PART B

2001

Please note that this answer book will be photocopied when returned and then

split so that answers are sent to the appropriate markers.

For this reason it is extremely important that you observe instructions 6 to 8.

Instructions to Student

1. You are allowed **10 minutes** to read this paper, and **3 hours** to complete the questions.

2. You are **not** permitted to refer to books, notes or periodic tables but you may use a non programmable electronic calculator.

3. All questions to be attempted. A guide for time allocation is supplied at the beginning of each question.

4. Data is supplied, where necessary, with each question.

5. Answers **must** provide **clearly laid out working** and **sufficient explanation** to show how you reached your conclusions.

6. Answers must be written in the blank space provided immediately below each question in the exam booklet. Rough working must be on the backs of pages. Only material presented in the answer boxes will be assessed.

7. Ensure that your name is written in the appropriate place on **each page** of your examination booklet.

8. Use only **black** or **blue** **pen** for your written answers, **pencil or other coloured pens are not acceptable**.

Question 1 (20 minutes)

Data: $h = 6.62608 \times 10^{-34}$ J s
$m_e = 9.10939 \times 10^{-31}$ kg
$c = 2.99792458 \times 10^8$ m s^{-1}

The molecules of polymethine dyes of the series:
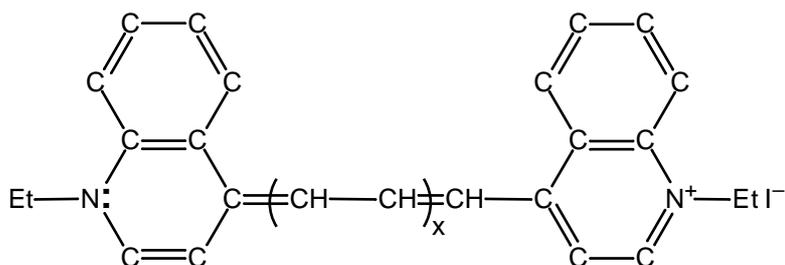
(where x = 0, 1, 2…) contain a conjugated π-electronic system. The absorption spectra of these dyes result from the transition of electrons between energy levels of the π system. The electronic states are commonly described using a simple particle-in-a-box model, where the molecule is presented as a one-dimensional box with infinitely high walls and the π electrons move freely within this box. In this assumption, only the kinetic energy of the electron needs to be considered.

a) Derive the formula of the energy levels of such a system if the box has length L. State and justify the assumptions you have made.

In the case of the dye, the length of the box L is assumed to be the distance between the nitrogen atoms:

$$L = b \cdot l + \gamma$$

Where b is the number of bonds in the chain between the nitrogen atoms, l is the average bond length in the conjugated system, and γ is the empirical parameter that accounts for the extension of the π system beyond each of the terminal nitrogen atoms. It is assumed that l and γ are the same for all dyes in this series. (That is, they are independent of x, NOT $l = \gamma$!)

b) For a dye molecule with a given x, determine the total number k of π electrons in the conjugated system between the nitrogen atoms, the total number b of bonds in the π system, and the number N of occupied orbitals in the ground electronic state. Remember that nitrogen atoms can contribute to the conjugated system due to their lone pair of electrons.

c) The maximum wavelength λ_{max} in the spectrum (the minimum energy difference) corresponds to the electronic transition from the highest occupied molecular orbital to the lowest unoccupied molecular orbital in the conjugated system. From your answer in a) and/or using any other information, derive the general expression of λ_{max} for a given x.

d) Given the maximum wavelength for the first two dyes of this series (λ_{max} = 592.2 nm and 706.0 nm respectively), calculate the average bond length l in the conjugated systems and the empirical parameter γ.

e) Determine the chemical formula of a dye that has an absorption band with the wavelength equal to 440.9 nm in the visible spectrum.

Question 2 (25 minutes)

a) The complex ion $[Co(en)_3]^{3+}$ is diamagnetic while the ion $[CoF_6]^{3-}$ is paramagnetic. Suggest a qualitative explanation for these observations. Include clearly labelled d-orbital splitting diagrams for these complex ions as part of your answer. Calculate the 'spin only' magnetic moments and the crystal field stabilization energies (in terms of Δ_O) of these species. Which ion absorbs at longer wavelength?

b) A series of cobalt complexes has been synthesized and their absorption maxima measured. These are listed in the following table:

Complexes	λ_{max} (nm)
$CoCl_3(NH_3)_6$	475
$Co(H_2O)(NO_3)_3(NH_3)_5$	495
$Co(CO_3)(NO_3)(NH_3)_5$	510
$CoF(NO_3)_2(NH_3)_5$	515
$CoCl_3(NH_3)_5$	534
$CoBr_3(NH_3)_5$	552

(i)   Rewrite these formulae according to the IUPAC guidelines and identify the complex part.

(ii) Give IUPAC names of the rewritten formula in (i).

(iii) What types of electrolytes would these complexes dissociate into when they are in solution?

(iv) What are the colours of these complexes?

(v)   Give a rationale for the different λ_{max} values observed for these complexes.

c)   A certain compound of chromium was synthesized. The elemental analysis shows its composition to be: Cr 27.1%, C 25.2% and H 4.25% by mass, the rest is due to oxygen.
  (i)   What is the empirical formula of this compound?
  (ii) If the empirical formula consists of one molecule of H_2O, what is the other ligand? What is the oxidation state of chromium?

  (iii) The study on magnetic property shows that this compound is diamagnetic, how would you explain the magnetic property of this compound? Sketch the possible structure of this compound.

Question 3 (45 minutes)

In both parts (a) and (b) make sure to state clearly any assumptions you make in your solutions. Moreover, you should justify your assumptions by showing that they are self-consistent. Data for both parts are given at the end of the question.

(a)   The dichromate anion can hydrolyse in aqueous solutions to form the related hydrogenchromate ion. The hydrogenchromate ion is in itself a weak acid, and so the solution behaviour of dichromate and its related species is indeed somewhat complex. The solution equilibria are dominated by the two systems:

$$Cr_2O_7^{2-} (aq) + H_2O (l) \rightleftharpoons 2HCrO_4^- (aq) \qquad\qquad pK_{hyd} = 1.36$$

$$HCrO_4^- (aq) + H_2O (l) \rightleftharpoons CrO_4^{2-} (aq) + H_3O^+ (aq) \qquad\qquad pK_a = 6.50$$
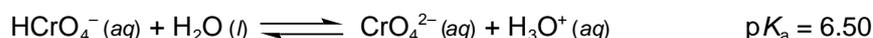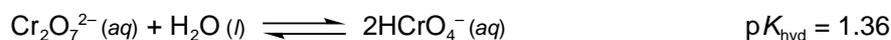
(i)   Calculate the pH of the following solutions
  1. 0.010 M K_2CrO_4
  2. 0.010 M $K_2Cr_2O_7$

(ii) Consider a solution initially containing $K_2Cr_2O_7$ at a concentration of 0.010 M and CH_3COOH at a concentration of 0.10 M. Calculate the concentration of the following species at equilibrium:
  1. H_3O^+
  2. CrO_4^{2-}
  3. $Cr_2O_7^{2-}$
  4. CH_3COOH

(b)   Potentiometric methods are widely used for the determination of equilibrium concentrations and equilibrium constants in solution.

Consider two separate solutions: Solution 1 contains an acidified aqueous mixture of $FeSO_4$ and $Fe_2(SO_4)_3$; solution 2 contains an aqueous mixture of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$. The concentration of iron-containing species in the two solutions are related by the two following equations:

$$[Fe^{2+}]_{solution\ 1} = [Fe(CN)_6^{4-}]_{solution\ 2}$$

$$[Fe^{3+}]_{solution\ 1} = [Fe(CN)_6^{3-}]_{solution\ 2}$$

The potential of a platinum electrode immersed into solution 1 is 0.652 V (relative to the SHE), while the potential of a platinum electrode immersed into solution 2 is 0.242 V (again relative to the SHE). The total concentration of iron-containing species in solution 2 is 0.1812 M. In

solution 2, you may neglect the presence of any species other than the completely complexed species.

(i) Give balanced redox equations for the half-cells represented by solutions 1 and 2.

(ii) Calculate the concentrations of the following species:
1. Fe^{3+} in solution 1
2. Fe^{2+} in solution 1

(iii) Calculate E°_{cell} ($[Fe(CN)_6]^{3-}$ / $[Fe(CN)_6]^{4-}$)

(iv) Calculate the ratio of the stability constants K_{stab} ($[Fe(CN)_6]^{3-}$) / K_{stab} ($[Fe(CN)_6]^{4-}$).
Hint: Consider how the half-cells in solutions 1 and 2 are related.

(v) Using your answer to (iv) above, or otherwise, calculate K_{stab} ($[Fe(CN)_6]^{3-}$)

Data: (All values are at 298 K and 1 atm) pK_a (CH_3COOH) = 4.76
pK_{stab} ($[Fe(CN)_6]^{4-}$) = -24.79
E^0 (Fe^{3+}/Fe^{2+}) = +0.77 V

Question 4 (45 minutes)

a) **Data:** R = 8.314 J K^{-1} mol^{-1}

The reaction between hypochlorite ions and iodide ions in basic solution is studied at 298K and the following data obtained:

Reaction: $I^- + OCl^- \rightarrow OI^- + Cl^-$
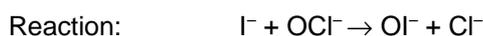
Run	$[I^-]_0$	$[OCl^-]_0$	$[OH^-]_0$	$(Rate)_0$ ($mol\,l^{-1}s^{-1}$)
1	0.0120	0.0120	1.00×10^{-5}	2.00×10^{-3}
2	0.0120	0.0120	2.00×10^{-5}	1.00×10^{-3}
3	0.0240	0.0120	2.00×10^{-5}	2.00×10^{-3}
4	0.0240	0.0240	4.00×10^{-5}	2.00×10^{-3}

(i) What is the rate law? What is rate constant k? If k triples on raising the temperature to 320.15K, what is the energy of activation?

Three possible mechanisms for the reaction are:

Mechanism I: $I^- + OCl^- \xrightarrow{k_1} OI^- + Cl^-$ slow

Mechanism II: $OCl^- + H_2O \xrightarrow{k_1} HOCl + OH^-$ fast

$HOCl + I^- \xrightarrow{k_2} HOI + Cl^-$ slow

$HOI + OH^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H_2O + OI^-$ fast

Mechanism III: $OCl^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + OH^-$ fast

$HOCl + I^- \xrightarrow{k_2} HOI + Cl^-$ slow

$HOI + OH^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H_2O + OI^-$ fast
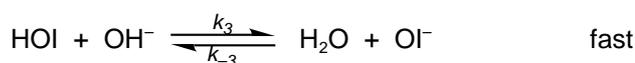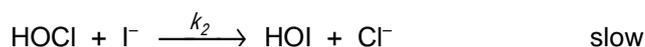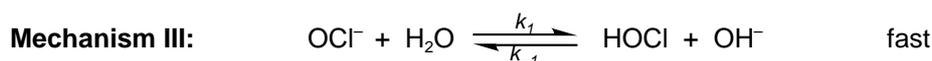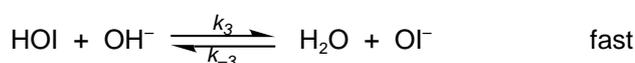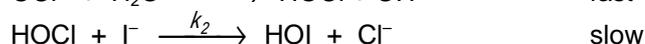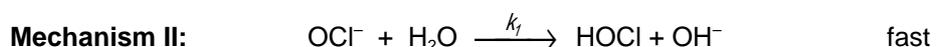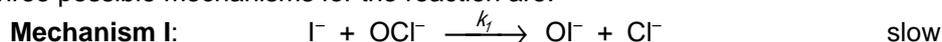
(ii) By using the steady state approximation, decide which of the above mechanisms is most appropriate for the observed kinetic behaviour.

(iii) What are the rate constant, Arrhenius factor and total activation energy in terms of the elementary step values?

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(iv) What is the order of the reaction in a buffer solution? Show that the hydronium ions catalyse the reaction above.

(v) Show that the catalytic rate constant in (iii) depends on pH.

b) It is often considered that two isotopes will have identical chemical reactivity; however, this is not precisely true. While details of the reasons need not concern us, it is useful to note that compounds featuring light isotopes (e.g. $^1H^{19}F$) have slightly lower bond strengths than analogous compounds featuring heavy isotopes (e.g. $^2H^{19}F$). This "isotope effect" can be crucial in the chemistry of low-temperature regions such as interstellar dust clouds (typically 10-20 K). Deuterium (D = ^2H) fractionation in cold interstellar clouds occurs by a variety of processes, including the following mechanism:

$$H_2 + D \longrightarrow HD + H \qquad (1)$$
$$HD + D \longrightarrow D_2 + H \qquad (2)$$
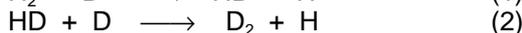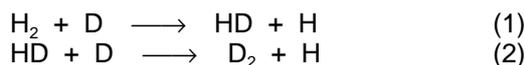
Thermochemical parameters relevant to reaction (1) are:

$\Delta H^\circ_f(H_2(g)) = 0 \text{ kJ mol}^{-1}$ $\Delta S^\circ(H_2(g)) = 130.57 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta H^\circ_f(HD(g)) = 0.33 \text{ kJ mol}^{-1}$ $\Delta S^\circ(HD(g)) = 143.69 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta H^\circ_f(H(g)) = 216.00 \text{ kJ mol}^{-1}$ $\Delta S^\circ(H(g)) = 114.60 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta H^\circ_f(D(g)) = 219.76 \text{ kJ mol}^{-1}$ $\Delta S^\circ(D(g)) = 123.24 \text{ J K}^{-1} \text{ mol}^{-1}$

[Enthalpies of formation are 0 K values (more appropriate to interstellar temperatures); entropies are 298 K values but can be assumed temperature-independent for our purposes.]

(i) Determine the free energy change ΔG° for reaction (1), at T = 20 K and T = 1000 K.

(ii) In which direction is this reaction spontaneous, if initial concentrations of all reactants and products are equal? What does the sign of ΔH° tell us about the respective bond strengths of H_2 and HD? What does the sign of ΔS° tell us about reaction (1) in the forward direction, and what is the physical basis for the sign of ΔS°?

(iii) Now consider reaction (2). What is the sign of ΔH°, and ΔS°, for the reaction in the forward direction? If you assume that enthalpy and entropy changes are equal in <u>magnitude</u> to those found in (i), calculate the free energy change and predict the direction of spontaneous reaction at 20 K, and at 1000 K.

(iv) Molecular hydrogen (in its various isotopic forms) is present in much higher concentrations than atomic hydrogen (and atomic deuterium) in interstellar clouds. Predict the dominant form of deuterium (D, HD or D_2) in interstellar clouds, assuming a temperature of 20 K, when n(D) << n(H), where n(X) is the total number of nuclei in whatever chemical form (this is the real-life situation). What is the dominant form when n(D) = n(H)? What is the dominant form of hydrogen under these conditions?

ORGANIC SECTION (45 minutes)

Question 5 (35 minutes)

Synthesis of haloperidol, a powerful tranquiliser.

Note that there is often more than one correct answer to synthesis questions, but a significant proportion of the marks for this question will be awarded for elegant and efficient syntheses (the less steps the better). Syntheses that work but are rather inelegant or complicated will only attract partial marks.

a) Propose a series of reactions to convert 4-chlorophenylmagnesium bromide into 4-chlorobenzoyl chloride. Show the product after each step, and all reagents and conditions necessary for each step.

When 4-chlorobenzoyl chloride is treated with an excess of vinylmagnesium bromide ($CH_2=CHMgBr$) in anhydrous ether, **B** is produced after aqueous workup. Treatment of **B** with excess HBr in anhydrous conditions in the presence of benzoyl peroxide gives **C**, which reacts with ammonia to form **D** ($C_{11}H_{14}ONCl$).

b) Draw out the reaction sequence showing the structures of **B**-**D**.

c)   Draw a mechanism for the conversion of **A** into **B** (to save time you may use "R-" to mean "4-chlorophenyl-".

d)   Convert 4-hydroxybutanoic acid into 4-chlorobutanoyl chloride.

In the presence of moderate amounts of aluminium trichloride, 4-chlorobutanoyl chloride reacts with fluorobenzene to give predominately a para-disubstituted compound **E**, which gives a precipitate when treated with 2,4-dinitrophenylhydrazine (2,4-DNP) but does not react with water.

e)   (i)   Give the structure of **E**.

      (ii)   Draw Whelan intermediates to explain why this substitution on fluorobenzene occurs at the para position rather than the meta position. Could this substitution occur at the meta position for other benzene derivatives? If so, give an example.

      (iii)   Draw the structure of the product of **E**'s reaction with 2,4-DNP.

              D reacts with **E** on a 1 to 1 mole basis in basic media to give **F**.

f)   Give the structure of **F**, which is haloperidol.

Question 6 (10 minutes)

The Dieckmann cyclisation is a mechanistically similar variant of the aldol reaction. Propose a mechanism for the following Dieckmann condensation:
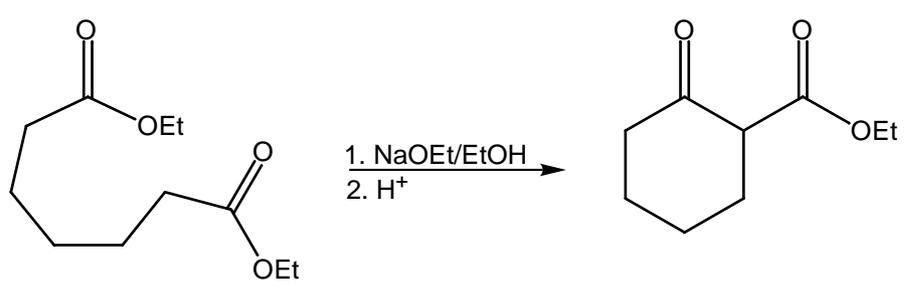
Treatment of the product of this Dieckmann condensation with sodium ethoxide in ethanol, followed by allyl bromide, then heating the product in acid gives an alkylated cyclohexanone, as shown below:
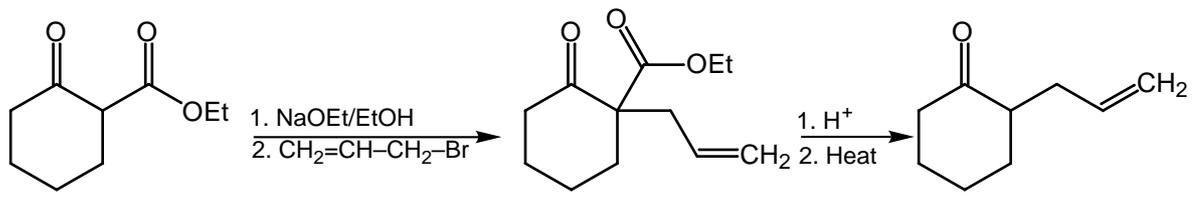
Propose a mechanism for these reactions.