

ANNEX A - THRESHOLD QUESTIONS

- A1** Hydrogen sulfide, H₂S, and sulfur dioxide, SO₂, are toxic components of natural gas which must be removed before gas is supplied to a customer. One possible reaction is:



- Using the data below, calculate the standard Gibbs free energy change for the reaction at 25 °C and 500 °C and comment on the values you obtain in terms of the feasibility of the reaction.
- Calculate the equilibrium constant, K_p, at both temperatures.
- Mixing H₂S and SO₂ does not in fact result in the above reaction. Comment.
- Predict the effect of (i) increasing the temperature and (ii) increasing the gas pressure on both the value of K_p and the extent of reaction of H₂S.
- How might the reaction conditions be changed to make it more acceptable in industrial terms?

| | H ₂ S(g) | SO ₂ (g) | H ₂ O(l) | S(s) |
|--|---------------------|---------------------|---------------------|-------|
| ΔH ^o _{f,298K} / kJ mol ⁻¹ | -22.2 | -296.6 | -285.8 | 0 |
| S ^o _{298K} / J K ⁻¹ mol ⁻¹ | 205.6 | 247.9 | 70.1 | 31.9 |
| c _p / J K ⁻¹ mol ⁻¹ | 34.23 | 39.87 | 75.29 | 22.64 |

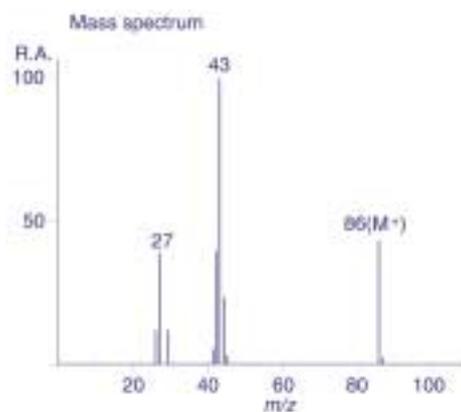
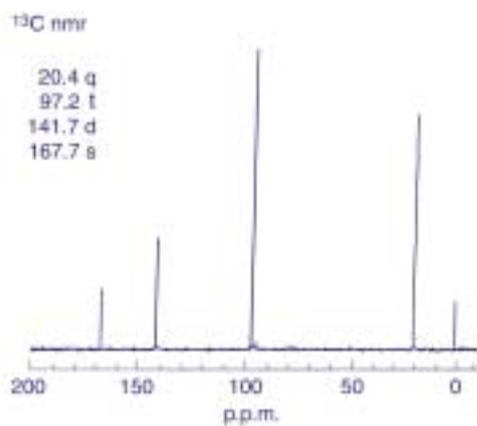
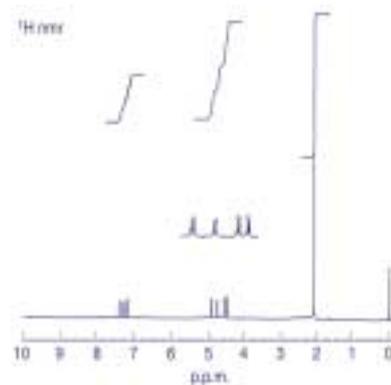
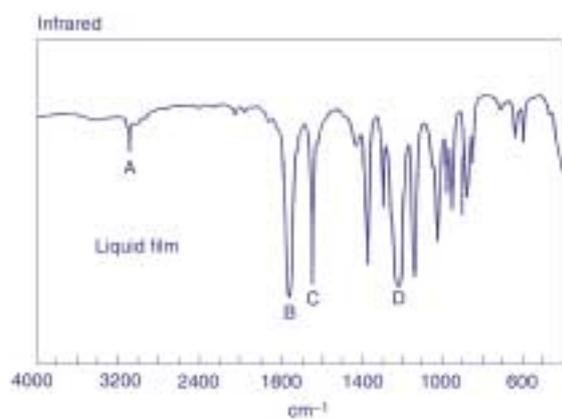
- A2**
- Write expressions for K₃, K₆, and β₃ for the stepwise replacement of water from [Cu(H₂O)₆]²⁺ by NH₃.
 - Stability constants K_n are given in the Table.

| Metal Ion | Ligand | n:1 | Log K _n | | | | 6 |
|------------------|-----------------|------|--------------------|-------|-------|------|-------|
| | | | 2 | 3 | 4 | 5 | |
| Sn ²⁺ | Cl ⁻ | 1.51 | 0.73 | -0.21 | -0.55 | | |
| Pd ²⁺ | Cl ⁻ | 6.1 | 4.6 | 2.4 | 2.6 | -2.1 | |
| Ni ²⁺ | NH ₃ | 2.67 | 2.12 | 1.61 | 1.07 | 0.63 | -0.09 |
| Cu ²⁺ | NH ₃ | 3.99 | 3.34 | 2.73 | 1.97 | -1.1 | |
| Cu ²⁺ | en | 10.6 | 9.1 | -1.0 | | | |



- Calculate the values of log β₄ and log β₅ for the Pd²⁺/Cl⁻ system.
- What are likely to be the predominant species in solution in the Pd²⁺/Cl⁻ and the Sn²⁺/Cl⁻ systems?
- Account for the variations in log K_n values for both the Ni²⁺/NH₃ and Cu²⁺/NH₃ systems.
- What is meant by the terms *chelate effect* and *macrocyclic effect*?
- Explain why log K₁ for Cu²⁺/en is larger than log β₂ for Cu²⁺/NH₃.
- Explain why log K₃ for Cu²⁺/en is so small.

A3 An aliphatic compound of *empirical* formula C_2H_3O has the IR, 1H , ^{13}C NMR and mass spectra shown below. Deduce the molecular structure and suggest structures for the fragmentation peaks at 43 and 27 mass units. Assign all the 1H and ^{13}C NMR signals and the IR bands labelled **A**, **B**, **C** and **D**. Finally sketch the ^{13}C NMR DEPT(135) spectrum.

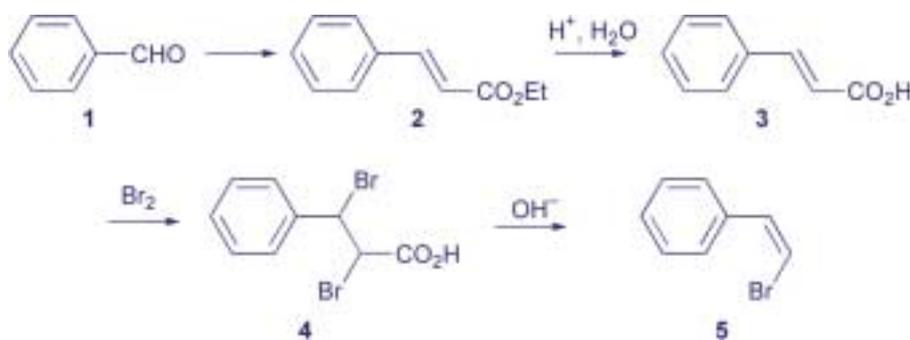


- A4** (a) A group 16 element chloride, **A**, reacts with ammonia to give a bright orange, cyclic product **B**. When **B** is heated with silver wool in *vacuo* ring contraction occurs to give **C** which, on sublimation, gives a lustrous golden polymer **D** that conducts electricity. Elemental analysis shows that **B**, **C** and **D** each contain 30.4% by mass of nitrogen. Identify, and draw the structures of **A**, **B**, **C** and **D**. Give equations to show each of the transformations. Why does **D** conduct electricity?
- (b) Use the following reactions to show how xenon fluorides can react as fluoride donors or as fluoride acceptors. Identify **A** to **C** and describe their structures.
- (i) $2\text{XeF}_2 + \text{SbF}_5 \rightarrow \text{A}$
- (ii) $\text{XeF}_6 + \text{AsF}_5 \rightarrow \text{B}$
- (iii) $\text{XeF}_6 + 2(\text{NOF}) \rightarrow \text{C}$
- (c) Write balanced equations for the following reactions and describe the structures of any xenon compounds in the products.
- (i) $\text{XeF}_6 + 3\text{H}_2\text{O} \rightarrow 2 \text{ products}$
- (ii) $\text{XeF}_4 + 2\text{H}_2\text{O} \rightarrow 4 \text{ products}$.

Alkaline solutions of the xenon-containing product which is common to both reactions are not stable and immediately begin to disproportionate slowly.

Write equations summarising this alkaline hydrolysis, describe the structure of the solid which is ultimately produced, and comment on its properties.

- A5** The following reaction sequence was used to prepare the Z-alkene **5**.



- (a) Suggest a reagent or reagents to effect the transformation from **1** to **2**, and account for the stereochemistry of **2**.
- (b) Give mechanisms for the reactions **2** to **3**, and **3** to **4**.
- (c) Only one diastereoisomer of **4** could be isolated. Draw its structure.
- (d) Give a mechanism for the last step. Why is the less stable Z-isomer formed?

- A6** (a) How can the adsorption of gases onto solids lead to a lowering of reaction activation energies and hence heterogeneous catalysis?
- (b) The experimental adsorption data for hydrogen on a sample of copper at 298 K are given below.

| | | | | | |
|---------------------------|-------|-------|-------|-------|-------|
| P / Torr | 0.19 | 0.97 | 1.90 | 4.05 | 7.50 |
| V / cm³ | 0.042 | 0.163 | 0.251 | 0.343 | 0.411 |

Show that these data fit the Langmuir model, with H₂ molecularly adsorbed. Calculate the value of K for the adsorption equilibrium and the adsorption volume of hydrogen (at atmospheric pressure) corresponding to monolayer coverage.

- (c) Data for the adsorption of krypton on graphite at 100 K do not fit the Langmuir model. Explain why and mention which model you would use to determine the surface area.
- (d) The following data were obtained from a decomposition of carbon monoxide on platinum at 773 K.

| | | | | | | | |
|-------------------------------|-----|-----|-----|-----|------|------|------|
| reaction half life / s | 6.9 | 7.0 | 6.8 | 7.5 | 16.1 | 31.9 | 65.0 |
| initial pressure / kPa | 1 | 2 | 4 | 8 | 16 | 32 | 64 |

Comment on the data in terms of the Langmuir model. Find the true rate constant and the Langmuir constant for the decomposition reaction.

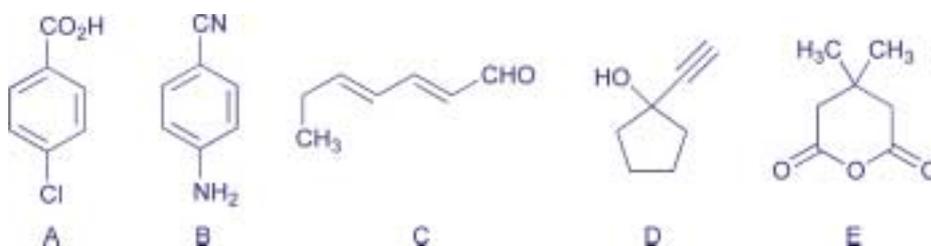
- A7** (a) Calculate the first 5 terms of the electrostatic potential energy, E , of a cation in a two-dimensional square array, A^+B^- , where the closest interionic distance is d . How are such calculations incorporated into the equation for the lattice energy of an ionic solid?
- (b) Use the data given below to show that, although BaF₃ has a favourable enthalpy of formation, the most stable fluoride of barium is BaF₂.

| | | $\Delta H / \text{kJ}$ |
|----------------------|---|--|
| Ba(s) | → | Ba(g) 180 |
| Ba(g) | → | Ba ⁺ (g) + e ⁻ 503 |
| Ba ⁺ (g) | → | Ba ²⁺ (g) + e ⁻ 965 |
| Ba ²⁺ (g) | → | Ba ³⁺ (g) + e ⁻ 3454 |
| F ₂ (g) | → | 2F(g) 159 |
| F ⁻ (g) | → | F(g) + e ⁻ 330 |

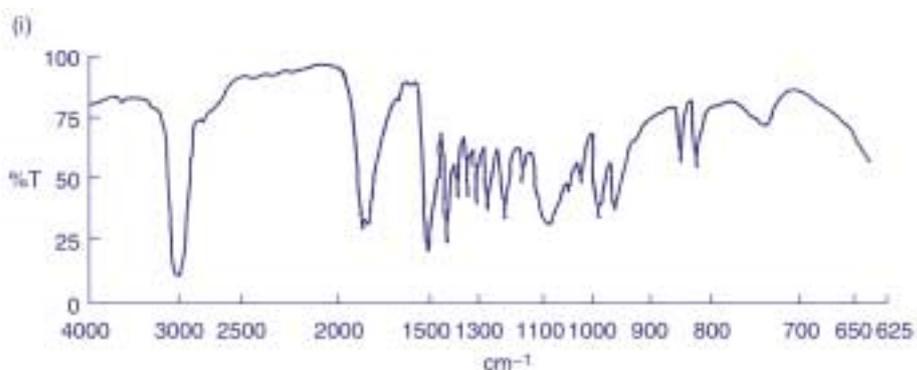
$r(\text{Ba}^{3+}) = 126 \text{ pm}$; $r(\text{Ba}^{2+}) = 136 \text{ pm}$; $r(\text{F}^-) = 133 \text{ pm}$.
Kapustinskii constant = 107 100 (with radii in pm)

- A8**
- (a) Hydrogen iodide cannot be prepared by the action of concentrated sulfuric acid on potassium iodide. The hydrogen iodide formed is oxidised to diiodine by the sulfuric acid, which is reduced to sulfur, hydrogen sulfide and sulfur dioxide in proportions that depend on the reaction conditions. Write three balanced equations for the reaction of hydrogen iodide with sulfuric acid to give diiodine plus either (i) sulfur, (ii) hydrogen sulfide, or (iii) sulfur dioxide.
- (b) In an experiment to test the stoichiometry of the reaction in part (a), potassium iodide (3.486 g) was added to an excess of concentrated sulfuric acid containing lead(II) sulfate (1.213 g) to trap any hydrogen sulfide as lead(II) sulfide. Some sulfur dioxide was lost to the atmosphere during the reaction. When oxidation of iodide to diiodine was complete the mixture was added to water and the acidity nearly neutralised. At this pH the remaining sulfur dioxide was oxidised to sulfate by some of the diiodine. The solid residue of lead(II) sulfate, lead(II) sulfide and sulfur was isolated (1.197 g), then washed with carbon disulfide to dissolve the sulfur and reweighed (1.149 g). Determine the molar ratios of potassium iodide that formed (i) sulfur, (ii) hydrogen sulfide, and (iii) sulphur dioxide.
- (c) The diiodine left after the adjustment of pH mentioned in (b) required 36.00 cm³ of sodium thiosulfate solution (0.5 mol dm⁻³) for reduction to iodide. Write a balanced equation for the reaction in (b) that occurred between diiodine and sulfur dioxide.
- (d) Determine the molar proportion of sulfur dioxide lost to the atmosphere.

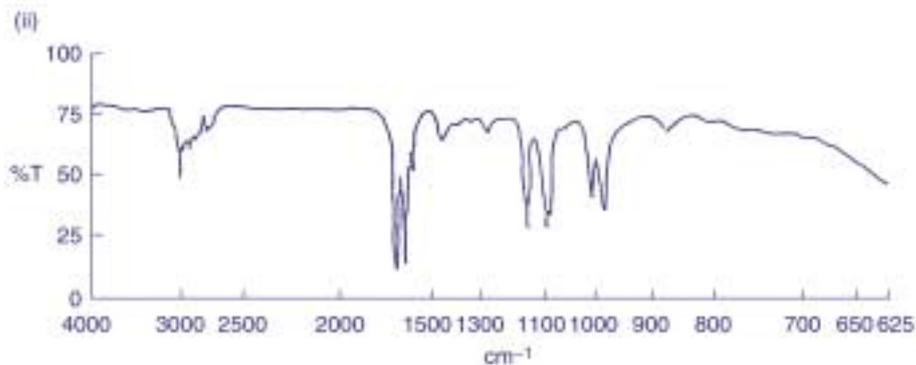
- A9**
- (a) The IR and ¹H NMR spectroscopic data of five organic compounds **A** - **E** (below), each of which contains seven carbon atoms, are provided below.



Indicate which structure gives rise to each set of spectroscopic data and assign the spectroscopic data for each compound.

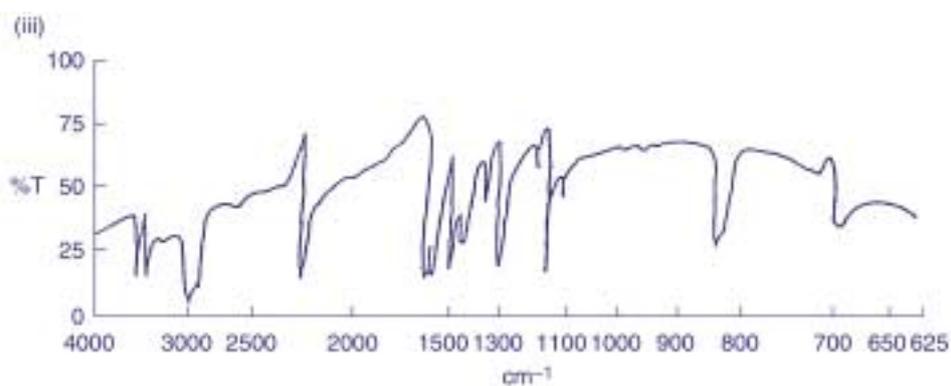


$\bar{\nu}_{\max}$ 3170–2860, 1820, 1775 cm⁻¹.
¹H NMR δ 2.61 (4H, s), 1.16 (6H, s).



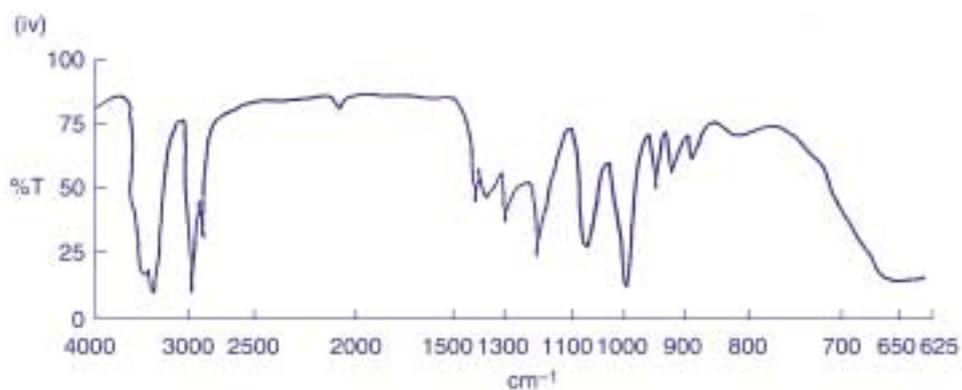
$\bar{\nu}_{\max}$ 3100–2630, 1680, 1645, 1595 cm^{-1} .

$^1\text{H NMR } \delta$ 9.53 (1H, d, $J = 7.4$ Hz), 7.10 (1H, dd, $J = 15.0$ and 10.5 Hz), 6.40–6.24 (2H, m), 6.08 (1H, dd, $J = 15.0$ and 7.4 Hz), 2.26 (2H, qd, $J = 7.5$ and 5.5 Hz), 1.09 (3H, t, $J = 7.5$ Hz).



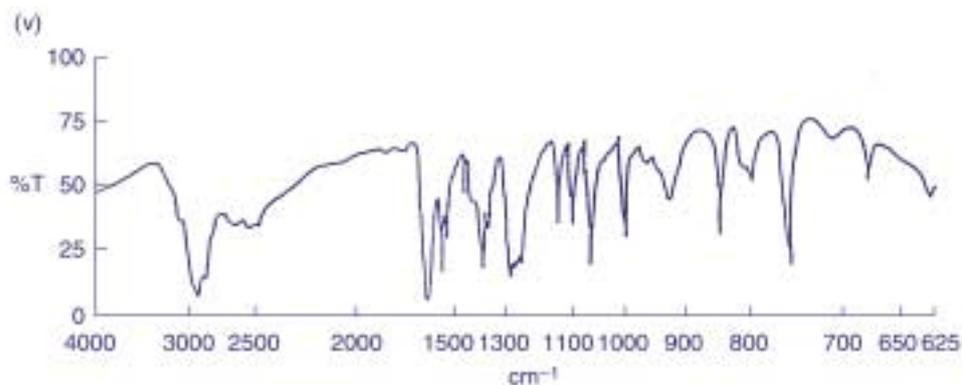
$\bar{\nu}_{\max}$ 3450, 3380, 3020–2860, 2220, 1610 cm^{-1} .

$^1\text{H NMR } \delta$ 7.38 (2H, d, $J = 9.0$ Hz), 6.63 (2H, d, $J = 9.0$ Hz), 4.31 (2H, broad s)



$\bar{\nu}_{\max}$ 3500–3010, 3300, 3010–2790, 2100 cm^{-1} .

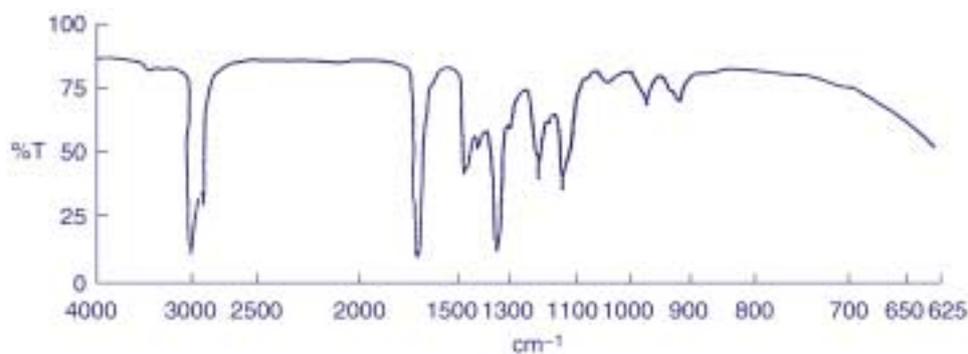
$^1\text{H NMR } \delta$ 2.50 (1H, s), 2.38 (1H, broad s), 2.00–1.88 (4H, m), 1.88–1.67 (4H, m).



$\bar{\nu}_{\max}$ 3350–2260, 1680 cm^{-1} .

$^1\text{H NMR } \delta$ 7.96 (2H, d, $J = 8.9$ Hz), 7.45 (2H, d, $J = 8.9$ Hz).

- (b) i) For each compound **A** - **E**, indicate how many signals you would expect to observe in its ^{13}C NMR spectrum
- (ii) Predict the values of m/z and the relative sizes of the two highest mass peaks in the mass spectrum of compound **A**
- (c) Another compound containing seven carbon atoms has the spectroscopic data shown below.
- (i) What is the structure of this compound?
- (ii) Assign its spectroscopic data.



$\bar{\nu}_{\max}$ 3010–2800, 1725 cm^{-1} .

m/z M^+ 114.

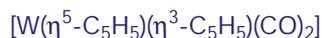
$^1\text{H NMR } \delta$ 2.33 (2H, s), 2.12 (3H, s), 1.01 (9H, s).

$^{13}\text{C NMR } \delta$ 208.4, 56.0, 32.3, 30.9, 29.8 (3C).

A10 Devise suitable analytical procedures to investigate each of the following situations (Your account should include the physical basis of the method, consider appropriate detection limits and interferences, indicate the advantages of your chosen method over other possible methods and also the steps necessary to ensure appropriate sampling and statistical significance of the results)

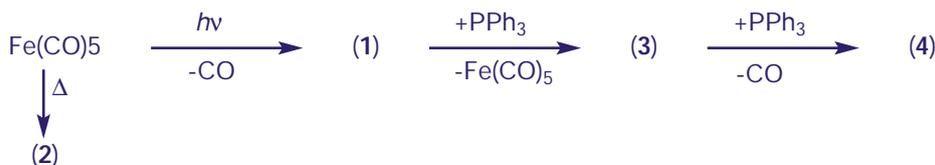
- A spillage of metal ion solutions into sea water.
- A mixture of tablets of analgesic drugs including aspirin, paracetamol and morphine.
- The concentration of lead in roadside vegetation.
- A mixture of organic dyes in aqueous solution.
- The concentration of hydrogen sulfide in natural gas.
- Trace levels of chlorinated hydrocarbons in river water.
- The composition of a mixture of several chiral sugars.
- The level of potassium cyanide in an aqueous industrial effluent.
- The concentrations of additives in a plastic food packaging polymer.

A11 (a) For the following molecules or ions, draw the structures, count the total number of valence electrons associated with the metal and work out the metal formal oxidation state and d-electron count:



- (b) Irradiation of $[\text{Fe}(\text{CO})_5]$ with UV light produces a gold-yellow solid (1) which gives rise to infrared absorptions indicating terminal and bridging carbonyl ligands in a 2:1 ratio. Direct heating of $[\text{Fe}(\text{CO})_5]$ yields a green black solid (2) with empirical formula FeC_4O_4 . Reaction of (1) with triphenylphosphine (PPh_3) at room temperature gives a compound (3) along with one equivalent of $[\text{Fe}(\text{CO})_5]$. Heating (3) with excess PPh_3 in cyclohexanol yields a compound (4) with composition $\text{C}_{39}\text{H}_{30}\text{FeO}_3\text{P}_2$ which gives rise to one resonance in its ^{31}P NMR spectrum.

Identify the compounds (1) to (4) and draw their structures. Indicate the possible isomers which exist for (4) and, using the data provided, indicate which geometry is most likely to be adopted and explain your reasoning.



- (c) The reaction of 2-butyne with PdCl_2 in hot ethanol as solvent gives a crystalline dimeric complex **A**. The metal atoms in the complex obey the 18-electron rule and its mass spectrum shows a molecular ion at 570 amu and additional fragment ions at 285 and 108 amu (but not 54 amu). The ^1H NMR spectrum of **A** shows only one signal: a singlet at 1.9 ppm, while its ^{13}C NMR spectrum has two signals at 26 and 130 ppm. Treatment of **A** with PPh_3 gives a new complex **B** which also obeys the 18-electron rule. Complex **B** shows a molecular ion at 547 amu in its mass spectrum and its ^1H and ^{13}C NMR spectra are similar to those of **A**, although with additional signals for PPh_3 .
- Give the structures of the complexes **A** and **B** and account for their formation.
 - Show how both complexes obey the 18-electron rule.
 - Account for the spectroscopic evidence given for complexes **A** and **B**.
 - Discuss the nature of the organic ligand present in these complexes and suggest why it is unstable as a free molecule but stable when coordinated to a metal.

- A12** (a) The experimental data given below were obtained for the temperature dependence of the rate constant, k , for the reaction:



- (b) From the units of k , what is the order of this reaction?
 (ii) Determine graphically the activation energy and pre-exponential (or frequency) factor for this reaction.

| Temperature / K | 430 | 450 | 470 | 490 | 510 | 530 |
|---|------|------|------|-------|-------|-------|
| $1000k / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ | 3.82 | 13.6 | 43.3 | 125.7 | 335.6 | 831.9 |

- (c) The ozone cycle comprises a series of photochemically-induced reactions which maintain the protective ozone layer in the upper atmosphere. Two key reactions in the cycle are:



- (i) If the Arrhenius parameters for reaction (2) are $A = 3.16 \times 10^{10} \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ and $E_a = 23.9 \text{kJ mol}^{-1}$, calculate the rate constant for the reaction at a temperature of 240 K, typical for the upper atmosphere.
 (ii) Derive an expression for the steady state concentration of O_3 using reactions (1) and (2).

- (d) Nitric oxide (NO) in the atmosphere can react with ozone by the reaction



By incorporating this reaction into the scheme, derive a new expression for the steady state concentration of ozone.

- (e) If $[\text{O}] = 8.30 \times 10^{-12} \text{mol dm}^{-3}$, $[\text{NO}] = 1.66 \times 10^{-13} \text{mol dm}^{-3}$ and $k_3 = 2.31 \times 10^6 \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$, calculate the ratio of ozone concentration in the presence and absence of nitric oxide. Comment on the practical significance of your calculated ratio.

A13

- (a) A 0.1001 g sample of a substance known to contain iron was weighed out, dissolved and all the iron converted to Fe(III). The Fe(III) was determined using the controlled current coulometric generation of Ti(III) ions from a solution of a Ti(IV) salt.
- Write out the reaction occurring at the cathode.
 - Write out the reaction between the Fe(III) ions and the Ti(III) ions.
 - Calculate the percentage of iron in the sample if a current of 1.732 mA for 119.0 seconds was needed to reach the end point.
 - Draw and label a diagram of the apparatus used for controlled current coulometry.
- (b) The data below were obtained for the reduction of Ni^{2+} at a dropping mercury electrode using the technique of sampled d.c. polarography.

| | | | | | | | | | | |
|-------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Potential/V | -0.564 | -0.591 | -0.616 | -0.625 | -0.648 | -0.664 | -0.684 | -0.711 | -0.750 | -0.800 |
| $I / \mu\text{A}$ | -0.2 | -1.1 | -4.6 | -6.9 | -13.8 | -18.4 | -20.7 | -21.6 | -21.9 | -22.0 |

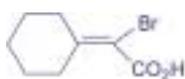
- (i) Determine, graphically or otherwise, the half-wave potential ($E_{1/2}$) for the reduction of Ni^{2+} and deduce whether or not the electron transfer process is reversible.

- (ii) Given that the sample of time for the measurement was 0.5 s and the mercury flow rate was 0.6 mg s^{-1} , use the Ilkovic equation to determine the concentration of the Ni^{2+} ions in the solution. The diffusion coefficient for Ni^{2+} can be taken as $6.12 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

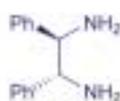
- A14**
- (a) Using a value for the Rydberg constant, R_H , of $1.09737 \times 10^5 \text{ cm}^{-1}$,
- calculate the wavelengths of the first three transitions in the absorption spectrum of a hydrogen atom in the 3s state;
 - determine the ionisation energy of the hydrogen atom in the 4s state, expressing your answer in kJ mol^{-1} .
- (b)
- Derive an expression for the energy levels of a particle of mass m in a one-dimensional box of length a .
 - A particle confined to a one-dimensional box of length $5.0 \times 10^{-9} \text{ m}$ has an energy of $1.0 \times 10^{-20} \text{ J}$ for $n = 2$. Calculate the mass of the particle.
 - Explain what happens to the energy levels for a one-dimensional box when,
 - the size of the box is doubled,
 - the mass of the particle is doubled,
 - one side of the box is removed to infinity.
- (c) An electron, mass m_e , is confined to a one-dimensional well of length $a = 1 \text{ nm}$. The potential energy is zero within the well and infinity elsewhere. Deduce the following information about the electron in this well.
- The wavelengths associated with the lowest five energy levels of the electron.
 - The wavelength of the light emitted when the electron moves from the third to the second energy level.
 - The number of energy levels available to the electron between 8 and 20 eV.
- (d) What are the degeneracies and energies, in units of $h^2 / 8m_e a^2$, of the first five energy levels when the electron is confined instead to a three-dimensional well (box) with equal sides of length a ?

A15 Indicate clearly those of the molecules **A** to **E** below that are:

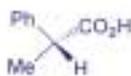
- chiral and contain a C_2 axis of rotation;
- achiral and contain a C_2 axis of rotation;
- chiral and lack a C_2 axis of rotation.



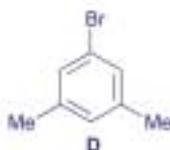
A



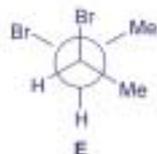
B



C



D



E

- A16** (a) Draw both chair conformers for each of the dibromides **H** and **I**.



- (b) (i) Using the data outlined below calculate the strain energy of the conformers of **H**.
(ii) Also calculate the additional strain energy of the conformers of **I** relative to cyclohexane.

| Interaction | Energy Cost / kJ mol^{-1} |
|---------------------|------------------------------------|
| 1,3-Diaxial H----Br | 1 |
| Gauche Br----Br | 3 |

- (c) In addition, use these data to calculate the percentage of the more stable conformer for both the dibromides **H** and **I** at 25 °C (298 K).
(d) Experimental evidence indicates that the diaxial conformer of **I** is more stable than the diequatorial conformer. Comment on this in the light of your answer to part (b) (ii).

A17 Cobalt(II) chloride hexahydrate was dissolved in water and 1,2-diaminoethane added. The solution was oxidised with H_2O_2 and a green complex (**A**) isolated after heating with hydrochloric acid. The green complex was shown to contain 1,2-diaminoethane and analysis also established that it contained 20.6% Co and 37.3% Cl. The green complex was diamagnetic and had two d-d bands at $19\,300\text{ cm}^{-1}$ and $26\,000\text{ cm}^{-1}$. In addition a single Co-Cl stretching frequency was observed in the IR at 370 cm^{-1} . The complex had a molar conductivity of $110\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ at 25 °C in water, and the conductivity was observed to increase with time finally reaching a value of $370\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ after several hours. Heating the green complex with hydrochloric acid gave a violet complex (**B**), which also contained 20.6% Co and 37.3% Cl. The violet complex had two d-d bands at $19,300$ and $26,000\text{ cm}^{-1}$, however, the extinction coefficients were roughly twice those observed for the green complex.

Reaction of the violet complex with 1,2-diaminoethane gave an orange complex (**C**), % Co = 17.1; % Cl = 30.8; % N = 24.3; which had two d-d bands at $21\,000\text{ cm}^{-1}$ and $28\,000\text{ cm}^{-1}$. When **C** (346 mg) was dissolved in water and passed through a cation exchange column in the hydrogen form, it released acid which required 60 cm^3 of aqueous sodium hydroxide (0.05 mol dm^{-3}) for neutralisation.

Suggest structures for the three complexes **A**, **B** and **C**; account for the experimental data provided and discuss the d-d spectra.

- A18** (a) The potential of the cell



at 298 K is 0.44 V. Calculate the standard electrode potential for the cell.

- (b) Given that the standard reduction potential for a $\text{Cu}^{2+} \mid \text{Cu}$ couple is +0.34 V calculate the standard reduction potential of the $\text{Ag}^+ \mid \text{Ag}$ couple.
- (c) Write the electrode reactions and the cell reaction for the following cell where m is the molal concentration



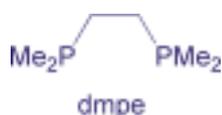
- (d) The e.m.f. of the cell in part (c) varies at 298 K with concentration as follows

| | | | | |
|--|--------|--------|--------|--------|
| $m / \times 10^{-3} \text{ mol kg}^{-1}$ | 2.70 | 5.63 | 9.22 | 14.88 |
| e.m.f. / V | 0.5291 | 0.4925 | 0.4684 | 0.4450 |

Use a graphical method to calculate the standard potential of the Ag, AgCl electrode. Hence calculate the activity coefficient, γ_{\pm} , of HCl in the most concentrated solution.

- (e) Use the Debye-Hückel limiting equation to obtain a value for γ_{\pm} in the most concentrated HCl solution ($A = 0.509 \text{ kg}^{0.5} \text{ mol}^{-0.5}$). Compare your value with that from part (d).

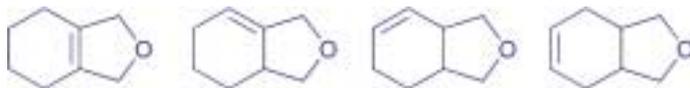
- A19** (a) Treatment of the square planar platinum(II) complexes $[\text{Pt}(\text{NH}_3)_{2+x}\text{Cl}_{2-x}]^{x+}(\text{Cl}^-)_x$ with silver nitrate is known to precipitate, as AgCl, only the chlorine present as ionic chloride. A solution containing 0.1671 g of one such platinum(II) complex required 13.33 cm³ of aqueous AgNO_3 (0.075 mol dm⁻³) to precipitate the ionic chloride. Determine the value of x .
- (b) Using structural diagrams, show which isomers are possible for the three following metal complexes:



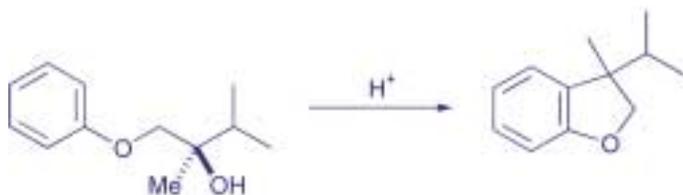
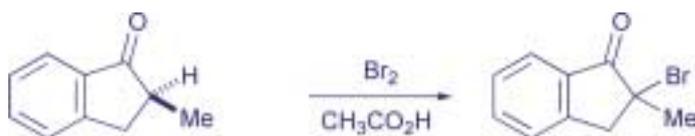
Assuming the spectra are first order, predict the ¹H-decoupled ³¹P NMR spectra you would expect to be shown by each isomer. [³¹P, I = 1/2]

- (c) The values of Δ_0 , for the complexes $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ are 156 and 275 kJ mol⁻¹ respectively. Given that the electron pairing energy is 251 kJ mol⁻¹, use these data to predict whether the complexes will be high or low spin and calculate the spin-only magnetic moment for each ion.
- (d) In the crystal structure of CuF_2 , the Cu^{2+} ion is 6-coordinate, with four F^- ions at a distance of 193 pm and two F^- ions at 227 pm. Explain this observation.

A20 (a) State, with explanation, which of the following molecules are chiral:



(b) Deduce, with mechanistic explanations, the stereochemistry of the products of the following reactions. All the starting materials are single enantiomers.



A21 (a) Sketch and fully label the phase diagram for pure ammonia, NH_3 , from the following data:

| | |
|----------------------|--------------------|
| triple point | 195.4 K; 6.12 kPa |
| critical point | 405.9 K; 11.35 MPa |
| normal boiling point | 239.8 K |
| normal melting point | 195.5 K |

(b) What would be observed if:

- a sample of gaseous NH_3 was cooled from 500 K to 150 K at a constant pressure of 50 kPa
- a sealed tube half-full of liquid NH_3 was heated from 200 K to 500 K.

(c) The vapour pressures (in bar) of liquid and solid benzene are given at low temperatures (in Kelvin) by the expressions

$$\ln p = -4110/T + 11.70 \quad (\text{liquid})$$

$$\ln p = -5320/T + 16.04 \quad (\text{solid})$$

- Calculate the pressure and temperature at the triple point of benzene and the enthalpy change of fusion of the solid.
- Close to its triple point, the molar volume of benzene increases on melting by approximately 10^{-5} m^3 . Assuming that the slope of the solid-liquid coexistence line is constant, estimate the temperature at which benzene melts under a pressure of 1 kbar

- A22**
- (a) For each of the following radionuclides, predict the decay mode, write a balanced equation for the nuclear transformation which occurs, and suggest a suitable detector.
- ^{95}Nb
 - ^{16}N
 - ^{230}U
- (b) Soil from south west Scotland is analysed by gamma ray spectroscopy. In May 2000, the activity of ^{137}Cs in the soil is found to be 2.74 Bq g^{-1} . Calculate
- the ^{137}Cs activity in the soil in May 1986, immediately following the Chernobyl nuclear accident,
 - the count rate which would be obtained if a 10 g sample of the soil was counted on a detector of 29% efficiency in May 1986.

DATA: Half life $^{137}\text{Cs} = 30.2\text{y}$

- (c) A contaminated soil sample is being analysed for Ni and Co by UV-visible spectroscopy. The Ni and Co from 10 g of the soil sample are extracted, filtered and made up to 100 cm^3 of solution. The ions were then complexed with 1,10-phenanthroline and the absorbencies of the solution measured to be 0.96 at 550 nm and 0.75 at 650 nm. Calculate the amount of Ni and Co in the soil sample in ppm given the molar absorptivities of the complexes in the table below.

| | ϵ (550 nm) / $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ | ϵ (650 nm) / $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ |
|------------|--|--|
| Ni complex | 20 533 | 7400 |
| Co complex | 9867 | 27 346 |

A23

The X-ray powder diffraction pattern of a complex nickel-iron oxide NiFe_2O_4 was recorded with radiation of wavelength 1.7902 \AA . The θ values of the first ten lines were as follows:

10.70 12.38 17.62 20.87 21.81 25.46 27.96 31.76 33.95 37.40

- Calculate the length of one side of the cubic unit cell.
- Index the lines.
- Given that the density of the material is 5.35 g cm^{-3} , calculate the number of formula units in the unit cell.

- A24** (a) Explain what is meant by the Net Present Value method. Apply this method to the data given in **Table 1** below, in order to decide which chemical manufacturing process (**A** or **B**) should be supported for commercial development. Comment upon the effect of "scale of operation" on the fixed costs and variable costs associated with the chosen process.

Table 1 - Capital Cost and Projected Cash-flows for Processes A and B

| Capital Cost/£ | | INCOME FLOW/£ /YEAR | | | | | Value of Equipment at End of Year 5/ £ |
|----------------|---------|---------------------|--------|---------|--------|--------|--|
| | | 1 | 2 | 3 | 4 | 5 | |
| Process A | 150,000 | 50,000 | 60,000 | -12,000 | 40,000 | 30,000 | 45,000 |
| Process B | 98,000 | 12,000 | 25,000 | 50,000 | 20,000 | 5,000 | 15,000 |

- (b) Using the data given in **Table 2**, evaluate the economic and technical feasibility of the following two synthetic routes to ethylamine. The answer should include all calculations.

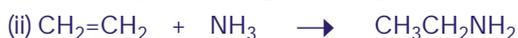
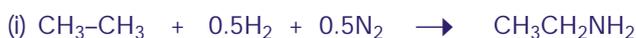
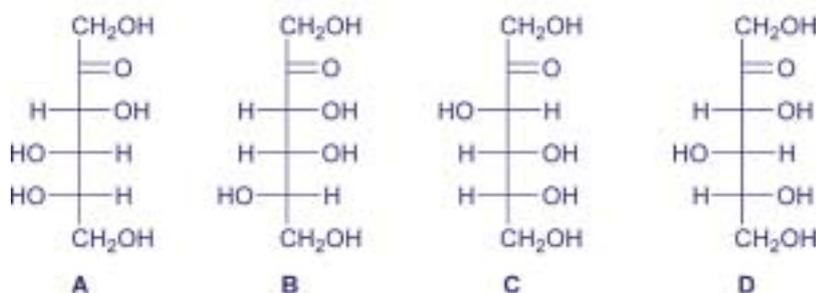
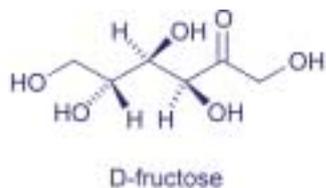


Table 2 - Market Value and Selected Thermochemical Data for Ethylamine Production

| Substance | Market Value/£ kg ⁻¹ | $\Delta G_f^\circ/\text{kJ mol}^{-1}$ | |
|-------------------------------------|---------------------------------|---------------------------------------|--------|
| | | 298 K | 1000 K |
| $\text{CH}_3\text{CH}_2\text{NH}_2$ | 0.95 | 37.7 | 255.1 |
| $\text{CH}_2=\text{CH}_2$ | 0.15 | 68.1 | 118.2 |
| $\text{CH}_3\text{-CH}_3$ | 0.07 | -32.9 | 109.3 |
| N_2 | 0.02 | 0 | 0 |
| H_2 | 0.04 | 0 | 0 |
| NH_3 | 0.165 | -16.15 | 62.14 |

State which route would merit further investigation and suggest the most favourable reaction conditions. Comment upon the usefulness of such assessments in the development of a large scale process.

- A25** (a) Which of the Fisher projections, **A** to **D** below, correctly represents the keto-sugar D-fructose?



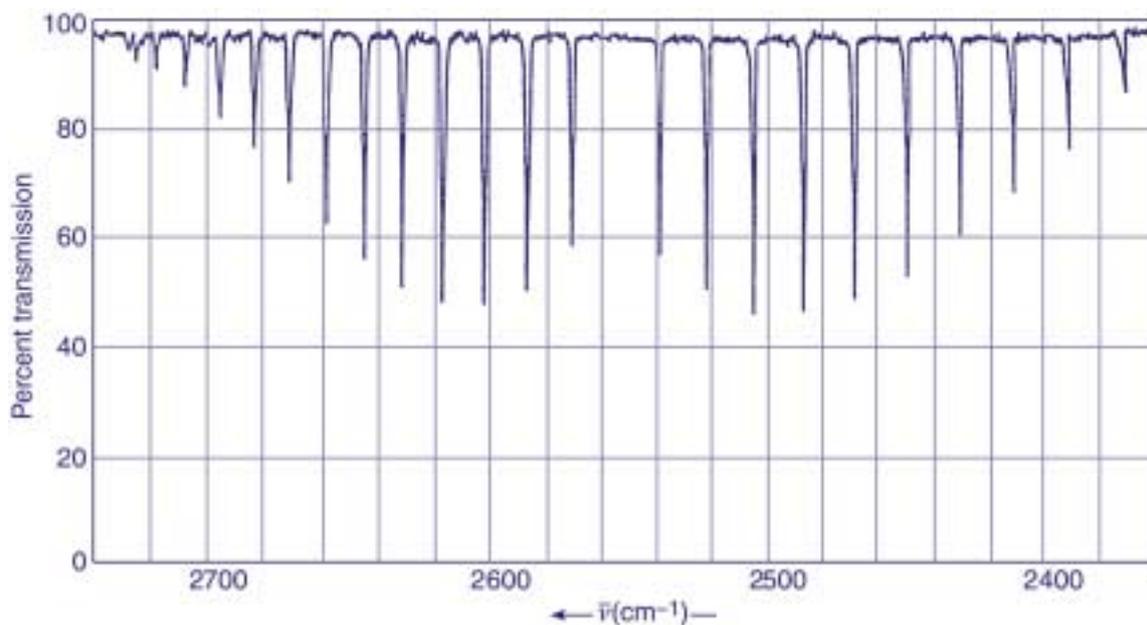
- (b) Treatment of D-fructose with NaBH_4 in methanol, and subsequent acidification, results in the formation of two products, **E** and **F**. What are their structures? (You may use any representation you see fit).
- (c) Exposure of the aldohexose D-mannose to NaBH_4 in methanol also affords compound **E**, whereas exposure of either of the aldohexoses D-glucose or L-gulose to the same conditions affords **F**. Explain. What are the structures of D-mannose, D-glucose and L-gulose? Assign the structures **E** and **F** exactly.
- (d) Treatment of **E** with acetone and an acid catalyst results in the formation of a new compound, $\text{C}_{12}\text{H}_{22}\text{O}_6$, which reacts with NaIO_4 to form two molecules of **G**, $\text{C}_6\text{H}_{10}\text{O}_3$. Give the structure of **G** and name the simple sugar of which it is a protected form.

A26

- (a) (i) Write down the selection rules for rotational excitation arising from the absorption of electromagnetic radiation and identify the region of the electromagnetic spectrum in which you would expect such absorption to occur.
- (ii) The first two lines in the rotational absorption spectrum of carbon monoxide lie at 3.84 cm^{-1} and 7.68 cm^{-1} respectively. Show that these results are in agreement with the predictions of the rigid rotor model and calculate the value of B , expressing the result in frequency units.
- (b) For each of the following molecules,



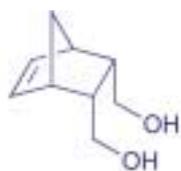
- (i) give the number of vibrational modes,
(ii) sketch the form of each vibration,
(iii) state, with your reasoning, whether or not each vibration is infra-red active.
- (c) The medium resolution gas phase infrared spectrum of hydrogen bromide is shown below.



Assuming the molar mass of bromine to be 80 g mol^{-1} :

- (i) make a rough estimate (within 5%) of the force constant of HBr;
(ii) make a rough estimate (within 5%) of the rotational constant of HBr;
(iii) explain, by means of an energy diagram, the origin of the spectrum.

- A27** (a) Propose syntheses of the following molecules from the indicated starting materials. Any commonly-available additional organic or inorganic reagents may be used. Show clearly your retrosynthetic analysis, and indicate any reasoning behind your choice of reagents and/or conditions.



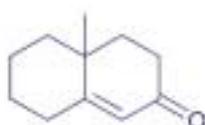
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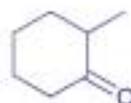
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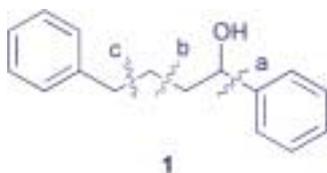
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- (b) Suggest three possible syntheses of target molecule (**1**), one based on a key disconnection at position **a**, one on a disconnection at position **b** and the third on a disconnection at position **c**. In each case show clearly the retrosynthetic analysis. Give reagents and mechanism for each synthesis.



A28

- (a) Write Lewis structures for the following:
- (i) 3 resonance forms of O_2NNH^-
 - (ii) 3 isomeric forms of HNSO
 - (iii) 2 resonance forms of HN_3 .
- (b) For a diatomic molecule X_2 show how suitable combinations of p-orbitals can lead to the formation of (a) σ -bonding, (b) σ^* - anti-bonding, (c) π -bonding and (d) π^* anti-bonding molecular orbitals. Assign the (+) and (-) symmetry notation and state whether the resulting molecular orbitals are gerade or ungerade.

Construct a molecular orbital energy level diagram for dinitrogen (N_2) and label clearly all the resulting molecular orbitals.

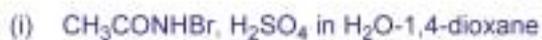
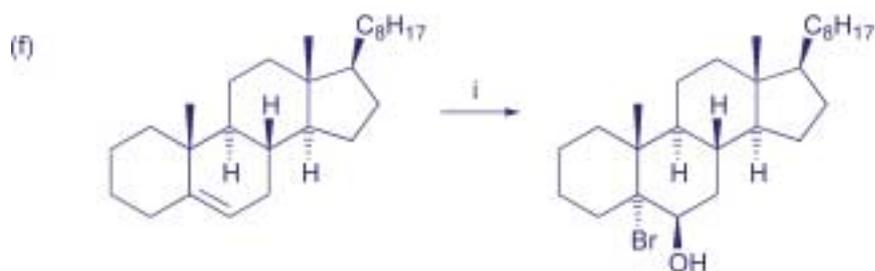
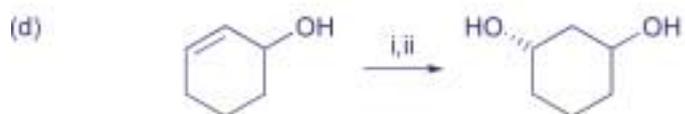
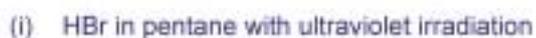
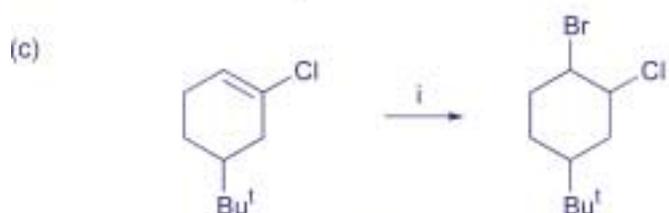
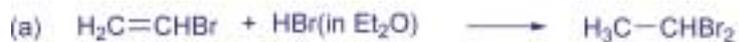
Using this diagram evaluate the most likely values for the data missing in the Table below and then rationalise the collective trends for the series.

| Diatomic Species | Bond distance/pm | Bond dissociation energy/kJ mol ⁻¹ |
|------------------|------------------|---|
| N_2 | 110 | 945 |
| N_2^- | | 765 |
| N_2^+ | 112 | |

Predict the magnetic behaviour (paramagnetic or diamagnetic) for each species.

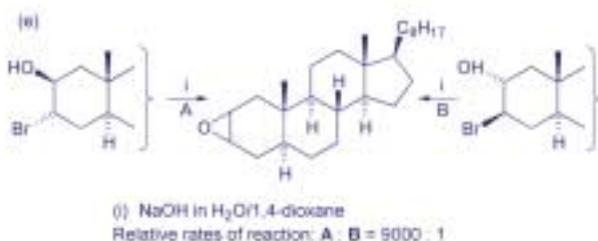
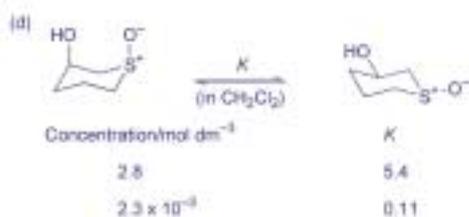
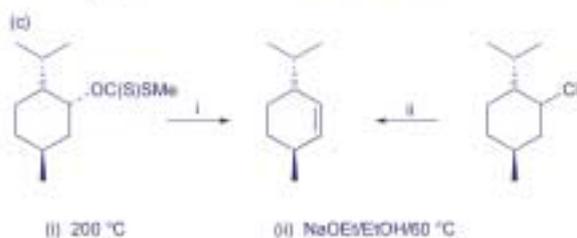
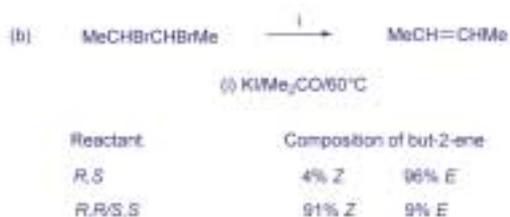
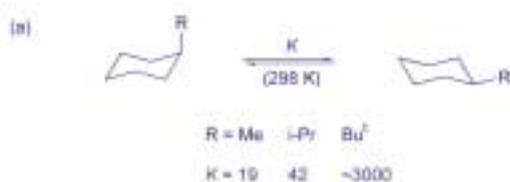
- (c) The diboron molecule, B_2 , is paramagnetic with a magnetic moment corresponding to two unpaired electrons per B_2 molecule. How can this be explained by Molecular Orbital Theory?

A29 Explain the regioselectivity, or stereoselectivity, or both, in the following additions to carbon carbon double bonds:



- A30**
- Calculate the wavelength, in Å, associated with a ball weighing 2 lb travelling at 50 mph.
 - The energy required to remove an electron from the 2s orbital of an excited H atom is 330 kJ mol^{-1} . Calculate the ionisation energy of Li^{2+} [i.e. of $\text{Li}^{2+}(1s^1) \rightarrow \text{Li}^{3+}(1s^0)$].
 - Use Slater's rules to calculate the effective nuclear charge for a valence electron in the Be and B atoms. Comment on the observation that the first ionisation energy of Be (900 kJ mol^{-1}) is greater than that of B (800 kJ mol^{-1}).
 - The enthalpies of formation of gaseous XeF_2 , XeF_4 and XeF_6 are -110 , -216 and -294 kJ mol^{-1} , respectively and the bond energy in F_2 is 159 kJ mol^{-1} . Calculate the average bond energy in each of these three compounds, and comment on the values obtained in relation to their fluorinating ability. Use the value for XeF_2 to obtain a value for the electronegativity of xenon, assuming the electronegativity of fluorine to be 4.0.

A31 Explain as fully as possible the following sets of observations:



- A32**
- (a) The efficiency of a certain strain of algae in producing oxygen via photosynthesis was measured by irradiating for 10 minutes with a 10 W lamp operating at a wavelength of 450 nm. The volume of oxygen evolved (measured at STP) was 7.58 cm³ and 50% of the incident light was absorbed. Assuming that each molecule of O₂ produced requires the absorption of four photons, calculate the quantum yield for the production of oxygen.
- (b) Comment on the result from (a) in terms of a possible mechanism for the reaction.
- (c) The intensity of fluorescence (I_f), observed from a solution containing a fluorescent substance (D), was progressively reduced by the addition of a quencher (Q). The results, measured in a spectrofluorimeter, were as follows:

| [Q] / dm ⁻³ mol | I_f (relative) |
|----------------------------|------------------|
| 0.000 | 100.0 |
| 0.001 | 81.0 |
| 0.002 | 69.0 |
| 0.003 | 61.0 |
| 0.004 | 52.3 |
| 0.005 | 47.4 |
| 0.006 | 42.5 |

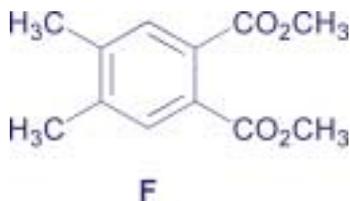
If the rate constant for the fluorescence decay is 10⁸ s⁻¹, and internal conversion and intersystem crossing are insignificant, calculate the rate constant for the energy transfer process.

- A33**
- (a) Explain the differences between the root mean square speed, the mean speed, and the most probable speed in the distribution of molecular speeds of a collection of gas molecules.
- (b) Calculate the most probable speed c^* of nitrogen molecules at 300 K.
- (c) Make a reasonable estimate of the volume of a nitrogen gas cylinder as usually used in the laboratory. Calculate the mass of nitrogen in the cylinder if the pressure of pure nitrogen is 200 atm (i) using the ideal gas model and (ii) using the van der Waals model.
The van der Waals constants for nitrogen are $a = 1.408 \text{ atm L}^2 \text{ mol}^{-2}$ and $b = 0.0391 \text{ L mol}^{-1}$.
- (d) Values of the molecular polarisability, α , and dipole moment, μ , are given along with the critical temperature, T_c , for four compounds.

| | Propane C ₃ H ₈ | Dimethyl ether (CH ₃) ₂ O | Epoxyethane C ₂ H ₄ O | Ethanol C ₂ H ₅ OH |
|----------------------------------|--|---|--|---|
| $\alpha / 10^{-24} \text{ cm}^3$ | 6.4 | 6.0 | 5.2 | 5.2 |
| μ / D | 0 | 1.3 | 1.9 | 1.7 |
| T_c / K | 370 | 400 | 467 | 516 |

Explain the connection between T_c and the first two quantities and discuss any trends in the data, highlighting and explaining any anomalies.

- A34** A compound **A** (C_3H_6O) was treated with magnesium amalgam followed by dilute hydrochloric acid to give **B** ($C_6H_{14}O_2$). Reaction between **B** and concentrated sulfuric acid gave **C** ($C_6H_{12}O$). Base-catalysed hydrogen-deuterium exchange on **C** gave $C_6H_9D_3O$. Vapour-phase dehydration of **B** gave **D** (C_6H_{10}). Reaction between **D** and $H_3CO_2C-C\equiv C-CO_2CH_3$ gave **E** ($C_{12}H_{16}O_4$) which could be dehydrogenated by heating with Pt/C to give **F**.



Using the following spectroscopic information deduce the structures of the compounds **A - E**.

Give the mechanism for the transformation of **B** into **C**.

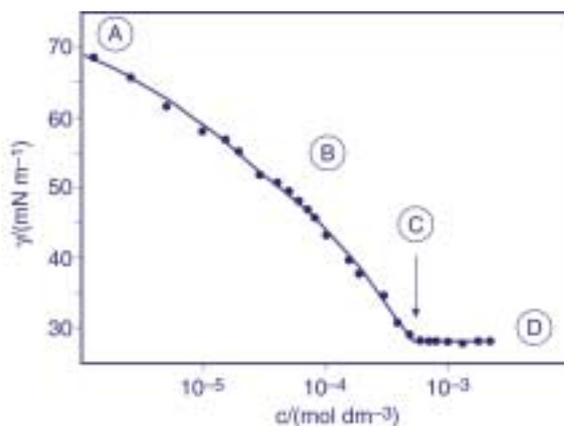
Spectroscopic data:

| | IR $\bar{\nu}$ / cm^{-1} | 1H NMR δ | ^{13}C NMR / ppm |
|----------|----------------------------|--|--|
| A | 1720 | 2.29 (s) | 206.3 (s) 30.7 (q) |
| B | 3350 | 1.25 (s, 12 H) 2.25 (s, 2H, disappears on treatment with D_2O) | |
| C | 1720 | 1.25 (s, 9H) 2.27 (s, 3H) | 206.3(s) 69.0 (s) 31.4 (q) 30.7 (q) |

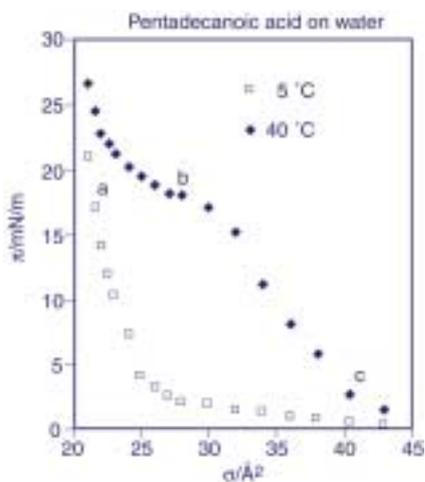
- A35** Describe a suitable chromatographic method to carry out FOUR of the following determinations. In each case give your reasons for the choice of mobile phase, stationary phase and detector and any sample treatment required.

- Methyl heptanoate in a fruit flavour
- Trace amounts of fluorobenzene in a mixture of solvents
- 1,2-Dihydroxybenzene in a wood preservative solution
- Ethylene glycol (1,2-dihydroxyethane) in a sample of wine
- Carbon monoxide in a car exhaust fumes
- Riboflavin in fruit juice

- A36** (a) The plot below shows the variation of surface tension, γ , with concentration, c , for aqueous solutions of a non-ionic surfactant $C_{10}H_{21}(OCH_2CH_2)_4OH$ (or $C_{10}E_4$) at a fixed temperature. Discuss the term *surface tension*, and hence explain the form of the curve, paying particular attention to the regions marked A, B, C and D.



- (b) The figure below gives π - σ plots for pentadecanoic acid on water at 5 °C and 40 °C. Explain what is meant by π and σ and describe the molecular structure of the film at (a), (b) and (c).



- (c) The data below give the surface tension of aqueous solutions of the surfactant $C_{12}H_{25}N(CH_3)_2HCl$ at 25 °C.

| Concentration/ mol dm ⁻³ | Surface Tension/ mN m ⁻¹ |
|-------------------------------------|-------------------------------------|
| 4.0×10^{-4} | 52 |
| 9.0×10^{-4} | 46 |
| 1.5×10^{-3} | 40 |
| 2.5×10^{-3} | 35 |
| 3.9×10^{-3} | 34 |
| 5.0×10^{-3} | 34 |

- Why does the surface tension fall to a constant value at high concentration? Give an answer both with respect to molecular events and in terms of the model leading to the Gibbs adsorption equation.
- Estimate the minimum occupied area at the surface per surfactant molecule.
- Given that the surfactant $C_{12}H_{25}N(CH_3)_2HCl$ forms spherical micelles of radius 1.6 nm calculate the number of surfactant molecules in each micelle.

- A37** (a) i) Sketch the π -MO diagram for ethylene (i.e. constructed from the two p-orbitals perpendicular to the molecular plane), labelling them with their g/u symmetry. What would be the consequences for the molecule of exciting an electron from the lower orbital to the upper one?
- (ii) Show how the form of the π -MOs of *trans*-butadiene can be derived by combining two sets of ethylene π -MOs. Give the g or u classification of each butadiene orbital and show the position of the nodal planes.
- (iii) Show, in the form of a correlation diagram of orbital energy versus chain length, n , how the stack of π -MOs evolves in the sequence of *even* number polyenes. Indicate how the HOMO-LUMO energy gap changes with n . In the case of butadiene ($n = 4$), explain how the bond orders between each pair of adjacent C atoms change on promoting an electron from the HOMO in the ground state to the LUMO. Is this transition allowed?
- (b) The valence bond wavefunction for H_2 has the form

$$\Psi = s_a(1)s_b(2) \pm s_b(1)s_a(2)$$

where s_a and s_b are orbitals centred on the two H atoms. The corresponding energy expression is

$$E_{\pm} = \frac{\alpha \pm \beta}{1 \pm S^2}$$

with

$$\alpha = 2\varepsilon_{1s} + J + 1/R$$

$$\beta = (2\varepsilon_{1s} + 1/R)S^2 + K,$$

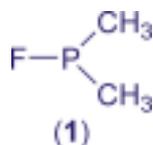
where

$$J = j - 2j'$$

$$K = k - 2Sk'$$

- (i) Give the meaning and physical significance of the terms that occur in the expressions for α and β .
- (ii) Is β negative or positive at the equilibrium bond distance in H_2 . Why?
- (iii) Which is the lower energy solution (a) + sign or (b) – sign?
The solution with the + sign corresponds to a singlet wavefunction and solution with the – sign is a triplet. What is the meaning of this statement?
- (iv) The MO wavefunction for H_2 contains *ionic* terms. Show how this arises by giving the MO wavefunction in valence bond configurations.
- (v) The MO method cannot correctly predict the dissociation products for homolytic dissociation. Discuss this statement.

- A38** (a) For compound, **1**, use labelled line diagrams to predict the appearance of:
- the ^1H NMR spectrum
 - the ^{31}P $\{^1\text{H}\}$ NMR spectrum
 - the ^{19}F NMR spectrum



You may ignore all interactions with the ^{13}C nucleus.

$$^1J(\text{P-F}) = 1500 \text{ Hz}; \quad ^2J(\text{P-H}) = 15 \text{ Hz}; \quad ^3J(\text{F-H}) = 2 \text{ Hz}$$

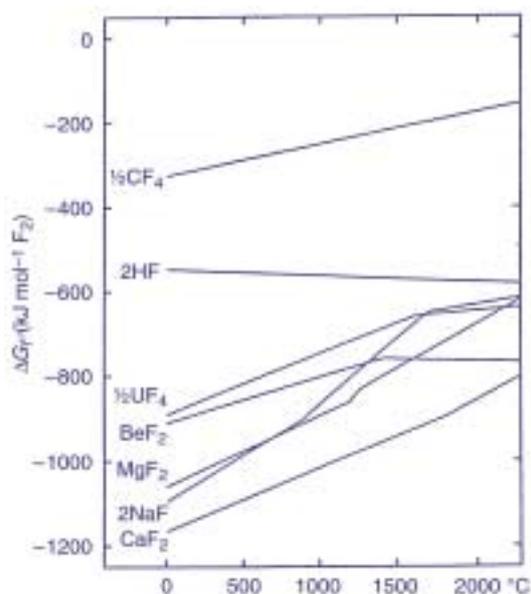
- (b) The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ consists of a doublet. (Note that ^{103}Rh has $I = 1/2$ and is 100% abundant.)
- Deduce the structure of the five-coordinate complex.
 - Sketch the signal that you would expect to see for the hydrido ligand in the ^1H NMR spectrum of the complex.
 - In what chemical shift region would you expect to find the signal due to the hydrido ligand in the ^1H NMR spectrum of the complex?
- (c) Treatment of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$ with acetyl chloride in the presence of anhydrous aluminium chloride affords compound A. The ^1H NMR spectrum of A consists of two complex multiplets at $\delta = 4.68$ and $\delta = 4.40$ (4 H each) and a singlet at $\delta = 2.12$ (6 H). There is a prominent peak at 1658 cm^{-1} in the infrared spectrum of A. Explain the spectroscopic data and suggest a structure for A. Note that the ^1H NMR spectrum of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$ consists of a singlet at $\delta = 4.04$.

- A39** (a) $H = A + B/\mu + C\mu$ is the general form of the van Deemter equation describing band broadening in packed column chromatography. Explain the terms and describe how A, B and C influence the separation efficiency of a column.
- Sketch and label a typical van Deemter plot for a packed gas chromatography column and show and explain how the plot would change;
- if a smaller particle size were used,
 - if a packed column were replaced by an open tubular capillary column.
- (b) Two components were injected onto a 20 metre long gas capillary column. Their retention times t_1 and t_2 are the retention times of components 1 and 2 respectively and W_B is the peak width of the second component. Calculate the efficiency of the column with respect to the second component in terms of the number of plates N and the plate height H .

- A40** (a) From the following thermodynamic data, with the assumption that the heat capacities of the components are negligible, calculate the temperature above which carbon could be used to reduce TiO_2 to titanium metal at standard pressure.

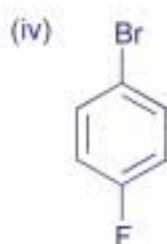
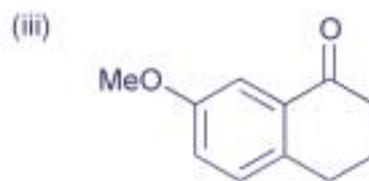
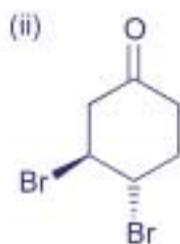
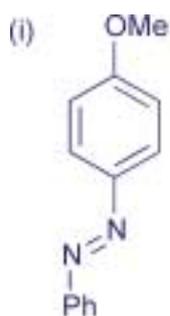
| | $\Delta H_f^\circ / \text{kJ mol}^{-1}$ | $S^\circ / \text{J K}^{-1} \text{mol}^{-1}$ |
|-----------------------------|---|---|
| $\text{C}(\text{graphite})$ | 0 | 5.74 |
| $\text{CO}(\text{g})$ | -110.53 | 197.67 |
| $\text{Ti}(\text{s})$ | 0 | 30.63 |
| $\text{TiO}_2(\text{s})$ | -944.7 | 50.33 |

- (b) The Gibbs free energies of formation of some fluorides (per mol of F_2 consumed) are plotted against temperature in the Ellingham diagram below.
- Comment on the feasibility of using carbon as a reductant to produce metals from their fluorides.
 - How could uranium be produced from uranium tetrafluoride?

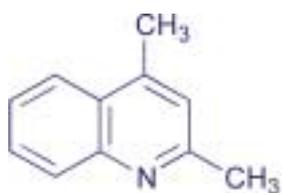


Ellingham diagram for the formation of several fluorides

- A41** (a) Show how you would prepare the following using a monosubstituted benzene as one of the starting materials.



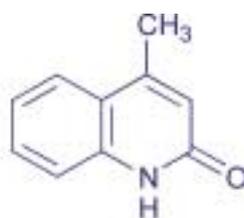
- (b) Describe synthetic routes to compounds **A** and **B** from aniline and other suitable building blocks and discuss the mechanisms of the reactions.



from PhNH₂

A

[Ph = C₆H₅]



from PhNH₂

B

A42 Answer *all* parts (a) to (g), using the standard electrode potentials for aqueous acid solutions (E^\ominus , in volts) given below.



- Give the oxidation state of Cl in each of these species.
- Write balanced half-cell reactions, with explicit inclusion of electrons, for the reduction of ClO_4^- to ClO_3^- and for the reduction of ClO_3^- to Cl_2 .
- Calculate the value of E^\ominus for the $\text{ClO}_4^-/\text{Cl}_2$ couple.
- State whether the ClO_3^- ion is expected to disproportionate in aqueous solution at pH 0 (standard conditions) to give ClO_4^- and Cl_2 , and show your reasoning.
- Write a balanced equation for the disproportionation reaction in part (d).
- Comment on the expected pH dependence of this disproportionation reaction.
- Which of the Cl species are, in principle, capable of oxidising water to oxygen under standard concentration conditions?

[$E^\ominus = +1.23 \text{ V}$ for $\text{O}_2/\text{H}_2\text{O}$].

A43 For the following species:



- Use the VSEPR method to predict the shapes, including any distortions from ideal geometries
- Assign each to the appropriate point group, listing and illustrating the diagnostic symmetry elements.

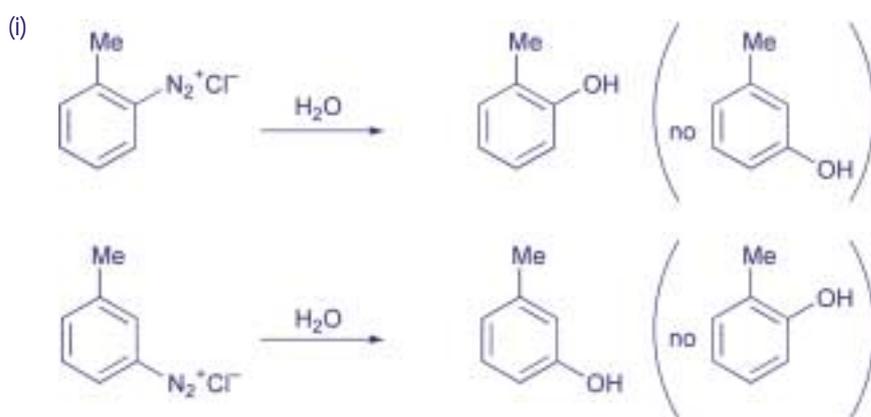
A44 The rate law for the reaction of benzenediazonium salts with weakly basic nucleophiles (H_2O , Br^- , Cl^- etc)



is of the form

$$\text{Rate} = k [(\text{PhN}_2)^+ \text{X}^-]$$

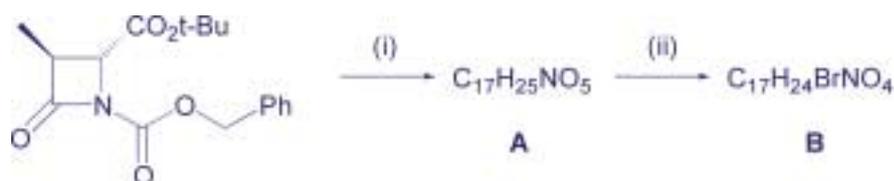
- (a) Suggest two possible mechanisms for the reaction that are consistent with the above rate law.
 (b) Show how the following additional data can be interpreted in favour of just one of your possible mechanisms.



- (ii) The entropy of activation for the reaction was large and positive
 (iii) $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 0.98$
 (iv) A Hammett plot indicates that the rate of reaction of substituted arenediazonium salts is accelerated by substituents in the *meta* and *para*-positions that have a negative σ value.

B1 Assign the spectral data where possible, suggest intermediates and propose mechanisms for the following processes.

(a)



(i) NaBH_4 , MeOH;

(ii) Ph_3P , CBr_4 .

Selected spectral data for A:

IR data, $\bar{\nu}_{\text{max}}$

3374 cm^{-1} (broad)

$1710\text{--}1730\text{ cm}^{-1}$ (broad, strong)

Selected spectral data for B:

IR data, $\bar{\nu}_{\text{max}}$

$1710\text{--}1730\text{ cm}^{-1}$ (broad, strong)

NMR data, δH (CDCl_3):

1.09 (3H, d, $J = 7\text{ Hz}$)

1.49 (9H, s)

2.34–2.37 (1H, m)

3.31 (1H, dd, $J = 10, 8\text{ Hz}$)

3.49 (1H, dd, $J = 10, 5.5\text{ Hz}$)

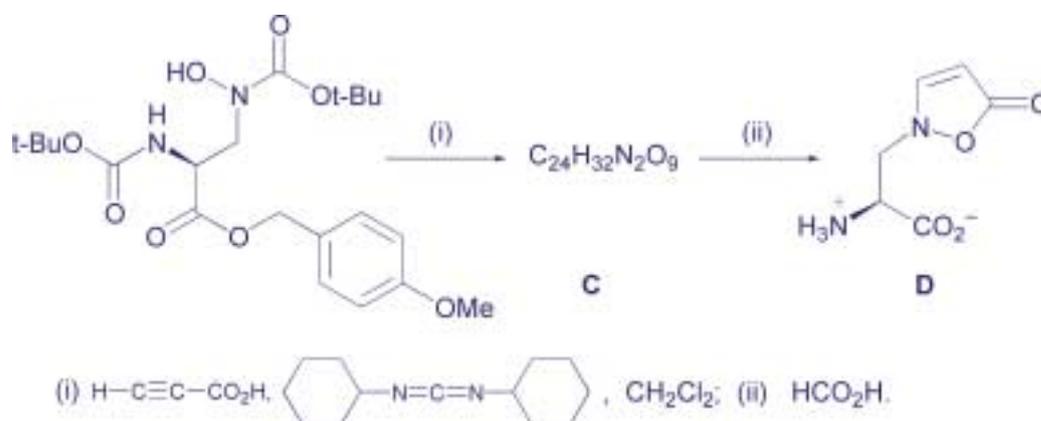
4.41 (1H, dd, $J = 8, 5\text{ Hz}$)

5.13 (2H, s)

5.52 (1H, d, $J = 8\text{ Hz}$, exch. D_2O)

7.33–7.41 (5H, m).

(b)



Selected spectral data for D:

IR data, $\bar{\nu}_{\max}$

1700 cm^{-1} (strong), 1600 cm^{-1} (strong)

NMR data, δH (D_2O):

3.98 (1H, t, $J = 5\text{Hz}$)

4.19 (2H, d, $J = 5\text{Hz}$)

5.15 (1H, d, $J = 3.5\text{Hz}$)

8.11 (1H, d, $J = 3.5\text{ Hz}$)

NMR data, δC (D_2O):

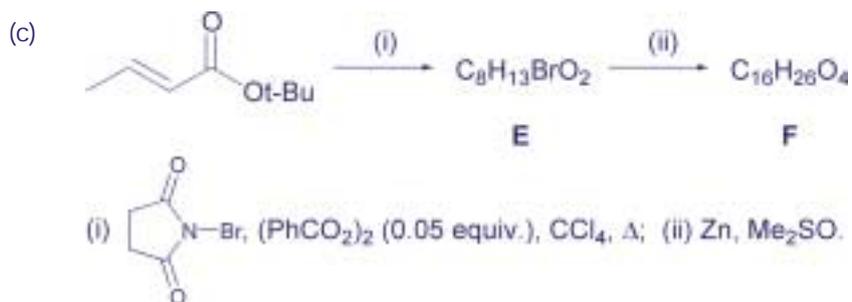
55.0 (two directly bonded hydrogens)

55.8 (one directly bonded hydrogen)

90.3 (one directly bonded hydrogen)

157.1 (one directly bonded hydrogen)

177.2 (no directly bonded hydrogens)



Selected spectral data for F:

IR data, $\bar{\nu}_{\max}$:

1720 cm^{-1} (strong),

1650 cm^{-1} (strong)

NMR data, δH (CDCl_3):

1.33 (9H, s)

1.35 (9H, s)

2.26 (1H, ddt, $J = 13.5, 1, 7\text{ Hz}$)

2.46 (1H, ddt, $J = 13.5, 1, 7\text{ Hz}$)

2.94 (1H, apparent q, $J = 7\text{ Hz}$)

5.00 (1H, dd, $J = 15, 1\text{ Hz}$)

5.01 (1H, dd, $J = 10, 1\text{ Hz}$)

5.60 (1H, dt, $J = 16, 1\text{ Hz}$)

5.62 (1H, ddd, $J = 15, 10, 7\text{ Hz}$)

6.60 (1H, dt, $J = 16, 7\text{ Hz}$).

- B2** (a) What is meant by the statement that a certain reaction in solution is *diffusion controlled*? What factors may contribute towards departure from the simple diffusion-control description?
- (b) The rate constant, k , of a diffusion-controlled reaction between neutral species A and B can be written as

$$k = 4\pi d(D_A + D_B)$$

where d is the collision diameter and D_A , D_B are the diffusion coefficients of the two species. Show that with some further approximations this expression can be used to relate k to the viscosity, η , of the solvent.

- (c) The data given below refer to the reaction



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

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

- B3** (a) The reaction cross section, S_r , can be expressed by the equation

$$S_r = \int_0^{\infty} 2\pi b P_r(b) db$$

where b is the impact parameter and $P_r(b)$ is the probability of reaction for that impact parameter. How is S_r related to the *collision cross section*, S_c ? Discuss briefly reasons why S_r might be (i) smaller, (ii) larger than S_c .

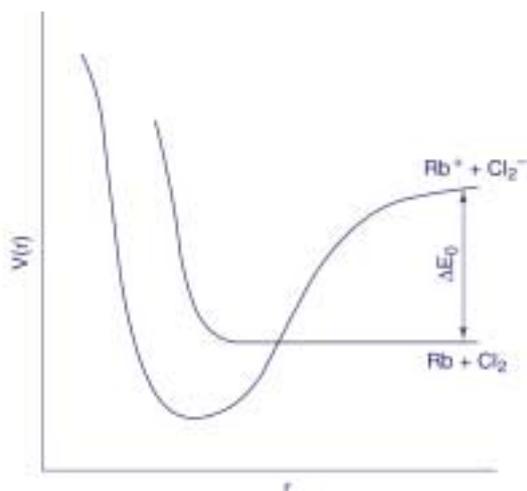
- (b) The reaction



proceeds extremely rapidly. Use the potential energy diagram below to suggest a possible mechanism for the reaction that would explain the kinetics of the process. Estimate the reaction cross section by assuming that the potential curve leading to $\text{Rb} + \text{Cl}_2$ is independent of r ($V(r) = 0$) at large r , and that the curve leading to $\text{Rb}^+ + \text{Cl}_2^-$ is dominated by electrostatic attraction for r beyond the potential minimum. Comment on your result.

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r} = \frac{-1.44}{r} \quad \text{for } V(r) \text{ in eV and } r \text{ in nm}$$

The ionisation potential of Rb is 4.2 eV and the electron affinity of Cl₂ is 2.4 eV.



B4

Interpret the following observations and accompanying data.

On refluxing with sodium cyclopentadienide (NaC₅H₅) in tetrahydrofuran (*thf*), molybdenum hexacarbonyl yields an orange, air-sensitive solution of a compound **A**, with evolution of three molar equivalents of a gas.

Treatment of **A** in *thf* with methyl bromide leads to precipitation of **B**, a white solid which proves soluble in water, and a compound **C** can be isolated from the *thf* solution. The latter is soluble in hydrocarbon solvents, and its ¹H NMR spectrum shows two singlet resonances at $\delta = 5.1$ and 0.4 ppm, with relative intensities 5:3. Reaction of **A** in *thf* with allyl bromide produces again a precipitate of **B**, together with a compound **D** which can be extracted as a yellow-brown oil having the empirical formula MoC₁₁H₁₀O₃.

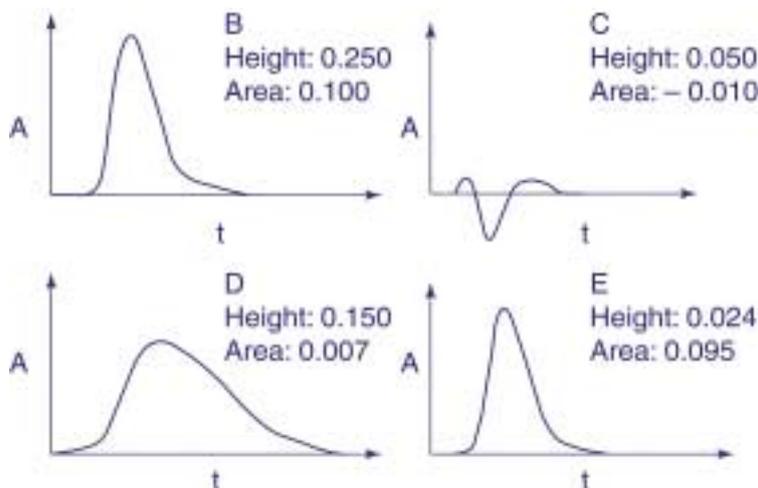
On photolysis or careful heating, **D** is converted to **E**, though the yield is improved by treating **D** with Me₃NO. The ¹H NMR of **E** shows a singlet ($\delta = 5.1$ ppm), a triplet (1:2:1) of triplets (1:2:1) ($\delta = 2.5$ ppm) and two doublets ($\delta = 1.5$ and 0.9 ppm) with the intensity ratio 5:1:2:2. The IR absorption spectrum of **E** shows two intense bands at 1835 and 1920 cm⁻¹; detailed spectroscopic studies at low temperature indicate that it is a mixture of two isomers.

Treatment of **A** with Fe(III) in ethanoic acid under carbon monoxide yields a red compound **F**, the mass spectrum of which shows a parent ion structure, centred about $m/z = 490$, with an isotope distribution pattern indicative of two molybdenum atoms per molecule. Photolysis of **F** in hexane with an argon purge leads to **G**, with a mass spectrum having the parent ion feature around $m/z = 434$ and displaying an isotope pattern very similar to that of **F**. The precursor **F** may be recovered by treating **G** with CO. Furthermore, **G** reacts with trimethylphosphine to form **H**, the ¹H NMR of which shows two singlets at $\delta = 4.5$ and 0.9 ppm, with relative intensities 5:9.

X-ray diffraction studies of **F** and **G** reveal Mo-Mo bond lengths of 323.5 pm and 244.8 pm, respectively.

[The metallic radius of molybdenum is 139 pm.]

The following signals were obtained for selenium by electrothermal atomic absorption spectrometry (ETAAS).



Details

- B 20 ng ml⁻¹ Se standard solution
 C 20 ng ml⁻¹ Se in diluted urine; D₂ background correction used
 D 20 ng ml⁻¹ Se in diluted urine; Zeeman-effect background correction used
 E 20 ng ml⁻¹ Se in diluted urine; Zeeman-effect background correction used platform atomization and a chemical modifier used

Answer the following:

- Compare signals B and C. Explain why the signals for Se are so different
- Compare signals C and D. Comment on why the Zeeman-effect background correct system has made a difference to the signal obtained.
- Compare signals B and D.
 - Calculate the extent of chemical interference caused by the urine matrix for both the height and area signals.
 - Comment on the most likely causes of the interference observed and on any differences between the two modes of measurement (height and area).
- Compare signals B, D and E.
 - Explain why the use of a platform and modifier has apparently reduced the extent of chemical interference.
 - Give an example of a possible modifier and explain its mode of action. Comment on any limitations in the use of the modifier you select.
- Describe how analysis of a time resolved peak (e.g. B) in ETAAS can be used to obtain an idea of the main mechanism of atom formation.

B6

Treatment of a tetrahydrofuran solution of $[(C_5H_5)Fe(CO)_2Cl]$ with propene, in the presence of $AlCl_3$, gave compound **(A)**.

Characterisation data for (A):

| | |
|-----------------------------------|---|
| Microanalysis: | C, 30.95; H, 2.85; Cl, 36.55% |
| IR($\bar{\nu}$ (CO), cm^{-1}) | 2070, 2035 |
| 1H NMR (ppm, $CDCl_3$) | 5.62 (s, intensity 5H), 5.20 (ddq, intensity 1H, $^3J_{HH} = 14.0$ Hz, 8.0 Hz, 6.0 Hz), 3.98 (d, intensity 1H, $^3J_{HH} = 8.0$ Hz), 3.53 (d, intensity 1H, $^3J_{HH} = 14.0$ Hz), 1.88 (d, intensity 3H, $^3J_{HH} = 6.0$ Hz). |

When compound **(A)** was reacted with one equivalent of $LiCH(CO_2Me)_2$ two products, **(B)** and **(C)**, were isolated.

Characterisation data for (B):

| | |
|-----------------------------------|--|
| Microanalysis: | C, 51.45; H, 5.14; Cl, 0.00% |
| IR($\bar{\nu}$ (CO), cm^{-1}) | 2005, 1955 |
| 1H NMR (ppm, $CDCl_3$) | 4.77 (s, intensity 5H), 3.62 (s, intensity 6H), 3.50 (dd, intensity 1H, $^3J_{HH} = 13.0$ Hz, 3.0 Hz), 2.60 (ddd, intensity 1H, $^3J_{HH} = 4.0$ Hz, 3.0 Hz, $^2J_{HH} = 3.0$ Hz), 2.10 (ddd, intensity 1H, $^3J_{HH} = 14.0$ Hz, 13.0 Hz, $^2J_{HH} = 3.0$ Hz), 1.6 (ddq, intensity 1H, $^3J_{HH} = 14.0$ Hz, 6.5 Hz, 4.0 Hz), 1.25 (d, intensity 3H, $^3J_{HH} = 6.5$ Hz). |

Characterisation data for (C):

| | |
|-----------------------------------|---|
| Microanalysis: | C, 51.45; H, 5.14; Cl, 0.00 % |
| IR($\bar{\nu}$ (CO), cm^{-1}) | 2003, 1954 |
| 1H NMR (ppm, $CDCl_3$) | 4.82 (s, intensity 5H), 3.65 (s, intensity 6H), 3.40 (d, intensity 1H, $^3J_{HH} = 14.0$ Hz), 2.80 (dddq, intensity 1H, $^3J_{HH} = 14.0$ Hz, 13.0 Hz, 7.0 Hz, 4.0 Hz), 2.40 (dd, intensity 1H, $^3J_{HH} = 13.0$ Hz, $^2J_{HH} = 3.0$ Hz), 2.10 (dd, intensity 1H, $^3J_{HH} = 4.0$ Hz, $^2J_{HH} = 3.0$ Hz), 0.95 (d, intensity 3H, $^3J_{HH} = 7.0$ Hz). |

Using the data provided answer all parts (i)–(v)

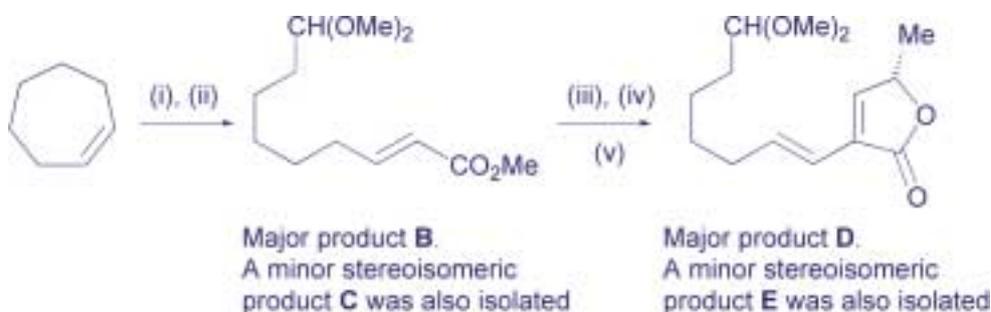
- Write a balanced equation for the formation of (A). Draw a structure for compound (A) and propose a mechanism for its formation.
- What is the oxidation state of iron in compound (A) and the overall electron count? Assign the spectroscopic data for compound (A) to confirm your answer to part (i).
- Using the Davies-Green-Mingos rules for nucleophilic attack at a coordinated polyene propose structures for products (B) and (C).
- Support your answer to (iii) by assigning the spectroscopic data provided (chemical shifts and coupling constants).
- Why are the IR stretching frequencies for (B) and (C) different from (A)?

Show all working and calculations in your answer to gain full marks.

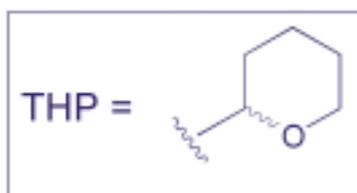
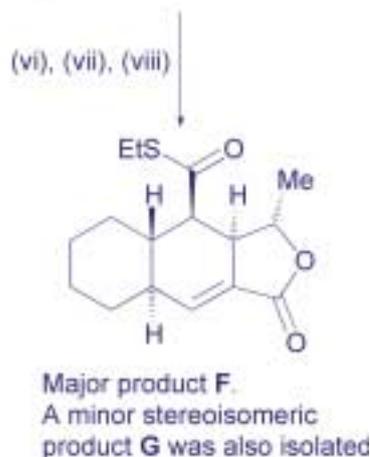
(open book question)

B7 The following schemes (I and II) illustrate steps from an asymmetric synthesis of the alkaloid himbacine **A**. Answer all questions.

Scheme I

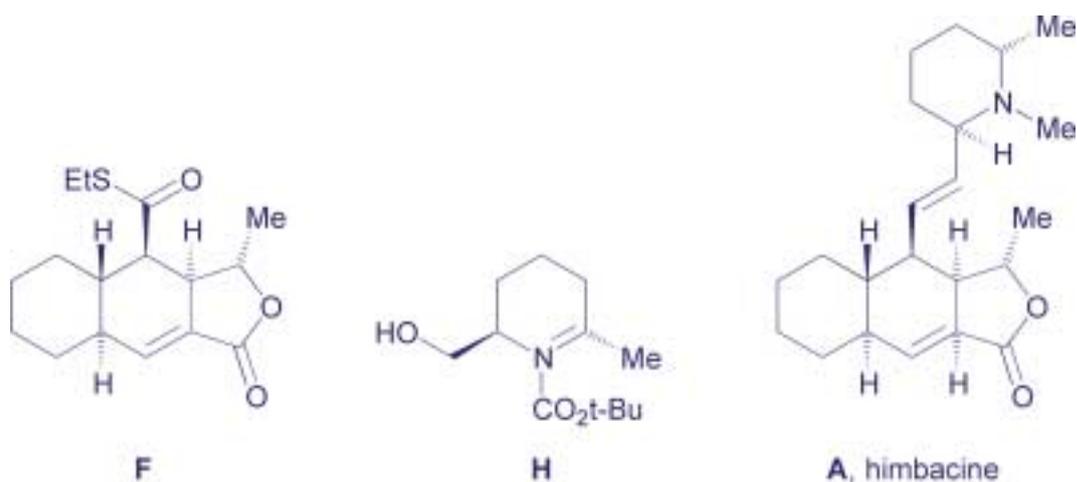


- O_3 , MeOH, TsOH then Me_2S , NaHCO_3 ;
- $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Me}$;
- $i\text{-Pr}_2\text{N}^-\text{Li}^+$, THF, $(\text{NMe}_2)_3\text{PO}$;
then $(2S)\text{-MeCH}(\text{OTHP})\text{CHO}$;
- TsOH, MeOH;
- MeSO_2Cl , Et_3N , CH_2Cl_2 ;
- Resin- SO_3^-H^+ , H_2O , Me_2CO ;
- $\text{Ph}_3\text{P}=\text{CHCOSEt}$;
- PhMe , Et_2AlCl , Δ .



- Suggest mechanisms for steps (i) and (ii). Rationalise the stereochemical outcome of step (ii) and predict the structure of the minor product **C** formed.
- Starting from **B** suggest mechanisms for steps (iii), (iv) and (v) and predict the structure of the minor product **E** formed.
- Suggest a method to convert **E** into **D**.
- Starting from **D** identify products formed in steps (vi) and (vii).
- Rationalise the stereochemical outcome of step (viii) and predict the structure of the minor product **G** formed.

Scheme II



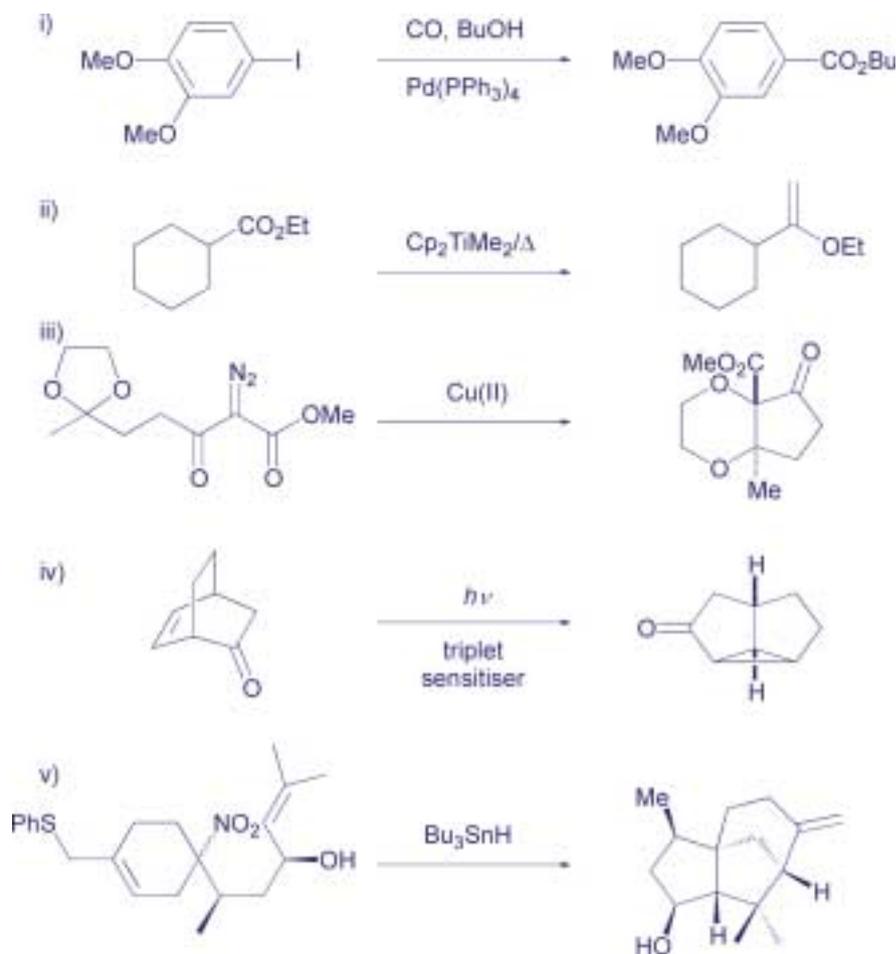
- Propose a synthesis of himbacine **A** from **F** and **H**. Briefly explain the reasons for your choice of reagents and indicate possible problems. Note that **F** and **H** may be modified before coupling.

- B8** (a) Describe briefly the different types of colloidal phase. Derive an expression for the surface area to volume ratio of a colloidal dispersion of spherical particles. Hence calculate this ratio for particles with a radius, a , of 5 nm at a volume fraction, ϕ , of 0.1.
- (b) Derive the critical polymer adsorption energy per segment for a cubic lattice. Plot the data below which represent a polymer layer adsorbed on a colloidal particle. Using the data, calculate the average layer thickness and the adsorbed amount of polymer, assuming that the polymer density is 1000 kg m^{-3} . From the calculations and the graph discuss to what kind of adsorbed polymer system(s) the data could refer.

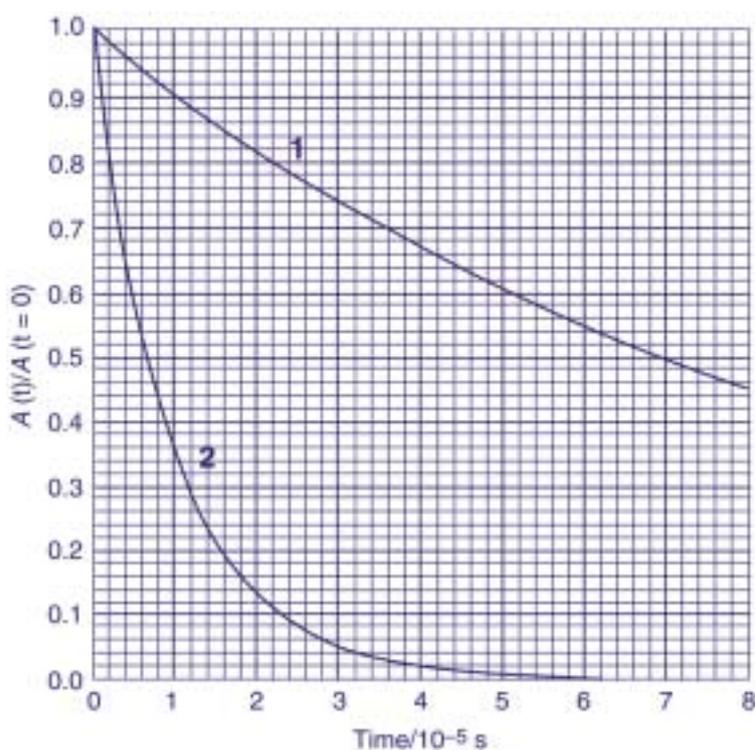
| $\phi(z)$ | 0.62 | 0.60 | 0.56 | 0.46 | 0.3 | 0.0 |
|------------------|------|------|------|------|-----|-----|
| $z / \text{\AA}$ | 100 | 200 | 300 | 400 | 500 | 600 |

- (c) The diffusion rate of an aqueous dispersion of a *monodisperse* colloid through a sintered glass disc was measured at 25°C . On one side of the glass membrane (area 1 cm^2 , thickness $1.50 \times 10^{-5} \text{ m}$) was 15 cm^3 of a $1.000 \times 10^{-3} \text{ mol dm}^{-3}$ solution of the colloid. On the other side there was 10 cm^3 of a solution with an initial colloidal concentration of $1.000 \times 10^{-5} \text{ mol dm}^{-3}$. After 3000 seconds, the colloidal concentration of the second solution had increased to $1.360 \times 10^{-5} \text{ mol dm}^{-3}$.
- (i) From these data and Fick's law, calculate the diffusion coefficient, D , of the colloid.
- (ii) Use the *Stokes-Einstein equation*, which relates D to particle size, to determine the radius of the colloidal particles.
- (iii) Scanning electron microscope measurements of colloidal size for this system produce a particle size measurement which is significantly different from the value obtained by these diffusional measurements. Compare and contrast the information obtained by the two measurements and hence suggest reasons for the discrepancy.

- B9** Propose mechanisms for the following reactions



- B10** (a) A sample of a polycyclic aromatic hydrocarbon is dissolved in *n*-hexane and, after removal of dissolved oxygen, is frozen in liquid nitrogen to form a glass. The fluorescence and phosphorescence decay lifetimes are measured and found to be 1.5×10^{-8} s and 8 s respectively. The rate constant for intersystem crossing from S_1 to T_1 is 2×10^7 s $^{-1}$. Calculate the ratio of the triplet and singlet concentrations under steady state illumination in the singlet absorption band of the aromatic compound. Outline briefly the processes that you consider in your calculations. What would happen to the triplet: singlet ratio if the glass was melted?
- (b) The triplet state of diphenylketone is quenched by small concentrations of naphthalene. The figure below shows transient triplet-triplet absorption decay curves for diphenylketone in *n*-hexane. Curve 1 was obtained in the absence of naphthalene, whereas curve 2 was recorded in the presence of 1×10^{-5} mol dm $^{-3}$ naphthalene. Analyse the decay curves to obtain information about the kinetics of the quenching process. Comment on the result of your calculations and suggest further experiments that could be used to test your conclusions.



Triplet-triplet absorbance decay curves. 1) no added naphthalene, 2) 10^{-5} mol dm $^{-3}$ naphthalene. (The curves have been normalised by dividing the absorbance at time t by the absorbance at $t = 0$.)

B11 Answer the following questions by reference to the paper, "A Novel [2,3] Intramolecular Rearrangement of N-Benzyl-*O*-allylhydroxylamines", S.G. Davies, S. Jones, M.A. Sanz, F.C. Teixeira and J.F. Fox, *Chem. Commun.*, **1998**, 2235-6, a copy of which is provided,

- Explain the term *intramolecular sigmatropic rearrangement* and what is meant by the notation [2,3] and [3,3] processes (paragraph 1).
- Why must the tetrahydrofuran solvent used for the rearrangements be dry (paragraph 4)? How would it have been dried?
- What changes in the ^1H NMR spectrum would you expect to signify the *essentially quantitative conversion* of **3a** into **4a** (paragraph 4)?
- Why do you think the rearrangement of **3c** to **4c** is harder to achieve than the other rearrangements (paragraph 4)?
- Explain why the rearrangement of the crotylhydroxylamine **3b** rules out the possibility of 1,2-anionic shift (paragraph 5).
- Explain the logic behind the test used to distinguish between inter- and intra-molecular rearrangements and hence explain why Scheme 3, as drawn, is misleading (paragraph 5).
- What is implied by the term *envelope transition state* (paragraph 6)?
- Redraw structure **8** to show more accurately all bonds being made or broken and redistribution of charge(s) in the transition state.
- Explain how the pK_a values quoted for EtOH and EtNH₂ relate to the driving force proposed for the reaction (paragraph 6) and also to the use of different bases (t-BuOK and n-BuLi) in the two deprotonation steps between oxime reactants **1** and hydroxylamine products **4**.

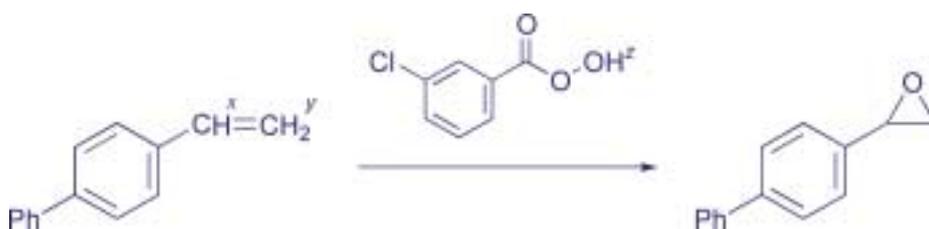
B12 (a) Plot a Hammett correlation and determine the value of the reaction constant for epoxidation of substituted *trans*-stilbenes ($\text{X-C}_6\text{H}_4\text{CH=CHPh}$) with *meta*-chloroperbenzoic acid, for which rate constants at 30°C ($k_2 / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) are as follows.

| X = | 4-OMe | 4-Me | 3-Me | H | 4-Cl | 3-Cl | 3-NO ₂ | 4-NO ₂ |
|------------|-------|-------|-------|------|------|------|-------------------|-------------------|
| k_2 | 31.4 | 14.9 | 7.46 | 6.64 | 4.28 | 2.76 | 1.14 | 0.98 |
| σ | -0.27 | -0.14 | -0.06 | 0.0 | 0.24 | 0.37 | 0.71 | 0.78 |
| σ^+ | -0.78 | -0.30 | | | 0.11 | | | |
| σ^- | | | | | | | | 1.23 |

(b) Discuss the mechanism and the nature of the rate-determining transition state for epoxidation of alkenes by peracids in the light of the following observations together with your result from part (a).

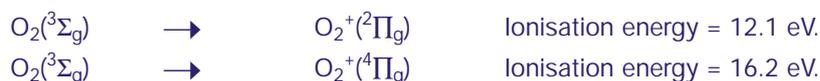
- Reactions of *trans*-PhCH=CHPh with substituted perbenzoic acids X-C₆H₄CO₃H correlate with Hammett's σ with $\rho = +1.4$.
- Rates of epoxidation in non-protic, non-basic solvents increase with increasing solvent polarity. In basic solvents the reactions are slow and depend little upon solvent polarity.
- The reaction below exhibits the following deuterium kinetic isotope effects:

$$k_{\text{H}}/k_{\text{D}^x} = 0.99 \quad k_{\text{H}}/k_{\text{D}^y} = 0.82 \quad k_{\text{H}}/k_{\text{D}^z} = 1.17$$



(iv) Epoxidations are stereospecifically *syn*.

B13 (a) Photoexcitation of molecular oxygen to its two lowest ionised states is summarised below.



Comment on the expected overall relative intensities for these two transitions.

(b) Account for the relative magnitudes of the vibrational wavenumbers for the molecular species tabled below.

| Molecule | Equilibrium bond length /nm | Vibrational wavenumber /cm ⁻¹ |
|---|-----------------------------|--|
| O ₂ (³ Σ _g) | 0.121 | 1580 |
| O ₂ ⁺ (² Π _g) | 0.112 | 1850 |
| O ₂ ⁺ (⁴ Π _g) | | 1200 |

(c) Estimate the equilibrium bond length for the excited O₂⁺(⁴Π_g) molecular ion.

(d) Methyl bromide, CH₃Br, a prolate symmetric top, has rotational constants $A = 5.082$ and $B = 0.319 \text{ cm}^{-1}$, respectively.

(i) Assuming that the CH₃Br has been cooled in a supersonic jet to a temperature of 15 K, show that only rotational levels in the $K = 0, 1$ and 2 stacks have significant populations.

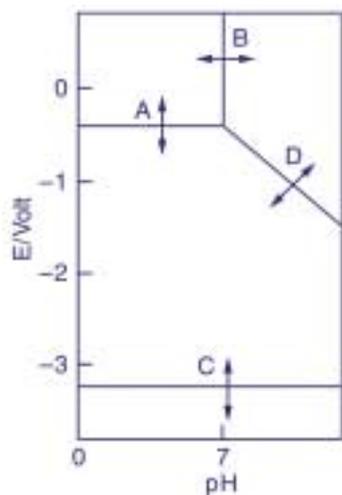
(ii) Sketch the expected appearance of a jet-cooled perpendicular rovibrational band of methyl bromide, taking care to label the K sub-bands.

(e) It is common to assume that rotational constants are unchanged by a vibrational transition. However, this is only an approximation.

(i) Derive formulae for the P - and R -branch rovibrational transitions in a parallel band of a linear molecule assuming that the rotational constants in the upper and lower vibrational levels differ slightly. (use B' and B'' to label the upper and lower state rotational constants, respectively).

(ii) Show that the R -branch reaches a turning point (a so-called bandhead) at some value of J'' if $B'' > B'$, whereas the P -branch has a turning point if $B'' < B'$.

- B14** (a) Shown below is the Pourbaix (standard potential vs. pH) diagram for a lanthanide element Ln.

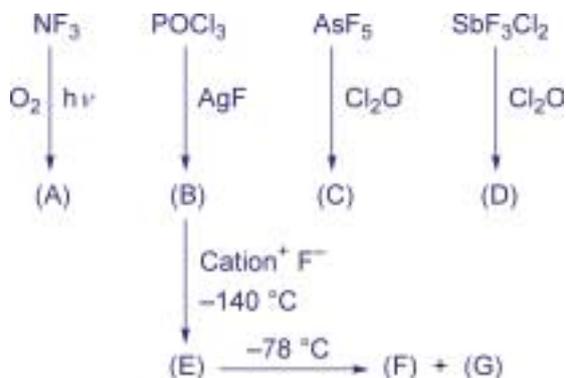


- Write equations for the half-cell reactions occurring at each of the points **A**, **B**, **C**, and **D** in the diagram.
 - Identify the element Ln, making clear your reasons.
 - What might be found were the diagram extended to higher pH?
- (b) What may be inferred from the standard potentials of the aqueous Ag(I)/Ag couple measured in the presence of unit activity of (i) perchlorate ions, + 0.80 V, (ii) chloride ions, + 0.22 V, and (iii) cyanide ions, - 0.02 V?
- (c) In acidic aqueous solutions a radioactive element **X** is believed to have the following standard reduction potentials (in V).



What can you deduce about the element **X** and its behaviour in acid solution?

B15 In the following scheme, some chemistry of elements from Group 15 is described.



(A), (B), (C) and (D) all have the same formula $[\text{MO}_x\text{F}_y]$ (where x and y are constant for $M = \text{N, P, As, Sb}$). However, (A) and (B), which are isostructural, are volatile gases whilst (C) and (D), which are also isostructural, are involatile solids.

The IR spectrum of (A) shows three stretching vibrations at $1691, 883$ and 743 cm^{-1} .

The ^{31}P NMR spectrum of (B) is a 1:3:3:1 quartet and the ^{19}F NMR spectrum of (B) is a 1:1 doublet. The couplings in the two spectra are identical.

- Deduce the empirical formulae of (A), (B), (C) and (D) and deduce the molecular structures of (A) and (B) accounting for all the spectroscopic data.
- Suggest reasonable structures for (C) and (D) and account for the difference in chemistry between the heavier and lighter elements of Group 15.

(E) is the first product from the reaction of (B) with a good source of fluoride ion. It is a 1:1 electrolyte which is stable in solution below -140°C ; at higher temperatures it decomposes into (F) and (G) which are formed in equimolar amounts and are both 1:1 electrolytes in solution.

The ^{31}P NMR spectrum of (E) contains one signal, a 1:2:1 triplet of 1:2:1 triplets. The ^{19}F NMR spectrum of (E) contains 2 signals in a 1:1 ratio. Both signals are 1:1 doublets of narrower 1:2:1 triplets. The ^{31}P NMR spectrum of (F) is a 1:2:1 triplet which is mutually coupled to a 1:1 doublet in the ^{19}F NMR spectrum of (F). The ^{31}P NMR spectrum of (G) is a 1:6:15:20:15:6:1 septet which is mutually coupled to a 1:1 doublet in the ^{19}F NMR spectrum of (G).

- Deduce the molecular formulae and draw the structures of (E), (F) and (G), accounting for all the NMR data.
- Suggest reasons why (A), (C) and (D) do not react with fluoride ion in solution.

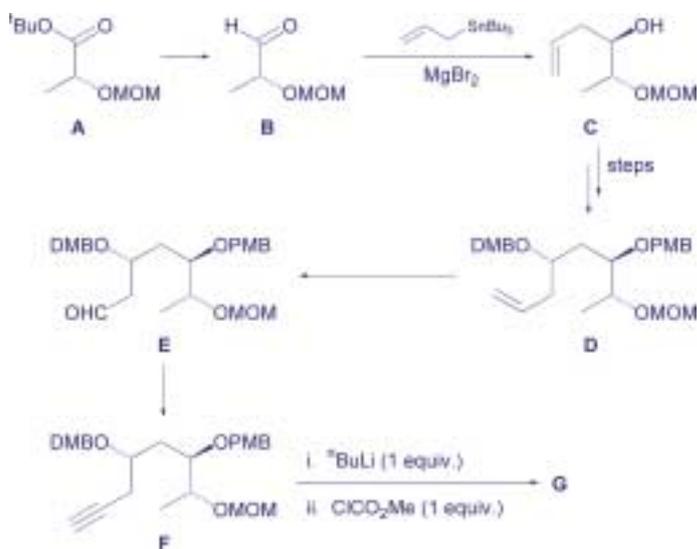
[NMR Data: ^{19}F , $I = \frac{1}{2}$, 100%; ^{31}P , $I = \frac{1}{2}$, 100%; ^{16}O , $I = 0$, 100%]

B16 (a) The synthesis of a fragment of the natural product, bryostatin, is shown below. (Note that MOM, PMB and DMBO are simply alcohol protecting groups).

(i) Suggest reagent(s) for the conversions $A \rightarrow B$, $D \rightarrow E$ and $E \rightarrow F$.

(ii) What is the structure of **G** and how is it formed?

(iii) Explain the stereoselectivity observed in the conversion of $B \rightarrow C$.

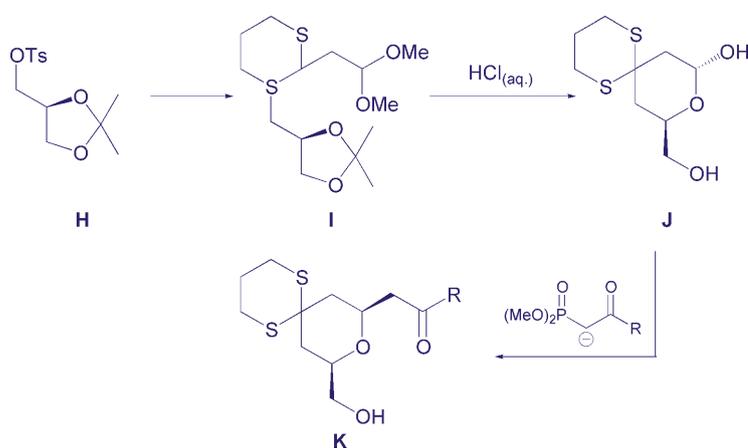


(b) The synthesis of a second bryostatin fragment is given below.

(i) Suggest reagent(s) for the conversion $H \rightarrow I$

(ii) Suggest a synthesis of **H** as a single enantiomer from an achiral starting material.

(iii) Provide a mechanism for the formation of **K**.



- B17** (a) The separation of ethanol and propanol by gas chromatography gave the following results.

| Run | Retention Time | | | Peak Width | |
|-----|-------------------------|-----------|------------|------------|------------|
| | Unretained compound/min | Ethanol/s | Propanol/s | Ethanol/s | Propanol/s |
| 1 | 1.01 | 131 | 173 | 19 | 26 |
| 2 | 1.00 | 129 | 165 | 16 | 23 |
| 3 | 1.03 | 133 | 177 | 21 | 28 |

From the above information, calculate:

- (i) the number of theoretical plates for each compound,
 - (ii) the capacity factor for each compound, and
 - (iii) the resolution between ethanol and propanol
- (b) After a disruption to the carrier gas supply, the mean retention times for ethanol and propanol were 196 and 249 seconds respectively. For a series of 3 injections, the relative standard deviation (RSD) was less than 5%. Comment on this result.
- (c) Explain with reasons, the method of sample introduction you would employ for the following gas chromatographic analyses:
- (i) ethanol in blood
 - (ii) benzene in petrol
 - (iii) a polymer

- B18** First order rate constants at 10°C for the oxidation of the $[\text{Mo}^{\text{V}}_2 \text{ ethylenediaminetetracetato}]$ complex $[\text{Mo}_2\text{O}_4(\text{edta})]^{2-}$ present in an excess concentration with $[\text{Fe}^{\text{III}}(\text{bipy})_3]^{2+}$:



have been determined by monitoring the formation of $[\text{Fe}^{\text{II}}(\text{bipy})_3]^{2+}$. There is no dependence of rate constants on $[\text{H}^+]$ in the range 0.02 - 0.40 mol dm⁻³. The ionic strength, I , was 1.0 mol dm⁻³ (LiClO₄).

- (a) From the data listed, determine k_1 by a graphical method for the rate law:

$$\frac{d[\text{Fe}^{\text{II}}]}{dt} = k_{\text{obs}}[\text{Fe}^{\text{III}}] = 2k_1[\text{Mo}_2^{\text{V}}][\text{Fe}^{\text{III}}]$$

| $10^6 [\text{Fe}^{\text{III}}] / \text{mol dm}^{-3}$ | $10^5 [\text{Mo}_2^{\text{V}}] / \text{mol dm}^{-3}$ | $10^3 k_{\text{obs}} / \text{s}^{-1}$ |
|--|--|---------------------------------------|
| 5.0 | 1.3 | 10.8 |
| 5.0 | 1.5 | 14.0 |
| 5.0 | 2.5 | 19.0 |
| 5.0 | 3.1 | 24.0 |
| 5.0 | 3.8 | 31.4 |
| 10.0 | 5.1 | 36.4 |

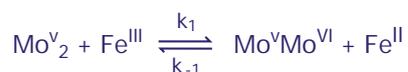
- (b) Further runs were carried out with a large excess of $[\text{Fe}^{\text{II}}(\text{bipy})_3]^{2+}$ over $[\text{Fe}^{\text{III}}(\text{bipy})_3]^{3+}$, when the following rate constants were obtained.

| $10^5 [\text{Mo}_2^{\text{V}}] / \text{mol dm}^{-3}$ | $10^5 [\text{Fe}^{\text{II}}(\text{bipy})_3^{2+}] / \text{mol dm}^{-3}$ | $10^3 k_{\text{obs}} / \text{s}^{-1}$ |
|--|---|---------------------------------------|
| 5.0 | 1.3 | 10.8 |
| 5.0 | 1.5 | 14.0 |
| 5.0 | 2.5 | 19.0 |
| 5.0 | 3.1 | 24.0 |
| 5.0 | 3.8 | 31.4 |
| 10.0 | 5.1 | 36.4 |

Show by graphical method that the following rate law applies and determine k_1 and k_{-1}/k_2 .

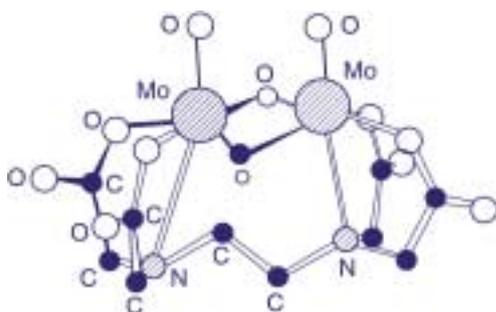
$$\frac{d[\text{Fe}^{\text{II}}]}{dt} = k_{\text{obs}} [\text{Fe}^{\text{III}}] = \frac{2k_1k_2[\text{Mo}_2^{\text{V}}]\text{Fe}^{\text{III}}}{k_{-1}[\text{Fe}^{\text{II}}] + k_2}$$

- (c) The above rate law is consistent with a mechanism:



Using the stationary-state approximation for $\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}$ derive a rate law of this form.

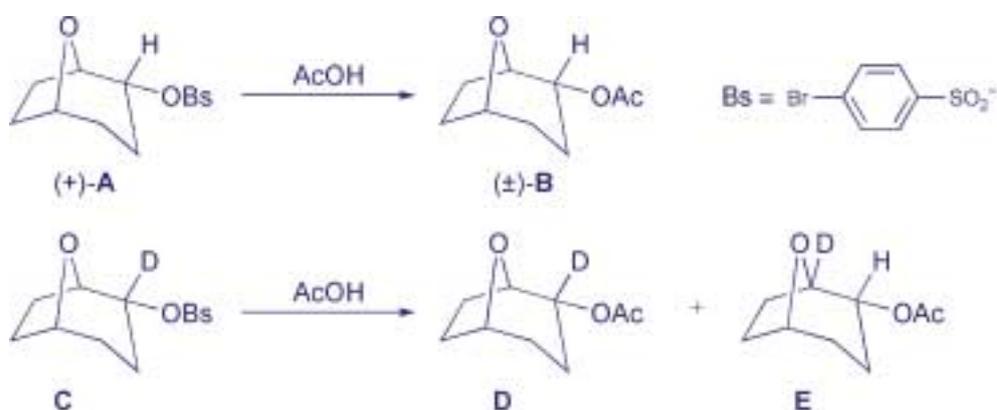
- (d) The structure of the Mo_2^{V} reactant is as shown.



- What influence will the edta have on the mechanism?
- What might happen with $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$ as the Mo_2^{V} reactant.
- What structure will Mo^{VI} have in such acidic solutions?

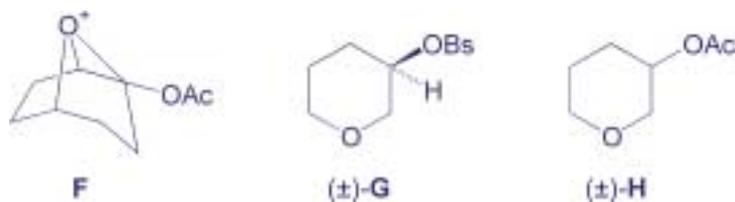
(open book question)

- B19** The optically active *endo*-brosylate (+)-**A** is solvolysed in buffered acetic acid yielding the racemic *endo*-acetate (±)-**B**. At 50° the first order titrimetric rate constant, k_t , for liberation of HOBs from (+)-**A** is 12 times larger than for its *exo*-isomer; and the polarimetric rate constant for (+)-**A**, k_α , is 4.6 times greater than the titrimetric rate constant, i.e. $k_\alpha/k_t = 4.6$. The deuteriated *endo*-brosylate **C** is solvolysed under similar conditions yielding an approximately 1:1 mixture of **D** and **E** (both racemic).



Use the above data to decide between the various possible solvolysis mechanisms (i.e. S_N1 and S_N2) and discuss the possible involvement of free carbocations and oxonium ions such as **F**.

Compare the behaviour of (+)-**A** with that of (+)-**G** which yields (±)-**H** on solvolysis under the same conditions with $k_\alpha/k_t \sim 1$.



B20

- (a) A 1.0 mol dm^{-3} solution of a nylon salt, $\text{H}_3\text{N}^+(\text{CH}_2)_8\text{COO}^-$, was polymerised in an inert solvent using a $0.001 \text{ mol dm}^{-3}$ solution of a catalyst. The concentration, C , of the salt was followed as a function of polymerisation time, t , with the results shown below.

| t / hr | 0 | 1 | 2 | 5 | 10 | 15 | 20 |
|--------------------------|-----|------|------|------|--------|--------|--------|
| $C / \text{mol dm}^{-3}$ | 1.0 | 0.22 | 0.14 | 0.07 | 0.0035 | 0.0026 | 0.0019 |

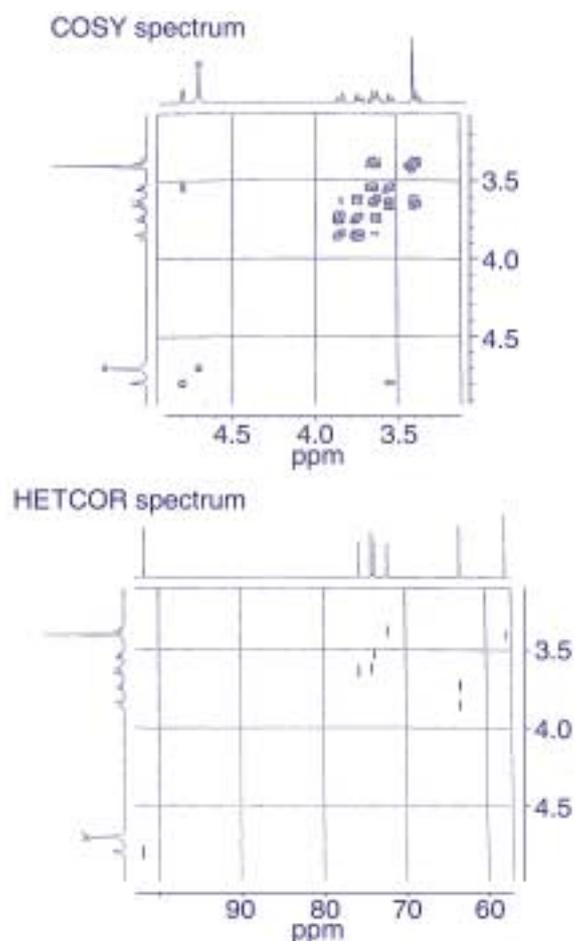
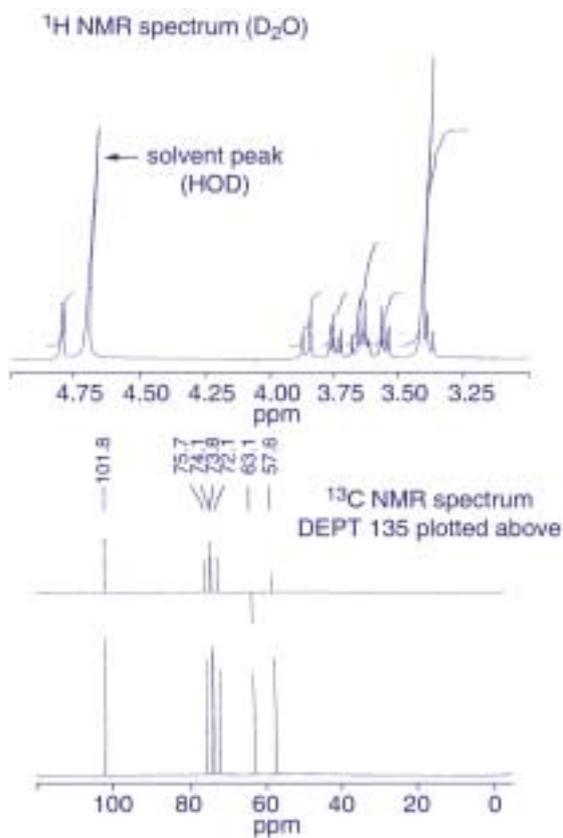
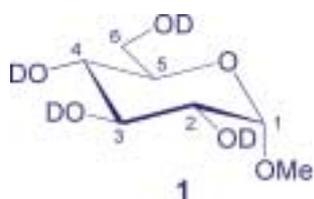
- (i) Derive an expression for C as a function of the polymerisation time and hence calculate the rate constant for the polymerisation reaction and the average molecular weight of the polymer recovered after a reaction time of 20 hr.
- (ii) Assuming that the reaction kinetics are unaffected, calculate the molecular weight that would be achieved after 20 hr if the nylon salt had been contaminated with 2 mol% of a monocarboxylic acid, $\text{CH}_3(\text{CH}_2)_7\text{COOH}$.
- (b) Polymerisation of a 1 mol dm^{-3} solution of acrylonitrile was initiated by $0.001 \text{ mol dm}^{-3}$ AIBN and the concentration of acrylonitrile $[M]$ was measured as a function of time.

| t / hr | 0 | 1 | 2 | 3 | 4 | 5 |
|----------------------------|-------|-------|-------|-------|-------|-------|
| $[M] / \text{mol dm}^{-3}$ | 1.000 | 0.959 | 0.919 | 0.881 | 0.845 | 0.810 |

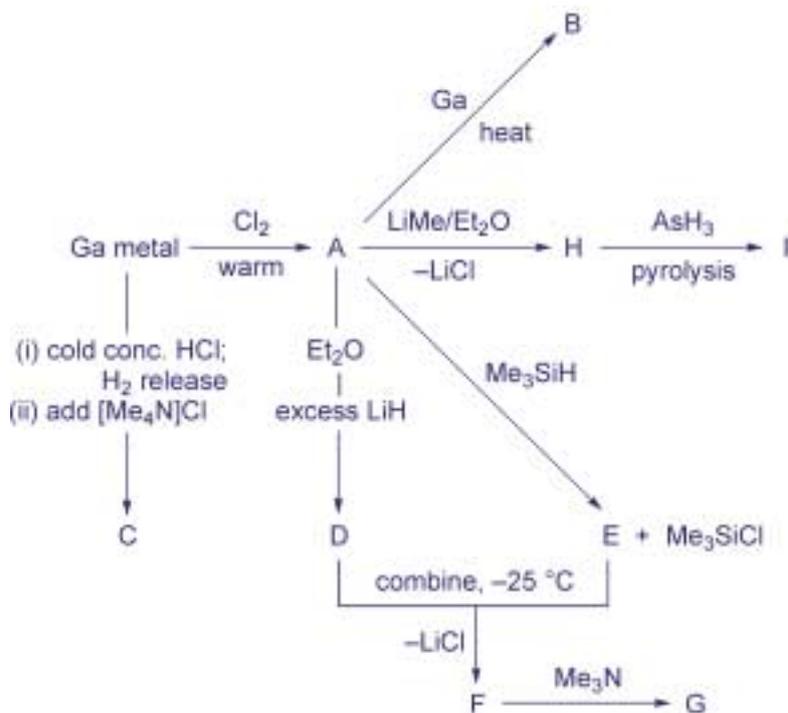
- (i) Calculate the rate constant for the polymerisation and comment on any assumptions you make in the calculation.
- (ii) The resulting molecular weight was too high for a particular application. Suggest two ways in which this parameter be controlled during the reaction and show the quantitative effect of the methods.
- (c) Two samples of polystyrene were prepared by different methods. Analysis by light scattering showed the molecular weight of both to be 100 000. The ideal osmotic pressures of solutions of the polymers with concentration 1.0 g dm^{-3} were 25.5 Pa and 49.1 Pa at 298 K. Calculate the polydispersities of the polymer and suggest, with reasons, the methods used for their preparation.
- (d) Polymerisation of two samples of MMA was separately initiated with benzoyl peroxide or with butyl lithium in an inert solvent. The polymerisations yielded polymers with the same number average molecular weights. Sketch the gel permeation chromatograms you would expect for the two samples, accounting for any differences. Comment on any differences you might expect in the ^1H NMR spectra and in the glass transition temperatures of the two polymers.

B21

Several NMR experiments (^1H , ^{13}C , COSY, HETCOR) were performed upon methyl- α -D-glucopyranoside (**1**) and are presented with this question. These experiments were performed using deuterium oxide (D_2O) as solvent, hence the hydroxyl protons are not observed in the ^1H NMR spectrum. Fully interpret the spectroscopic data and use this information to assign the ^1H and ^{13}C NMR spectra of compound **1**. The numbering system indicated below should be used in your answer.



B22 Identify the gallium compounds **A – I** in the reactions described below. Comment on their structures and properties, on the reactions taking place, and on how gallium compares with other members of its periodic group in the properties thus revealed.



| compound | properties |
|----------|---|
| A | Low-melting white solid with a molecular mass of 352 g mol^{-1} both in non-polar solvents and in the vapour phase. |
| B | Involatile, white, diamagnetic solid containing 49.5% Ga. The molten compound shows two resonances of equal intensity in its ^{71}Ga NMR spectrum. |
| C | Crystalline, diamagnetic salt of the $[\text{NMe}_4]^+$ cation containing 27.9 % Ga and 42.6 % Cl |
| D | White solid containing no chlorine and with a Raman spectrum similar to that of GeH_4 . |
| E | Viscous liquid with a molecular mass of 214 g mol^{-1} both in non-polar solvents and in the vapour phase. There are no coincidences between the bands in the IR and Raman spectra of E , and the only features observed in either spectrum at wavenumbers exceeding 800 cm^{-1} occur close to 2000 cm^{-1} ; these shift to about 1400 cm^{-1} for the deuterated version of E . Its ^1H NMR spectrum shows just a single resonance. |
| F | A highly volatile compound which decomposes at room temperature. The vapour shows two strong IR bands at 1993 and 1976 cm^{-1} , and two more at 1273 and 1202 cm^{-1} . The ^1H NMR spectrum of a solution at 210 K consists of two resonances with relative intensities of 2:1. |
| G | A volatile solid which is more stable than compound F ; the high-frequency region of its IR spectrum resembles that of AsH_3 . |
| H | A volatile liquid with a molecular mass of 115 g mol^{-1} both in non-polar solvents and in the vapour phase. |
| I | Lustrous solid with semiconductor properties. |

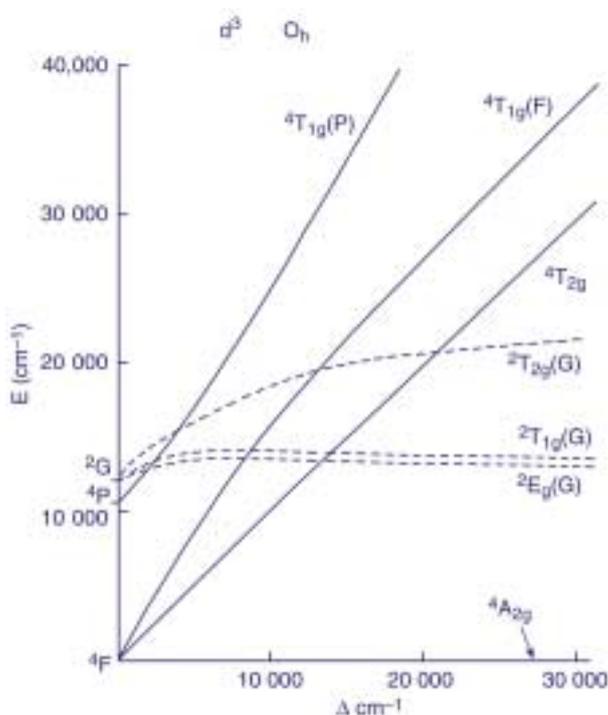
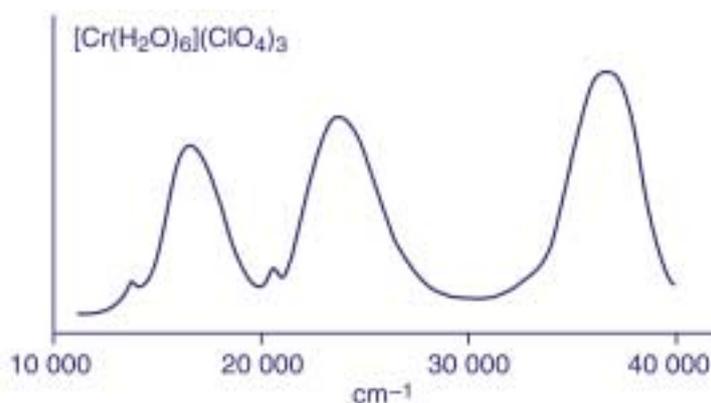
Nuclei other than ^1H ($I = 1/2$) and ^{71}Ga (39.9% abundance, $I = 3/2$) do not contribute significantly to the NMR spectra described, while no H-Ga nuclear spin coupling is resolved.

B23 (a) The magnetic moments (Bohr magnetons) of the tetrahedral cobalt(II) complexes CoX_4^{2-} vary as below:

| X | μ_{eff} |
|----|--------------------|
| Cl | 4.59 |
| Br | 4.69 |
| I | 4.77 |

What value would you expect using the spin-only formula? Comment on the observed values of μ_{eff} in relation to the positions of the ligands in the Spectrochemical Series.

- (b) Using, as necessary, the appropriate energy level diagram, the descent in symmetry correlation table, and the table of rules for the evaluation of direct products (*all assumed available*).
- Assign the bands in the attached electronic spectrum of $[\text{Cr}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$ and evaluate an approximate value for the ligand field strength parameter, Δ , for H_2O in octahedrally coordinated Cr(III). Why are these bands allowed?
 - Given that chloride, when in octahedral Cr(III), has a ligand field strength $\Delta = 13\,000\text{ cm}^{-1}$, sketch the electronic spectrum (spin-allowed bands only) you would expect for $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}](\text{ClO}_4)_2$, the cation of which has C_{4v} symmetry, and explain any differences from the spectrum of $[\text{Cr}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$.



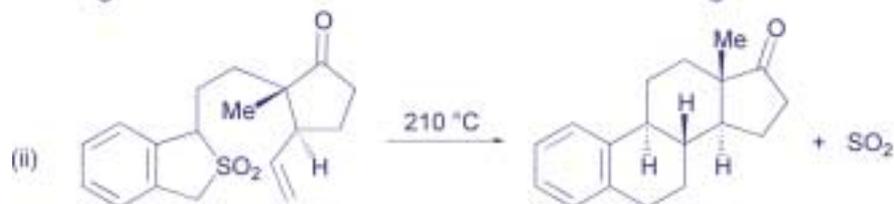
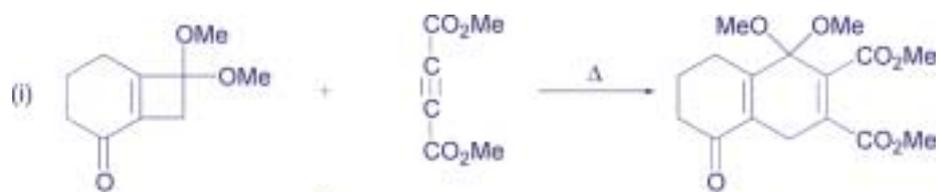
B24 Soil samples, collected from four different sites are digested in acid and then analysed for Cd by atomic emission spectrometry. At each site, five separate samples are collected and subsequently analysed. The concentration of Cd, in $\mu\text{g g}^{-1}$ in the 20 samples is shown in the table below.

| Sample Replicate | Site 1 | Site 2 | Site 3 | Site 4 |
|------------------|--------|--------|--------|--------|
| 1 | 15 | 14 | 8 | 15 |
| 2 | 11 | 12 | 11 | 9 |
| 3 | 9 | 9 | 13 | 12 |
| 4 | 7 | 7 | 14 | 16 |
| 5 | 10 | 10 | 9 | 13 |

- Construct a one-way ANOVA layout, indicating the level means and variances, as well as the grand mean.
- Determine the total sum of squares (SS_T), the residual sum of squares (SS_R) and the between column sum of squares (SS_A).
- Construct a one-way ANOVA table. Include SS_T , SS_R and SS_A , along with their respective degrees of freedom and the appropriate mean sums of squares (variance). Calculate the value of the F -statistic.
- From the accompanying table of critical F -values, determine whether any significant difference exists between the average Cd concentration at the four sites, at the 95% confidence level.

| Critical F -values for 95% Confidence Level | | | | | |
|---|--------|--------|--------|--------|--------|
| dof_1/dof_2 | 1 | 2 | 3 | 4 | 5 |
| 1 | 161.45 | 199.50 | 215.71 | 224.58 | 230.16 |
| 2 | 18.51 | 19.00 | 19.16 | 19.25 | 19.30 |
| 3 | 10.13 | 9.55 | 9.28 | 9.12 | 9.01 |
| 4 | 7.71 | 6.94 | 6.59 | 6.39 | 6.26 |
| 5 | 6.61 | 5.79 | 5.41 | 5.19 | 5.05 |
| 6 | 5.99 | 5.14 | 4.76 | 4.53 | 4.39 |
| 7 | 5.59 | 4.74 | 4.35 | 4.12 | 3.97 |
| 8 | 5.32 | 4.46 | 4.07 | 3.84 | 3.69 |
| 9 | 5.12 | 4.26 | 3.86 | 3.63 | 3.48 |
| 10 | 4.96 | 4.10 | 3.71 | 3.48 | 3.33 |
| 11 | 4.84 | 3.98 | 3.59 | 3.36 | 3.20 |
| 12 | 4.75 | 3.89 | 3.49 | 3.26 | 3.11 |
| 13 | 4.67 | 3.81 | 3.41 | 3.18 | 3.03 |
| 14 | 4.60 | 3.74 | 3.34 | 3.11 | 2.96 |
| 15 | 4.54 | 3.68 | 3.29 | 3.06 | 2.90 |
| 16 | 4.49 | 3.36 | 3.24 | 3.01 | 2.85 |
| 17 | 4.45 | 3.59 | 3.2 | 2.96 | 2.81 |
| 18 | 4.41 | 3.55 | 3.16 | 2.93 | 2.77 |
| 19 | 4.38 | 3.52 | 3.13 | 2.9 | 2.74 |
| 20 | 4.35 | 3.49 | 3.1 | 2.87 | 2.71 |

B25 Give mechanistic explanations for the following reactions (i) to (iii), which involve pericyclic reactions.



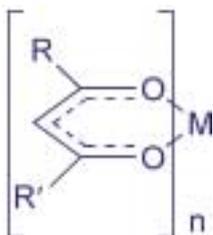
- B26** The ionic conductivity of two samples of KCl, labelled **A** and **B**, was measured as a function of temperature under a large applied voltage, with the following results:

| Sample A | | Sample B | |
|---------------|--|---------------|--|
| Temperature/K | Conductivity/ $\text{ohm}^{-1} \text{cm}^{-1}$ | Temperature/K | Conductivity/ $\text{ohm}^{-1} \text{cm}^{-1}$ |
| 1049 | 1.848×10^{-4} | 1049 | 1.842×10^{-4} |
| 996 | 5.996×10^{-5} | 996 | 6.010×10^{-5} |
| 952 | 1.880×10^{-5} | 952 | 1.906×10^{-5} |
| 915 | 7.233×10^{-6} | 915 | 7.181×10^{-6} |
| 878 | 2.192×10^{-6} | 903 | 4.803×10^{-6} |
| 846 | 8.151×10^{-7} | 843 | 2.268×10^{-6} |
| 828 | 4.263×10^{-7} | 782 | 1.146×10^{-6} |
| 802 | 2.555×10^{-7} | 733 | 5.056×10^{-7} |
| 787 | 1.817×10^{-7} | 693 | 2.387×10^{-7} |
| 769 | 1.431×10^{-7} | | |
| 749 | 9.833×10^{-8} | | |

One sample had been carefully purified by repeated recrystallisation, while the other had been doped with a small amount of SrCl_2 . Use the measurements and an appropriate graphical method to answer the following questions.

- Which sample (**A** or **B**) is the doped material?
- What are the approximate temperatures at which the ionic conductivity of each of the materials changes from extrinsic to intrinsic behaviour, and what is the mechanism of conduction in each case in each of these regimes?
- Use the data to calculate both the energy of formation and the activation energy for migration of the charge carriers in KCl.
- The ionic conductivity of KCl is too low for it to be useful as a solid electrolyte for most applications. Discuss the factors that favour fast-ion conductivity, with references to materials that display this phenomenon.

- B27**
- Briefly discuss the relative advantages and disadvantages of the preparation of thin films using physical vapour deposition (PVD) and chemical vapour deposition (CVD) techniques.
 - Thin films of the high temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) can be prepared by CVD from b diketonate precursors of the form



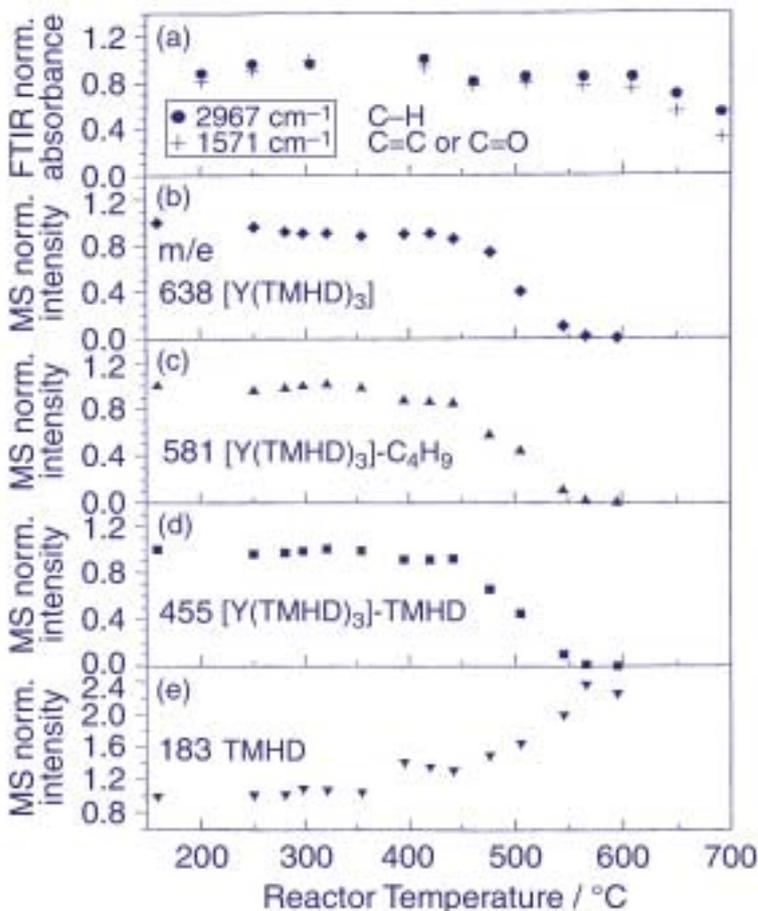
where $n = 2$ for Ba and Cu and $n = 3$ for Y. If $R = R' =$ tertiary butyl, the compounds can be represented by the acronym $[M(TMHD)_n]$. All the precursors are solids at the typical evaporation temperatures of 145°C, 180°C and 110°C for Y, Ba and Cu respectively. Other typical deposition conditions are:

| | |
|-------------------------------|---------------------------------------|
| Ar carrier gas flow | 100 cm ³ min ⁻¹ |
| O ₂ gas flow | 100 cm ³ min ⁻¹ |
| Deposition temperature | 700°C |
| Total pressure in the reactor | 1.33 x 10 ³ Pa |
| Precursor partial pressure | 1 Pa |

Sketch a suitable CVD system, including the gas handling facilities, the reactor, and the post-reactor treatment of the exit gases, which could be used for the deposition of YBCO. Discuss possible problems which might be encountered in the CVD of YBCO.

- (c) The figure overleaf shows the mass spectra and FTIR signals obtained for analysis of the vapour phase for the decomposition of $[Y(TMHD)_3]$ as a function of substrate temperature. Discuss these results in terms of the break up of the $[Y(TMHD)_3]$ molecule.

Comparison of (a) FTIR and (b)–(e) Mass Spectroscopy signals for the decomposition of $[Y(TMHD)_3]$



B28

- (a) Explain what is meant by the Fixed, Variable and Capital components of the manufacturing cost of a bulk polymer such as polystyrene. What is the effect of production scale on these costs?

Comment on the principal cause of the fluctuations in polystyrene price shown below and identify the components which contribute to the difference in price between styrene monomer and polystyrene. Which of these components are fixed costs and which are variable or capital?

| Year | Styrene / \$/lb | Polystyrene / \$/lb | Year | Styrene / \$/lb | Polystyrene / \$/lb |
|------|-----------------|---------------------|------|-----------------|---------------------|
| 1983 | 0.32 | 0.38 | 1989 | 0.42 | 0.54 |
| 1984 | 0.30 | 0.38 | 1990 | 0.41 | 0.49 |
| 1985 | 0.24 | 0.34 | 1991 | 0.30 | 0.43 |
| 1986 | 0.20 | 0.32 | 1992 | 0.24 | 0.42 |
| 1987 | 0.38 | 0.48 | 1993 | 0.24 | 0.43 |
| 1988 | 0.46 | 0.58 | 1994 | 0.33 | 0.46 |

- (b) SFA Chemicals has developed a new polymer for which market research predicts European sales of 40 000 tonnes in 2001 and a further 40 000 tonne per annum (tpa) in 2002. The cost of the manufacturing plant must be committed at the start of the construction period and plants take one year to build and commission. Fixed costs and capital costs are assumed to be incurred once the plant has been commissioned. SFA must decide whether to invest either in a single 100 000 tpa plant on Humberside or a 50 000 tpa plant on Humberside with a second 50 000 tpa plant in Germany started one year later. The cost of the second plant is the same as that of the first and does not change if the start is delayed.

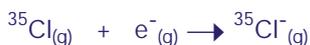
Which of these options is cheaper

- (i) over the three years period from the start of 2000 ?
 (ii) over the five year period from the start of 2000 to the end of 2004 ?

| | |
|---|---------------------------|
| Energy costs | £25 per tonne of polymer |
| Raw material costs | £225 per tonne of polymer |
| Labour for 50 ktpa plant | £1M |
| Site and other fixed costs for 50 ktpa plant | £4M |
| Labour for 100 ktpa plant | £1.5M |
| Site and other fixed costs for 100 ktpa plant | £5.5M |
| Capital for 50 ktpa | £5M |
| Capital for 100 ktpa plant | £8M |

- (c) What other financial or non-financial considerations should the board of SFA take into account when making their decision?

- B29**
- (a) What is the electronic contribution to the molecular partition function and internal energy of $^{35}\text{Cl}_{(\text{g})}$ at 25°C and 2707°C, given that the ground state and first excited state are four-fold and two-fold degenerate respectively and they are separated by 878 cm^{-1} .
- (b) Calculate the translational contribution to the molar entropy of $^{35}\text{Cl}_{(\text{g})}$ at 25°C and 1 bar.
- (c) Evaluate the molar entropy change at 25°C for



given that the ground state degeneracies of e^{-} and Cl^{-} are 2 and 1 respectively.

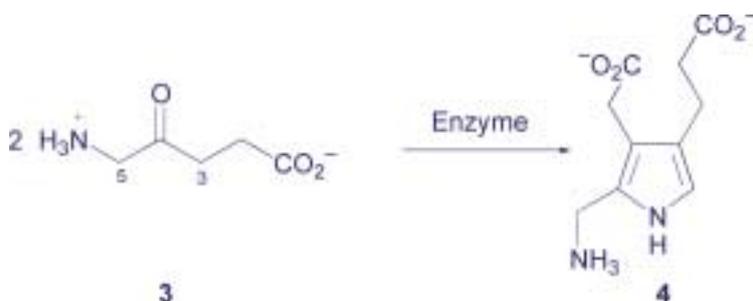
- (d) The vibrational partition function of the Cl_2 molecule increases from $f_{\text{vib}} = 1.07$ at 300 K to $f_{\text{vib}} = 1.57$ at 800 K. What physical significance can be attached to these numbers?

- B30**
- (a) Give a mechanism for the interconversion of butyryl CoA, **1**, and isobutyryl CoA, **2**, catalysed by the B_{12} -dependent enzyme isobutyryl CoA mutase.



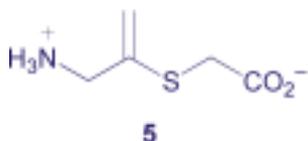
Explain the following isotopic labelling results:

- (i) If $[3,3\text{-}^2\text{H}_2, 2\text{-}^{13}\text{C}]$ butyryl CoA, **1**, is incubated with the enzyme then the **2** produced is almost entirely $[2,3\text{-}^2\text{H}_2, 3\text{-}^{13}\text{C}]$ isobutyryl CoA.
- (ii) If $[3,3\text{-}^2\text{H}_2, 2\text{-}^{13}\text{C}]$ butyryl CoA, **1**, is mixed with an excess of unlabelled **1** and incubated with the enzyme then most of the molecules of product **2** which have ^{13}C at C-3 do not have a deuterium atom attached to C-3.
- (b) Give a possible mechanism for the enzymic conversion of **3** to **4** which is consistent with the observations given below, explaining what each of the observations tells us about the mechanism and why



- The enzyme is irreversibly inhibited by NaBH_4 in the presence of **3** but not in its absence.

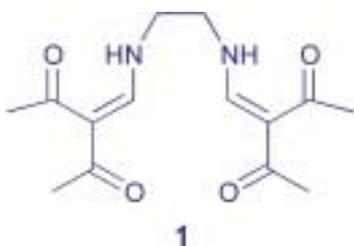
- Thioester **5** irreversibly inhibits the enzyme at a rate which is proportional to the square of its concentration.



- The k_{cat} value for the reaction is 3.5 times slower when **3** is deuteriated at C-3 but unchanged if **3** is deuteriated at C-5. The K_{M} value is unchanged in either case. The **3** recovered after 50% reaction has not lost any deuterium.

B31

- (a) In order to maximise the yield of macrocyclic ligands chemists often rely on **template reactions**. Explain, with appropriate examples, what is meant by a template reaction.
- (b) Reaction, in a 1:1 mole ratio, of $[\text{Ni}(\text{CH}_3\text{CO}_2)_2] \cdot 4\text{H}_2\text{O}$ with the tetradentate ligand **1** in warm methanol (55°C) results in the precipitation of an orange crystalline material (**A**), and the production of $\text{CH}_3\text{CO}_2\text{H}$ (2 moles) and H_2O (4 moles). Compound (**A**) has a molecular mass of $337.03 \text{ g mol}^{-1}$, and analyses for C, 49.99; H, 5.40; N, 8.33; O, 19.04; Ni, 17.24%. It displays two intense bands in the IR spectrum (nujol mull) at 1650 cm^{-1} and 1590 cm^{-1} .



Refluxing (**A**) with excess 1,2-diaminoethane for 1 hour, followed by cooling and addition of water, results in the precipitation of a red crystalline material (**B**). Compound (**B**) has a molecular mass of $361.11 \text{ g mol}^{-1}$, and analyses for C, 53.22; H, 6.14; N, 15.52; O, 8.86; Ni, 16.25%. The $^1\text{H NMR}$ (CDCl_3) of (**B**) displays four resonances at δ 7.5 (2H), 3.2 (8H), 2.42 (6H) and 2.26 (6H). It also displays a broad intense band in the IR spectrum (nujol mull) at 1600 cm^{-1} .

- Identify and draw the structures of the products (**A**) and (**B**).
- Assign the resonances in the $^1\text{H NMR}$ of (**B**) as far as you are able.

B32 Chromium(II) chloride crystallizes in an orthorhombic unit cell with $a = 6.64$, $b = 5.98$, $c = 3.48$ Å, which contains two molecules. The two Cr atoms occupy the special positions $(0,0,0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ of space group Pnm, and one of the four symmetry related Cl atoms is at $(x = 0.36, y = 0.28, z = 0)$.

- Calculate the density of CrCl_2 .
- Give the site symmetry of the Cr atoms, and of the Cl atoms.
- Draw a projection of one complete unit cell as seen down the c axis direction.
- Show that the Cr atom is surrounded by two Cl atoms at 2.92 Å and four at 2.37 Å. Describe the Cr atom coordinate geometry. Give a possible explanation for this geometry.
- The unit cell derived from the neutron diffraction pattern of CrCl_2 is four times larger than the X-ray determined cell. Give a qualitative explanation for this observation.

B33 Attempt to assign the ^{13}C -NMR signals to the structure presented. Those carbons that were enriched with ^{13}C following a feeding experiment with 2- ^{13}C -acetate are marked with an asterisk (*). On the basis of this information, propose a plausible biogenesis for the natural product.

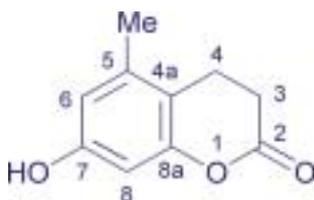
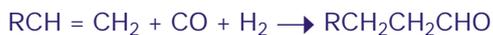


Table - proton-coupled natural abundance spectrum

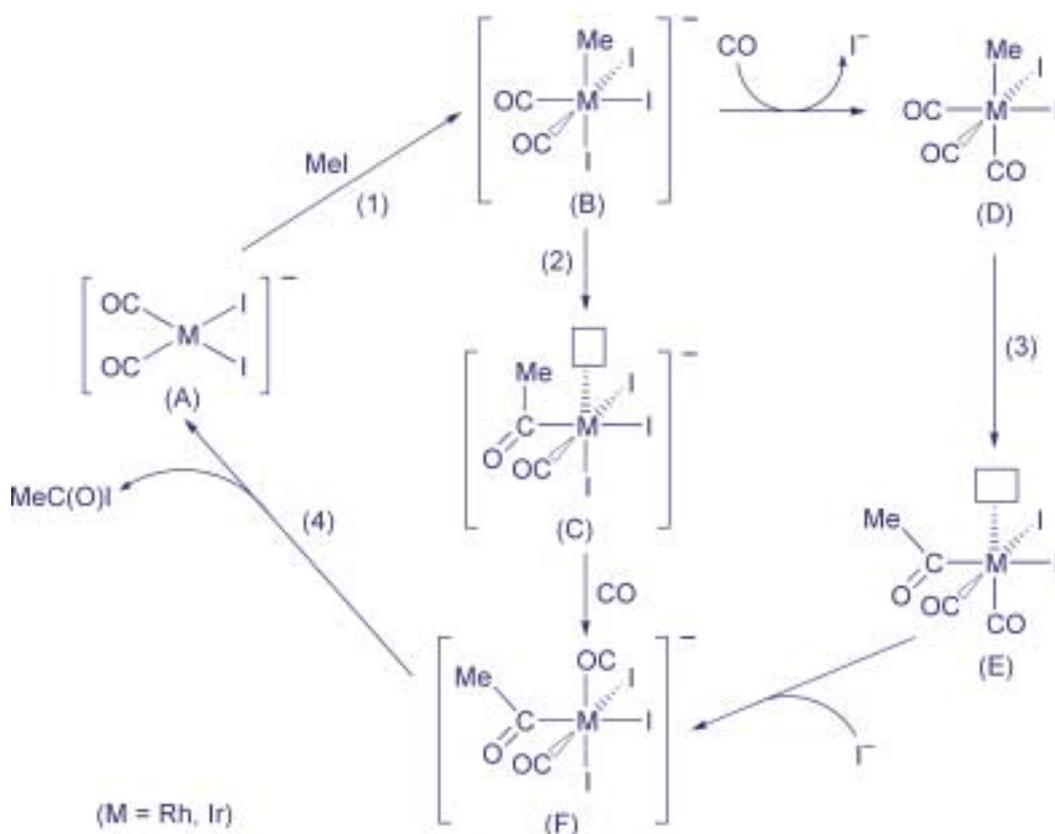
| δ -value | Multiplicity | |
|-----------------|--------------|-----|
| 25.2 | q | (*) |
| 41.6 | t | |
| 44.2 | t | (*) |
| 110.9 | s | |
| 114.5 | s | (*) |
| 122.3 | d | (*) |
| 131.4 | d | (*) |
| 140.5 | s | |
| 149.2 | s | |
| 175.1 | s | |

B34 (a) The complex $[\text{RhCl}(\text{PPh}_3)_3]$ will catalyse the hydroformylation of alkenes:



Write a mechanistic cycle for this reaction, giving the oxidation state of the Rh for each intermediate species.

- (b) Explain in detail why the hydroformylation of an equilibrium mixture of but-1-ene and but-2-ene affords $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$ as the major product.
- (c) Parts of the catalytic cycles involved in the carbonylation of methanol with a rhodium or iridium catalyst are shown below.



- (i) Classify the key reaction steps (1) to (4).
- (ii) Using the data given below, identify which cycle $\text{A} \rightarrow \text{B} \rightarrow \text{C} \rightarrow \text{F} \rightarrow \text{A}$ or $\text{A} \rightarrow \text{B} \rightarrow \text{D} \rightarrow \text{E} \rightarrow \text{F} \rightarrow \text{A}$ is correct for each metal, identify the rate determining step in each case and hence deduce which species is most likely to have the highest concentration in each case. Explain all reasoning.

For Rh rate = $k[\text{Rh}][\text{MeI}]$

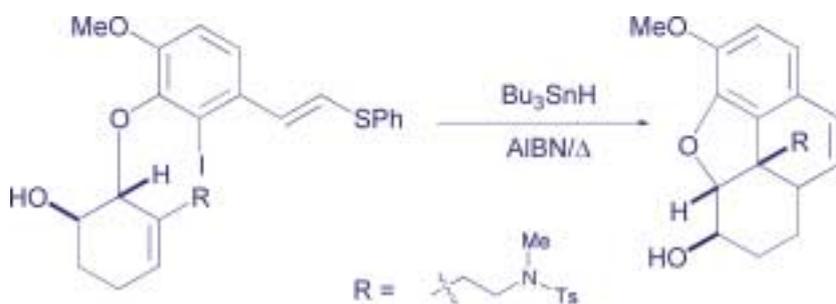
For Ir rate = $k[\text{Ir}][\text{CO}]$ independent of MeI above a threshold level

$\text{A} \rightarrow \text{B}$ is 120 times faster for Ir,

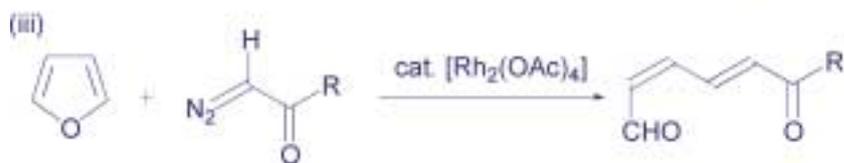
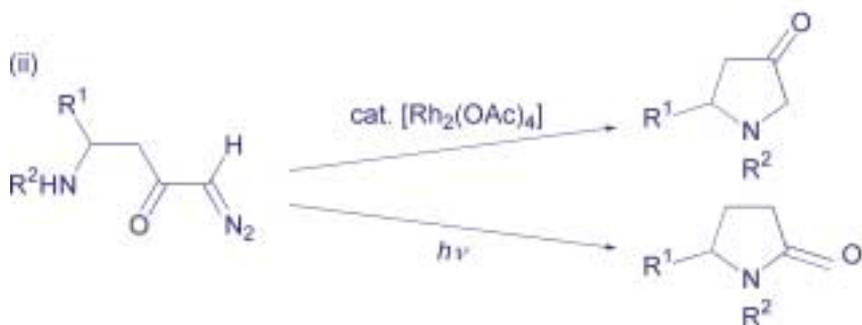
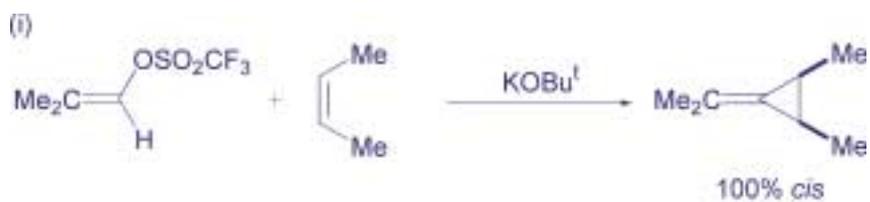
$\text{D} \rightarrow \text{E}$ is 10^5 times slower than $\text{B} \rightarrow \text{C}$.

- (iii) How are acetic acid and methyl iodide generated in the carbonylation process?

- B35** (a) In a synthesis of the painkiller codeine, free-radical chemistry has been used to assemble part of the multiple ring system. The key step shown below, involves three consecutive radical processes which occur after initial radical generation. Identify these processes, explaining the transformation mechanistically.



- (b) Rationalise the following transformations, giving as much mechanistic detail as possible:



B36

A regression model for the determination of potassium in a variety of geological samples using X-ray fluorescence is required. Multivariate regression is to be used in order to compensate for interferences from other components of the sample matrix. A total of 30 different natural geological samples are obtained and the concentration of potassium is determined in each sample by the use of a reference method. The 30 samples are divided into a calibration set (20 samples), a test set (5 samples) and a validation set (5 samples). X-ray fluorescence spectra of the calibration, test and validation samples are obtained and it is decided to use principal component regression (PCR) to build the model.

- (a) Describe the rationale for the choice of principal component regression, rather than multiple linear regression, for this particular problem.
- (b) The predicted concentration of potassium in each of the 5 test set samples obtained from models using a different number of principal components is shown in table 1 along with the concentration of potassium determined by the reference method. Determine the optimum number of principal components to be included in the PCR model.

| Test set sample number | Table 1 | | | | | | Reference method concentration / $\mu\text{g g}^{-1}$ |
|------------------------|--|------|------|------|------|------|---|
| | Concentration of potassium predicted by PCR model / $\mu\text{g g}^{-1}$ | | | | | | |
| | Number of PCs in model | | | | | | |
| | 1 | 2 | 3 | 4 | 5 | 6 | |
| 1 | 4.05 | 3.85 | 3.06 | 2.95 | 3.02 | 3.95 | 3.02 |
| 2 | 3.98 | 2.25 | 1.65 | 1.75 | 1.65 | 1.09 | 1.74 |
| 3 | 12.07 | 5.84 | 5.13 | 5.21 | 5.82 | 4.63 | 5.07 |
| 4 | 6.16 | 3.85 | 2.08 | 2.36 | 2.33 | 1.38 | 2.12 |
| 5 | 5.88 | 5.62 | 3.68 | 3.73 | 4.02 | 4.45 | 3.77 |

- (c) Give the equations for the standard error of prediction and for the bias, with respect to an independent validation data set. Explain how these statistics test the predictive performance of a multivariate regression model.
- (d) The predicted concentration of potassium of each of the validation set is shown in table 2, for PCR models with a different number of principal components, along with the concentration of potassium determined by the reference method. Using your answer from (b) to determine the optimum number of PCs for the model, comment upon the predictive ability of the regression model.

| Validation sample number | Table 2 | | | | | | Reference method concentration / $\mu\text{g g}^{-1}$ |
|--------------------------|--|------|------|------|------|------|---|
| | Concentration of potassium predicted by PCR model / $\mu\text{g g}^{-1}$ | | | | | | |
| | Number of PCs in model | | | | | | |
| | 1 | 2 | 3 | 4 | 5 | 6 | |
| 1 | 3.89 | 2.58 | 1.59 | 1.66 | 1.41 | 1.33 | 1.55 |
| 2 | 6.00 | 3.66 | 2.59 | 2.59 | 2.90 | 2.54 | 2.69 |
| 3 | 54 | 6.14 | 4.86 | 5.02 | 5.16 | 4.85 | 4.95 |
| 4 | 8.97 | 4.62 | 3.75 | 3.75 | 4.32 | 3.99 | 3.66 |
| 5 | 3.96 | 3.00 | 1.52 | 1.24 | 1.84 | 1.36 | 1.29 |

- (e) State, giving reasons, whether the calibration model for K should be used in the following circumstances:
- For the prediction of the concentration of potassium in geological samples whose composition is similar to those used in the calibration set.
 - For the prediction of the concentration potassium in geological samples whose composition differs from those used in the calibration set.
 - For the prediction of the concentration of potassium in plant material.

- B37** (a) $[\text{PtH}_4]^{2-}$ is used as a model for the theoretical study of electronic structure and bonding in column-stacked mixed valence square planar platinum complexes. Given the D_{4h} character table, derive symmetry-adapted linear combinations of the four H atom 1s orbitals and give their symmetry species (irreducible representations). Give the symmetry species of all the Pt valence orbitals ($5d$, $6s$, and $6p$). Hence construct a qualitative molecular orbital energy level diagram for $[\text{PtH}_4]^{2-}$, taking the H 1s orbitals to be of lower energy than the orbitals of Pt. Indicate clearly which Pt orbitals remain non-bonding, and which molecular orbitals contain electrons.
- Now consider the approach of two axial (z axis) ligands with only σ -bonding capability. Construct symmetry adapted linear combinations of these two orbitals and show which orbitals on Pt can interact with them.
- (b) A new volatile molecular compound of low thermal stability is believed to be PF_2H_3 . Its infrared and Raman spectra show bands assigned to stretching vibrations at the following wavenumbers (in cm^{-1}):

| Infrared | Raman |
|---------------|---------------------------|
| 2488 <i>w</i> | 2488 <i>m</i> , <i>dp</i> |
| 722 <i>vs</i> | 2419 <i>s</i> , <i>p</i> |
| | 578 <i>s</i> , <i>p</i> |

s = strong; *vs* = very strong; *m* = medium; *w* = weak;
p = polarised ($\rho < \frac{3}{4}$); *dp* = depolarised ($\rho = \frac{3}{4}$).

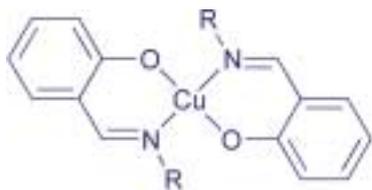
Consider whether these results are consistent with the formulation of the compound as PF_2H_3 and, if so, what they tell you about the likely structure of the compound.

B38

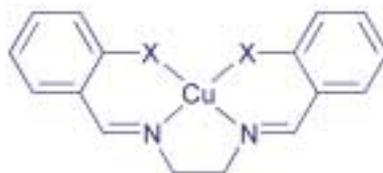
- (a) Explain *briefly* the term *zinc-finger peptide*
- (b) Artificial analogues of zinc fingers with metal ions other than zinc at the metal-binding sites can be prepared. For a cobalt-containing peptide of this type, the dissociation constant for Co^{2+} , determined spectrophotometrically, is $3.8 \times 10^{-6} \text{ mol dm}^{-3}$. The affinity of the peptide for zinc ions may be determined by titrating the Co^{2+} peptide with $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ in the presence of an excess of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (equation 1), giving a value of $2.8 \times 10^{-9} \text{ mol dm}^{-3}$ for the dissociation constant for Zn^{2+} , from peptide- Zn^{2+}



- (i) Calculate the free energy change for displacement of Co^{2+} by Zn^{2+} in the peptide.
- (ii) Given that $\Delta o \approx 9300 \text{ cm}^{-1}$ for $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $\Delta t \approx 4900 \text{ cm}^{-1}$ for $[\text{peptide-Co}^{2+}]$, estimate the change in ligand-field stabilisation energy that accompanies the displacement reaction.
- (iii) Compare your answers to (i) and (ii) and comment on the implications for the selection of zinc in nature in such peptides. How would you expect the binding of Mn^{2+} to compare with that of Co^{2+} ?
- (c) Discuss the importance of the coordination geometry at the metal-binding site, and the nature of the ligating atoms, on the chemistry of copper proteins in electron-transfer reactions and in oxygen transport. Include in your discussion an interpretation of the standard electrode potential, E^0 , for the $\text{Cu}^{2+}/\text{Cu}^+$ process in the model compounds below.



| R | E^0 |
|---------------------------|---------|
| CH_3 | -0.90 V |
| $(\text{CH}_3)_3\text{C}$ | -0.66 V |



| X | E^0 |
|---|---------|
| O | -1.21 V |
| S | -0.83 V |

- B39** (a) Three different kinds of Fe/S cluster are used in nature. Draw a clear diagram of each cluster, indicate which oxidation states are used for electron transfer, and explain how redox information would be obtained experimentally.
- (b) First-order rate constants, k_{obs} , for oxidation of *Clostridium pasteurianum* ferredoxin with a range of inorganic oxidants (298 K; pH 8.0; [ferredoxin] = 10^{-6} mol dm $^{-3}$) are tabulated below.

| | | | | | |
|---|-----|------|------|------|------|
| $10^4[\text{Co}(\text{C}_2\text{O}_4)_3^{3-}] / \text{mol dm}^{-3}$ | 2.0 | 4.0 | 7.0 | 10.0 | 20.0 |
| $k_{\text{obs}}/\text{s}^{-1}$ | 1.0 | 2.0 | 3.2 | 4.8 | 9.5 |
| $10^4[\text{Co}(\text{edta})^-] / \text{mol dm}^{-3}$ | 5.0 | 8.0 | 12.1 | 16.1 | 20.1 |
| $k_{\text{obs}}/\text{s}^{-1}$ | 5.6 | 9.1 | 13.0 | 16.5 | 23.8 |
| $10^4[\text{Co}(\text{acac})_3] / \text{mol dm}^{-3}$ | 0.8 | 1.7 | 3.4 | 5.4 | 7.8 |
| $k_{\text{obs}}/\text{s}^{-1}$ | 3.0 | 5.5 | 10.4 | 16.9 | 23.8 |
| $10^4[\text{Pt}(\text{NH}_3)_6]^{4+} / \text{mol dm}^{-3}$ | 0.8 | 1.5 | 2.9 | 3.2 | 5.8 |
| $k_{\text{obs}}/\text{s}^{-1}$ | 8.8 | 14.5 | 22.0 | 23.8 | 29.4 |

- (i) Plot the data in a suitable graphical form and propose a mechanism for the reaction.
- (ii) What does the graph suggest about the nature of the electron transfer site for the inorganic complexes? Give an expression for k_{obs} and use this to account qualitatively for the different behaviour of each complex.
- (iii) For the complex ion $[\text{Pt}(\text{NH}_3)_6]^{4+}$, show how linearisation of the data can be used to gain additional mechanistic information. Hence calculate the magnitude of the association constant and the rate constant for the electron transfer (giving units).

[edta = ethylenediaminetetraacetate; acac = acetylacetonate]

- B40** (a) The bulk scale benzoylation of glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) is monitored by ^1H NMR spectroscopy. After the first stage of the reaction the product mixture contains some unchanged diol, the monobenzoate and the dibenzoate, and the ^1H spectrum shows bands for the methylene groups $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{OBz}$ in the ratio 0.54:1.00. A second stage of the reaction is carried out at a lower temperature such that the monobenzoate will not react further. After this second stage the diol is totally consumed and the ^1H spectrum shows that the ratio of the methylene groups is now 0.33:1.00. Determine the molar percentage composition of the mixture after the first stage.
- (b) Describe the rules which determine the number and relative intensity of lines in an NMR multiplet when coupling is present to spins with $I = 1/2$ and $I = 1$. Illustrate your answer with reference to the species F_3CCD_3 .

B41 (a) Identify the isomers which would be possible for the cluster of molecular formula $K[H_2RhOs_3(CO)_{12}]$.

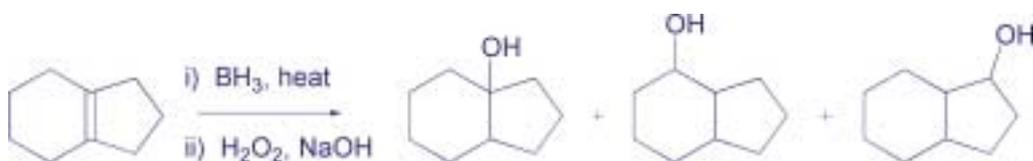
The 1H NMR spectrum of a solution of $K[H_2RhOs_3(CO)_{12}]$ shows two doublets of relative intensity 1:10 with a coupling constant of 20 Hz for the doublet of intensity 1 and 10 Hz for the doublet of intensity 10. The relative intensity of the lines was found to vary with the temperature. There was a number of bands in the IR spectrum in the region of 1900 cm^{-1} and weak bands in the region of 1500 cm^{-1} . On deuteration the bands at 1900 cm^{-1} were unaffected whilst the bands at 1500 cm^{-1} were replaced by absorption at 1100 cm^{-1} . The IR spectrum also showed a variation in the relative intensity of the bands at 1900 and 1500 cm^{-1} with temperature. On thermolysis, two new complexes were isolated, $HRhOs_4(CO)_{15}$ and $HRhOs_4C(CO)_{14}$.

Suggest possible structures for the above species.

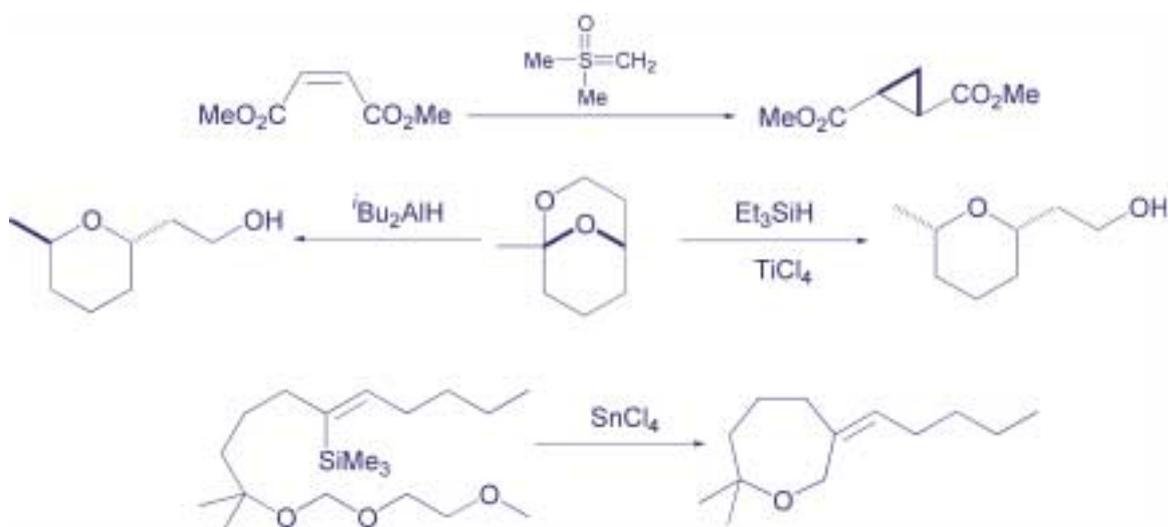
$[Rh, I = \frac{1}{2}, 100\%]$

(b) Pentanuclear clusters are found in a wide variety of structural types. Give examples of these and show how Wade Mingos rules and the extended 18e-rule can be used in structure rationalisation. Include in your answer the following pentanuclear compounds; Pb_5^{2-} , Bi_5^{3+} , Tl_5^{7-} , $Fe_3(CO)_9(Se)_2$, and $C_2B_3H_5$.

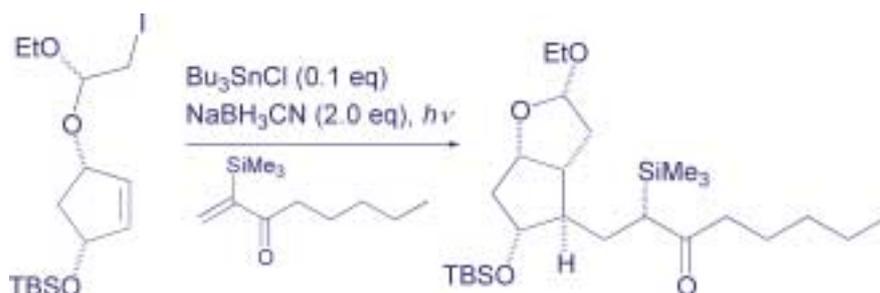
B42 (a) Account mechanistically for the formation of the following mixture of isomeric alcohols, and predict the likely stereochemistries.



(b) Account mechanistically for the products formed in each of these reactions and explain any selectivity.

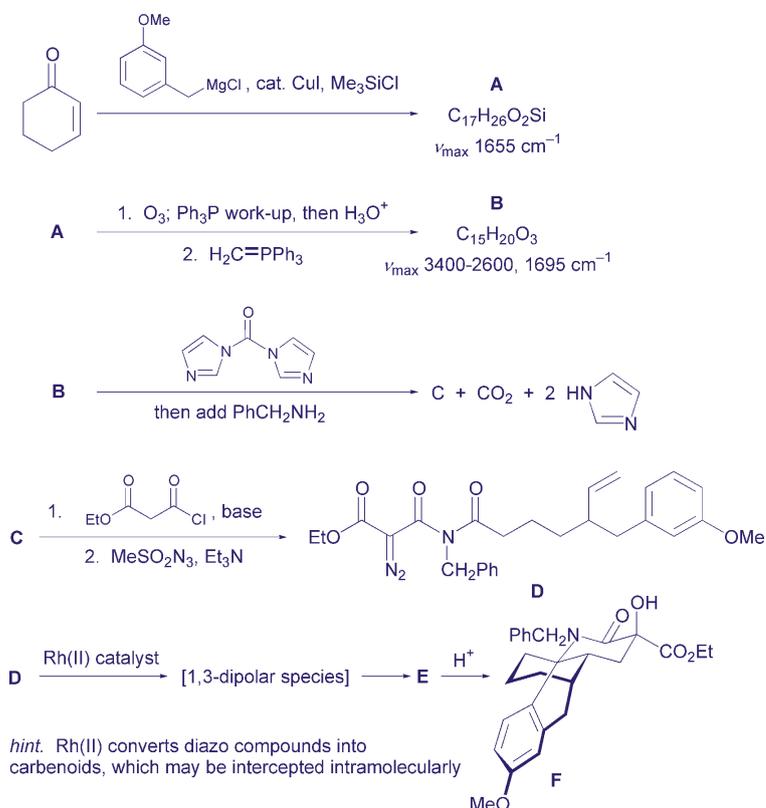


- (c) Account for the following reaction, explaining the selectivity. Why was this procedure preferred to the simple use of a stoichiometric amount of Bu_3SnH ?



B43

Suggest structures for the lettered compounds **A**, **B**, **C** and **E** in the synthetic sequence below, which was developed as part of a programme directed towards the synthesis of the alkaloid lycopodium. Assign the infrared data given for **A** and **B**. Give a mechanism for the conversion of **B** into **C**, the formation of **E** from **D**, and of the cyclisation reaction which occurs to give **F** when **E** is treated with acid.



B44 An electrochemical cell is set up in which the reduction process



occurs at the cathode when a suitable potential is applied. The current flowing as the cathode is made increasingly negative depends on the rate of potential change, and has the form indicated in Figure 1.

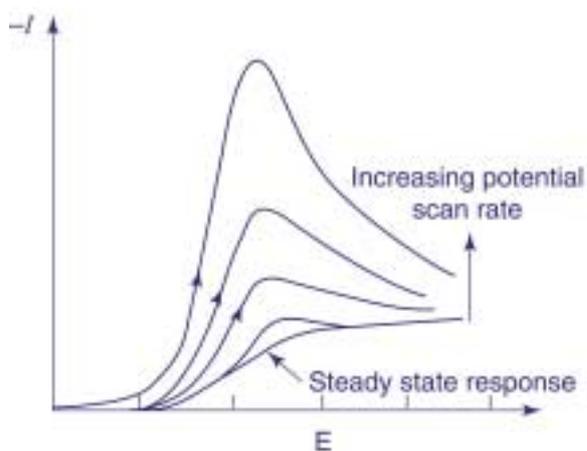


Figure 1

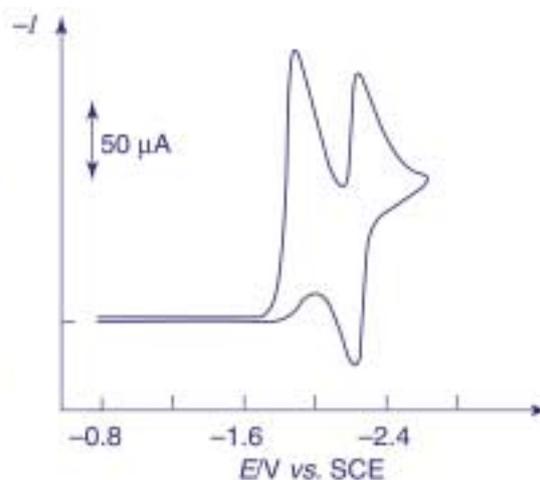
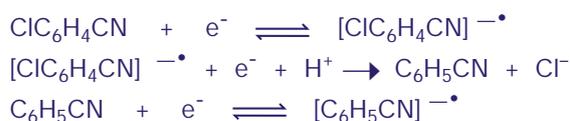


Figure 2

- (a) Explain the appearance of the curves in Figure 1, labelling any key values on the potential axis. What might the current response look like when the potential sweep is reversed? Discuss the types of information that can be obtained from measurements of the currents produced by cyclic forward and reverse potential sweeps.
- (b) The reduction of 4-chlorobenzonitrile is postulated to occur via the mechanism



The second step is assumed to be irreversible. A cyclic voltammogram for a solution of 4-chlorobenzonitrile in dimethylformamide is shown in Figure 2. Show that this voltammogram is consistent with the proposed mechanism. Predict the appearance of the cyclic voltammogram for unsubstituted benzonitrile.

B45 The molecular ion group ($m/z = 138, 139, 140$) in the 70 eV electron bombardment mass spectrum of an organic compound showed the following relative intensities:

| | | |
|------------------|-----------------|--------|
| M^+ | ($m/z = 138$) | 84.30% |
| $\text{M}^+ + 1$ | ($m/z = 139$) | 6.17% |
| $\text{M}^+ + 2$ | ($m/z = 140$) | 0.52% |

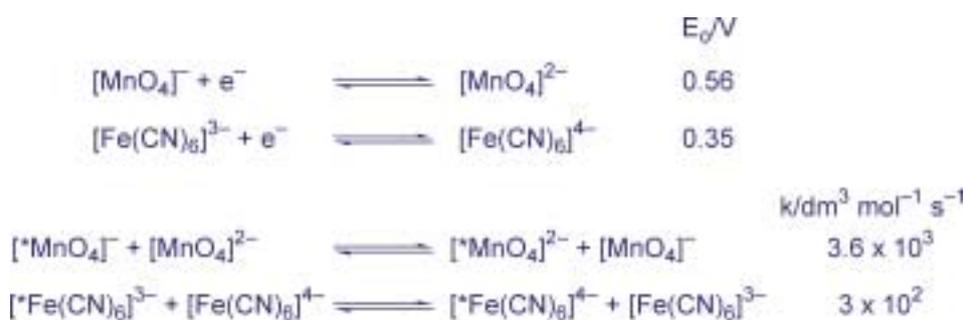
The relative abundance of the ^{15}N and ^{18}O isotopes are 0.36% and 0.20% respectively. Calculate the empirical formula of the molecular ion.

The major fragment ions in the spectrum occurred at $m/z = 122, 92, 76, 75, 74$ and 52. Identify the molecular formula of the compound as completely as possible.

- B46**
- (a) Assuming a dissociative (D) mechanism show how calculations of CFAE for octahedral transition metal complexes may be used to predict the relative labilities of the aqueous ions of Cr^{2+} ($3d^4$), Ni^{2+} ($3d^8$), Cr^{3+} ($3d^3$) and Ga^{3+} ($3d^{10}$). Assume that for a square pyramidal complex the relative energies of the d-orbitals (in units of Dq , where $\Delta_o = 10 Dq$) are as follows: d_{xz} , d_{yz} , -4.57 ; d_{xy} , -0.86 ; d_{z^2} , $+0.86$; $d_{x^2-y^2}$, $+9.14$.
- (b) Given the reagents PPh_3 , pyridine and $[\text{PtCl}_4]^{2-}$, propose efficient syntheses of the *cis* and *trans* isomers of $[\text{Pt}(\text{PPh}_3)(\text{py})\text{Cl}_2]$. Explain the stereochemical outcome of each synthetic step.
- (c) Calculate the rate constant for the following reaction using the Marcus equation.



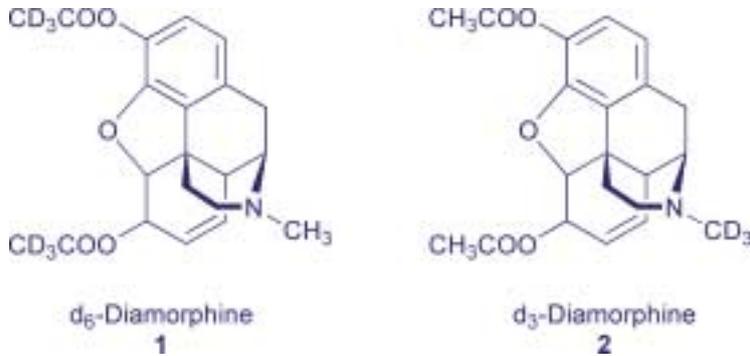
Use the following data for the isotopic exchange reactions at 25 °C.



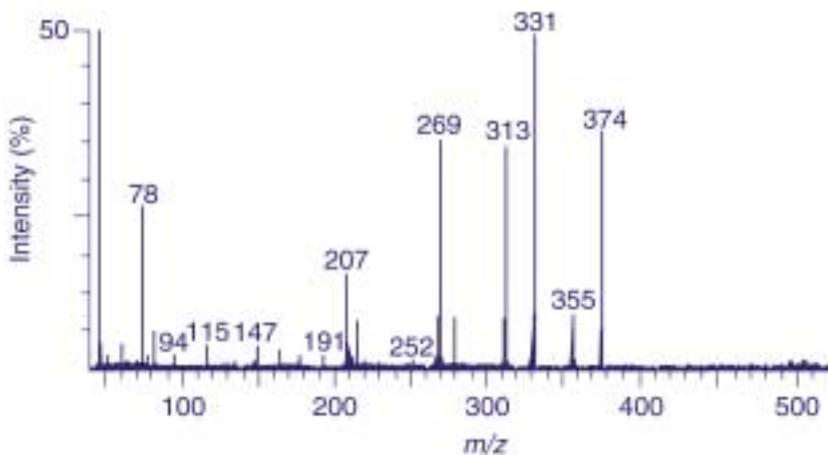
B47

You have been requested to develop a method for the quantitative determination of diamorphine in a sample of heroin, using gas chromatography–mass spectrometry (GC-MS), with a deuterated internal standard.

- Explain the desirable characteristics of a suitable internal standard for such an analysis.
- Deuterated internal standards are not available and you are requested to synthesise your own standard.



- Evaluate why d₆-diamorphine (1) is a more suitable internal standard than d₃-diamorphine (2).
 - Explain how you would synthesise and purify d₆-diamorphine from the commonly available opiate morphine.
- c) The electron impact mass spectrum of d₆-diamorphine, after GC-MS analysis, is shown below



Interpret this mass spectrum as far as you are able.

- d) Explain how you would use the d₆-diamorphine to quantify diamorphine in a heroin sample.



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