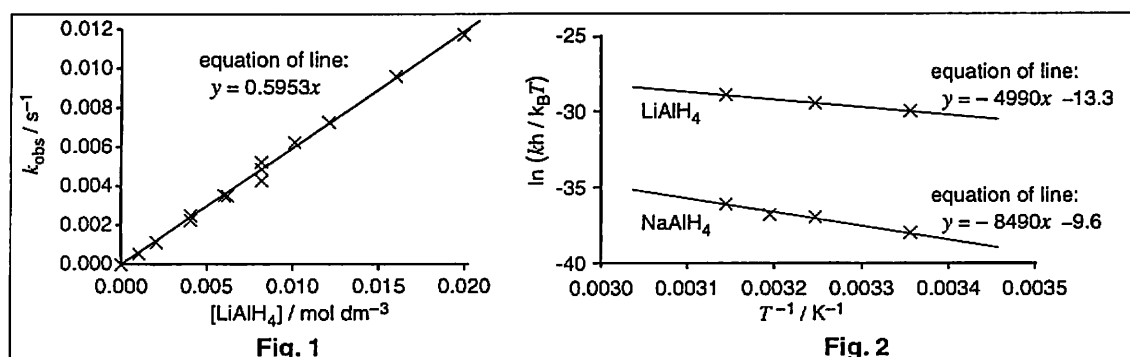
Sodium aluminium hydride was found to react with the ketone about eleven times more slowly than lithium aluminium hydride. The reaction rates for both $LiAlH_4$ and $NaAlH_4$ with the ketone were measured at varying temperatures and a graph of

$\ln\left(\dfrac{k\,h}{k_B T}\right) vs \dfrac{1}{T}$ was plotted, and the result are shown in **Fig. 2** [where k is the rate constant,

h is Planck's constant, k_B is Boltzmann's constant and T is the temperature in Kelvin].

If lithium aluminium deuteride is used in place of the hydride, the reaction is found to proceed 1.3 times more slowly.

When one equivalent of **1** is added to the $LiAlH_4$ / ketone mix, the reaction stops. On addition of lithium iodide, the reduction continues.

[Continuation of Question A10]

1
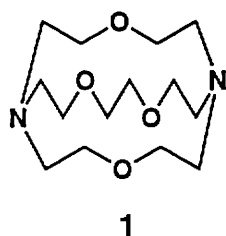
(a) Suggest how 1 inhibits the reaction. What does this tell us about the mechanism?

(b) Determine the following parameters and say what information each reveals about the reaction mechanism between $LiAlH_4$ and the ketone.

    (i) The rate equation and rate constant, k.

    (ii) The enthalpies of activation for both the $LiAlH_4$ and $NaAlH_4$ reductions.

    (iii) The entropies of activation for both the $LiAlH_4$ and $NaAlH_4$ reductions.

    (iv) The kinetic isotope effect.

(c) Suggest a suitable mechanism for the reduction that is consistent with all the available data, drawing any key transition states.

Approximate division of marks: (a) 10%; (b) 70%; (c) 20%.

[END OF PAPER]

NATURAL SCIENCES TRIPOS Part 1B

Wednesday 6th June 2001   1.30 to 4.30

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 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.

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A11

Answer *all* parts of the question

Write down the Schrödinger equation for a particle of mass m moving in one dimension in a potential $V(x)$ with energy E and wavefunction ψ.

(a)   Consider the potential $V(x) = -\dfrac{3\hbar^2}{m}\,\text{sech}^2 x$.

    (i) Using the fact that $\text{sech}\,x = \dfrac{1}{\cosh x}$, and
    $\cosh 0 = 1$, $\cosh\infty = \infty$, $\cosh-\infty = \infty$, freely sketch $V(x)$.

    (ii) By substitution show that the ground-state wavefunction is $\psi = \text{sech}^2 x$ (you may assume that $\dfrac{d^2\psi}{dx^2} = 4\,\text{sech}^2 x - 6\,\text{sech}^4 x$). What is the energy?

    (iii) Why is the energy, E, of the ground state greater than the minimum $V(0)$ of $V(x)$? Sketch ψ.

(b)   Consider the harmonic oscillator potential $V(x) = \tfrac{1}{2}m\omega^2 x^2$. Sketch $V(x)$ and the associated ground-state wavefunction $e^{-m\omega x^2/2\hbar}$. Determine the ground-state energy by substitution.

(c)   Show that if $\omega = \dfrac{2\hbar}{m}$, then $E - V(0)$ has the same value for both (a) and (b).

    Why is the potential in (a) not a good model for molecular vibrations?

Approximate division of marks: (a) 40%, (b) 55%, (c) 5%.

A12

Answer *all* parts of the question

(a) The spin wavefunctions $\alpha(v), \beta(v)$ are eigenfunctions of the spin angular momentum operators $\hat{S}_z$, $\hat{S}^2$. Write down the equations which represent this.

Write down the eigenvalues for $\hat{S}_z$, $\hat{S}^2$ for the two electron spin functions:

(i) $\qquad \alpha(v_1)\alpha(v_2)$ $\qquad\qquad\qquad\qquad$ [1]

(ii) $\qquad \alpha(v_1)\beta(v_2) - \alpha(v_2)\beta(v_1)$ $\qquad\qquad$ [2]

(b) Wavefunctions for the excited 1s 2s states of He may be constructed from the orbital functions:

$$1s(r_1)2s(r_2) + 1s(r_2)2s(r_1) \qquad\qquad [3]$$

$$1s(r_1)2s(r_2) - 1s(r_2)2s(r_1) \qquad\qquad [4]$$

and the spin functions [1] and [2]. Use the Pauli Principle to give the allowed products of [1], [2] with [3], [4]. Give the atomic term symbols for the allowed forms.

(c) Give Hund's first rule, and use the above to explain why it should be true.

(d) Give the electronic configuration (in terms of molecular orbitals) for the ground state of O_2. Give the form of each molecular orbital in terms of atomic orbitals, and sketch them. Obtain and explain the term symbol for the ground state of O_2.

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

A13

Answer *all* parts of the question

(a) What is the symmetry group of 1,4-difluorobenzene?

(b) Using only the six p_π orbitals from the carbon atoms, construct and assign the symmetry orbitals for this system.

(c) Using Hückel theory, find the molecular orbital energies.

Approximate division of marks: (a) 10%, (b) 45%, (c) 45%.

A14

Answer *both* parts of the question

(a) State the conditions for a molecule to be aromatic, and compare and contrast the bonding in benzene (C_6H_6) and borazine ($B_3N_3H_6$).

(b) All the P–N bonds in dichloro-cyclophosphazene, $(PCl_2N)_3$, are identical, having a bond length which is intermediate between that expected for a single P–N and a double P=N bond.

   (i) Show how the P–N bonding in $(PCl_2N)_3$ may be strengthened by $d\pi$-$p\pi$ bonding. Why is there debate as to whether the molecule should be considered fully aromatic?

   (ii) Suggest why the π stabilisation energy of $(PX_2N)_3$ may be highly sensitive to the substituent (X).

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

A15

Answer *all* parts of the question

(a) Approximate wavenumbers of rotational fine structure observed in the P and R branches of an IR spectrum of $^{14}N^{16}O$ in its electronic ground state are listed below. Transitions of maximum intensity are marked with asterisks.

1869.91, 1873.32, 1876.73, 1880.14, 1883.54*, 1886.95, 1890.36, 1893.77, 1897.18, 1900.59, 1907.41, 1910.82, 1914.23, 1917.64, 1921.05, 1924.46, 1927.86*, 1931.27, 1934.68, 1938.09, 1941.50

Assign the different features, explaining your reasoning.

(b) Use the information in (a) to deduce what you can about the $^{14}N^{16}O$ molecule, including the sample temperature, explaining your reasoning.

(c) Given that there is a low-lying electronic state 121.1 cm^{-1} above the ground state, and that both states are doubly degenerate, estimate the molar internal energy of the NO sample, making clear any assumptions or approximations you make.

(d) Indicate, with reasoning, which degrees of freedom of the NO molecule contribute significantly to the molar specific heat at the sample temperature. What changes would you expect to see at a temperature of 1200K?

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

A16

Answer *all* parts of the question

(a) Using the general form of the partition function, write down an expression for the rotational partition function of a diatomic molecule. In your answer you should make clear how the different terms in your expression are related to fundamental properties of that molecule.

(b) Derive an expression for the rotational partition function of a diatomic molecule in the high-temperature limit, explaining any assumptions or approximations you make.

(c) Using the formula obtained in (b), derive expressions for the rotational contribution to the internal energy and the entropy for a system of N heteronuclear diatomic molecules.

(d) Given that the bond length of H_2 is 74.1 pm, use the formula obtained in (b) to evaluate the rotational contribution to the molar internal energy of the H_2 molecule at 100K. Comment on the likely accuracy of your result.

(e) Evaluate the partition function of the H_2 molecule at 100K to an accuracy of better than 1%, and hence obtain an improved estimate of the rotational contribution to the molar internal energy at that temperature.

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

A17

Answer *all* parts of the question

(a)   Explain what is meant by the work function, Φ, of a metal surface, illustrating your answer with a diagram showing the electrostatic potential just inside and outside the surface. How can Φ be measured optically?

(b)   The thermionic electron current density emitted from a tungsten surface is 2×10^{-3} Am^{-2} at 1500K and 22 Am^{-2} at 2000K. What is the value of the work function of the metal surface?

(c)   A tungsten filament, coated with a monolayer of lanthanum, is used as the thermionically emitting cathode of an electron gun. If the electron-beam current density of the W:La filament operating at 1000K is the same as that of a pure W filament operating at 2000K, by how much is the work function reduced by the La overlayer? State any assumptions made. Explain, with the aid of a suitable diagram, why La has this effect.

(d)   Explain briefly, giving reasons, what is the effect on Φ for a W surface covered with a close-packed monolayer of rare-gas atoms.

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

A18

Answer *all* parts of the question

(a)   The pressure of a gas, in equilibrium with its adsorbate on a metal surface at a fractional coverage of $\theta = 0.5$ is 0.64 atm at 200K and 35 atm at 300K. Estimate the corresponding heat of adsorption, making clear the assumptions made in obtaining this result. From the magnitude of the energy so obtained, is the molecule involved likely to be physisorbed or chemisorbed on the metal surface?

(b)   Obtain an estimate for the half-life time, $t_{1/2}$, for the adsorbate at a temperature of 300K. Any formulae used should be derived and any assumptions made should be stated. (The desorption attempt frequency may be taken to be $v = 10^{13}$ Hz.)

(c)   Hence estimate the sticking coefficient of the adsorbed molecule, $s(\theta, T)$, at $\theta = 0.5$ and $T = 300$K, given that the mass of the gaseous adsorbant is 32 amu, and the surface density of adsorption sites of the metal surface is $N_s = 10^{19}$ m^{-2}.

Approximate division of marks: (a) 20%, (b) 45%, (c) 35%.

[TURN OVER

A19

Answer *all* parts of the question

(a) Describe the key assumptions behind transition state theory.

(b) Derive a formula relating the rate constant of a reaction to the enthalpy of activation, $\Delta H_0^{\ddagger}$, and entropy of activation, $\Delta S_0^{\ddagger}$.

(c) Use the data below to calculate $\Delta H_0^{\ddagger}$ and $\Delta S_0^{\ddagger}$ for the reaction:

$$CH_3I + C_6H_5ONa \xrightarrow{\text{Ethanol}} CH_3OC_6H_5 + NaI$$
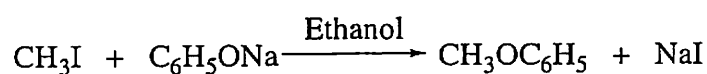
| Temperature/ ^0C	Rate constant/ $M^{-1} s^{-1}$
0	5.6×10^{-5}
6	11.8×10^{-5}
12	24.5×10^{-5}
18	48.8×10^{-5}
24	100×10^{-5}
36	208×10^{-5}

(d) Comment on the sign and magnitude of $\Delta H_0^{\ddagger}$ and $\Delta S_0^{\ddagger}$ for this reaction. What do you predict the effect of hydrostatic pressure will be on this reaction? Explain your reasoning.

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

A20

Answer *all* parts of the question

Alkynes react with aqueous acid to form ketones *via* the following proposed mechanism:
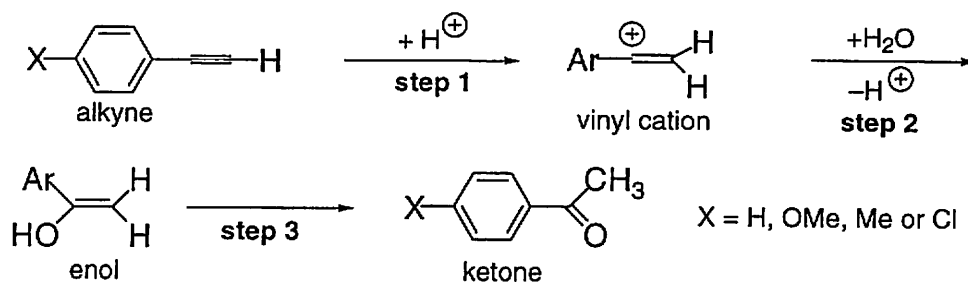
(a)   Sketch the form of the reaction profile for the hydration of phenylacetylene (i.e., Ar = Ph, X=H) assuming –

(i).   step 1 is the rate-determining step.

(ii)   step 2 is the rate-determing step.

You should indicate on your graphs the observed activation energy for the reaction.

(b)   (i)   The rate of reaction is found to be first order with respect to the concentrations of both the alkyne and H^+ ions. How does this help to determine which step is rate determining?

(ii)   The rate of hydration of substituted phenylacetylenes is extremely sensitive to the nature of the substituent, X, with a Hammett ρ value of -3.84. What information does this reveal about the rate-determining step?

(c)   To see if the hydration of *p*-methoxyphenylacetylene ($X = $ OMe) undergoes general acid catalysis, the reaction rate was measured at 45 °C at a fixed pH of 3.36 with varying concentrations of formic acid / formate buffer. The results are shown in the graph below.

[Question A20 continues on the next page]

[Continuation of Question A20]
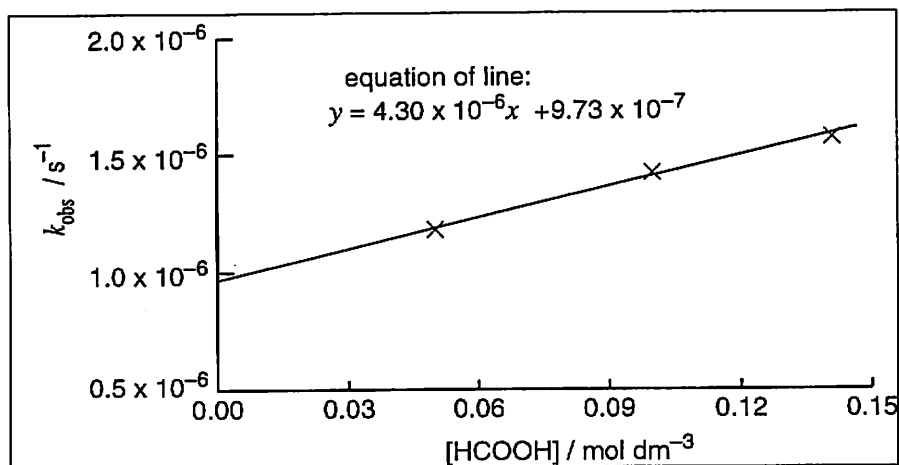
(i) Assuming the uncatalysed rate to be negligible, write an expression for k_{obs} in terms of k_{H^+} and k_{HCOOH}, the rate constants for the reaction as catalysed by H_3O^+ and formic acid respectively.

(ii) Determine the values of k_{H^+} and k_{HCOOH} and comment on your answers.

(iii) How does the result in (ii) help to determine which step is rate determining?

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

[END OF PAPER]