

THE UNIVERSITY OF EDINBURGH
College of Science and Engineering
School of Chemistry



Chairman of the Board of Examiners: Professor S K Chapman
External Examiners: Professors P G Edwards, R J K Taylor and B Vincent
Senior Internal Examiners: Professors R J Donovan, D A Leigh and D W H Rankin and
Dr R M Paton

CHEMISTRY 2

PAPER 2

Thursday 12th May 2005, 09.30 - 12.30

Answer ALL questions.

Please answer each question in a separate book.

[The bracketed numbers shown against part of a question are only a guide to the likely allocation of marks in that question.]

This examination will be marked anonymously.

Please enter your student examination number on each answer book.

A data sheet is provided with this examination paper.

Unassembled molecular model kits may be used in this examination.

Only the calculator provided may be used in this examination.

1. Answer **ANY FOUR** of the following **six** parts (a), (b), (c), (d), (e), and (f).
- (a) Outline synthetic routes to each of the following compounds.
- (i) SnI_4
 - (ii) Anhydrous AlCl_3
 - (iii) ND_3
 - (iv) DCl
 - (v) $\text{DC}\equiv\text{CD}$ **[5]**
- (b) Use the following bond-dissociation energies (in kJ mol^{-1}) to explain why NF_3 is more stable than NCl_3 with respect to decomposition to N_2 and the respective halogen.
- | | | |
|------------------------------|--------------------------------|--|
| $\text{D}(\text{N-F}) = 278$ | $\text{D}(\text{N-Cl}) = 190$ | $\text{D}(\text{N}\equiv\text{N}) = 946$ |
| $\text{D}(\text{F-F}) = 158$ | $\text{D}(\text{Cl-Cl}) = 243$ | [5] |
- (c) Astatine, At, is a short-lived radioactive element. Predict the types of structures adopted by CaAt_2 and BAt_3 under normal conditions, and the products formed if these compounds were added to water. **[5]**
- (d) Explain the concept of electronegativity. How does electronegativity affect heteronuclear bond dissociation energies? **[5]**
- (e) How do the first ionisation energies of the elements vary along the first period (Li-Ne) and down most groups? Account for these variations. **[5]**
- (f) Explain why compounds containing multiple bonds are more common for elements of the first period (Li-Ne) than for those of the second and subsequent periods. **[5]**

2. Answer **all** of part (a) and **EITHER all** of part (b) **OR all** of part (c).

- (a) At 298 K the standard enthalpy of formation for $\text{NH}_3(\text{g})$ is $\Delta H_f^\ominus = -46.1 \text{ kJ mol}^{-1}$. The molar heat capacities of the species involved can be written in the form:

$$C_p^\ominus = \alpha + \beta T,$$

with α and β given in the Table below.

	$\alpha/\text{J K}^{-1} \text{ mol}^{-1}$	$\beta/\text{J K}^{-2} \text{ mol}^{-1}$
$\text{N}_2(\text{g})$	28.58	3.77×10^{-3}
$\text{H}_2(\text{g})$	27.28	3.26×10^{-3}
$\text{NH}_3(\text{g})$	29.75	25.1×10^{-3}

- (i) Write down the balanced chemical equation for which the enthalpy change of reaction is the standard enthalpy change of formation of $\text{NH}_3(\text{g})$. **[3]**
- (ii) For the reaction in part (a) (i), write down an expression for $\Delta C_p^\ominus$ in terms of the heat capacities of the reactants and products. Use the data in the Table to express $\Delta C_p^\ominus$ in the form:

$$\Delta C_p^\ominus = A + BT,$$

and compute the parameters A and B . **[7]**

- (iii) The standard entropies at 298 K of $\text{NH}_3(\text{g})$, $\text{H}_2(\text{g})$ and $\text{N}_2(\text{g})$ are $192.5 \text{ J K}^{-1} \text{ mol}^{-1}$, $130.7 \text{ J K}^{-1} \text{ mol}^{-1}$ and $191.6 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. Use these data to calculate the standard entropy change of the reaction you have written in part (a) (i) at 298 K. **[2]**

- (b) You are given the relation:

$$\Delta H_f^\ominus(T_2) = \Delta H_f^\ominus(T_1) + \int_{T_1}^{T_2} \Delta C_p^\ominus dT.$$

- (i) Calculate, by integration, an expression for $\Delta H_f^\ominus(T_2)$ in terms of A and B using the relation $\Delta C_p^\ominus = A + BT$ as in part (a) (ii). Calculate also $\Delta H_f^\ominus(T_1)$. **[4]**
- (ii) Using the expression obtained in part (b) (i), calculate the standard enthalpy change of formation of $\text{NH}_3(\text{g})$ at 1000 K using the values of A and B that you found in part (a) (ii). **[4]**

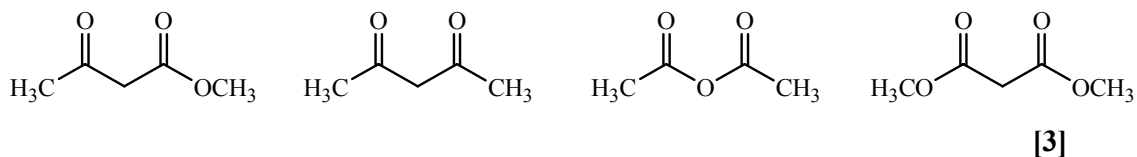
- (c) You are given the relation:

$$\Delta S_f^\ominus(T_2) = \Delta S_f^\ominus(T_1) + \int_{T_1}^{T_2} \frac{\Delta C_p^\ominus}{T} dT.$$

- (i) Calculate, by integration, an expression for $\Delta S_f^\ominus(T_2)$ in terms of A and B using the relation $\Delta C_p^\ominus = A + BT$ as in part (a) (ii). Calculate also $\Delta S_f^\ominus(T_1)$. **[4]**
- (ii) Using the expression obtained in part (c) (i), calculate the standard entropy change of formation of $\text{NH}_3(\text{g})$ at 1000 K. **[4]**

3. Answer **all** of part of (a) and **EITHER** part (b) **OR** part (c).

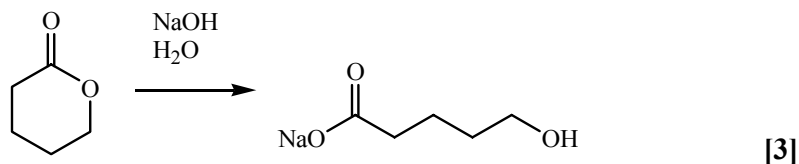
(a) (i) Place the following compounds in order of acidity (most acidic first).



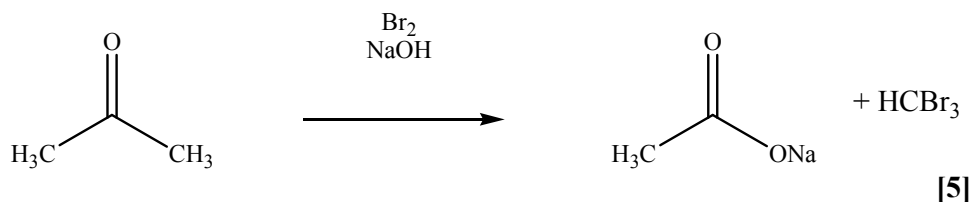
(ii) What is the product **A** from the following reaction? Show the mechanism by which it is produced.



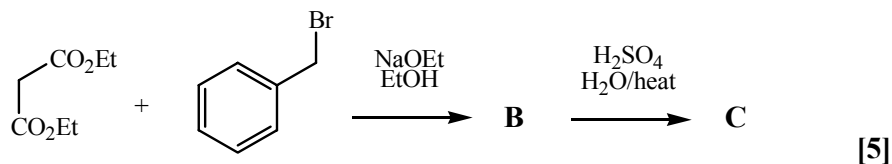
(iii) Give the mechanism for the following transformation.



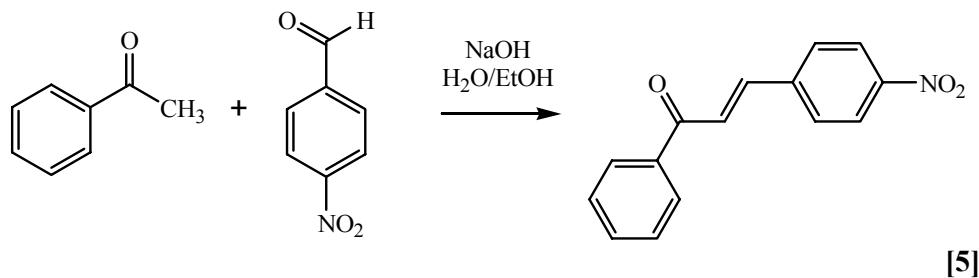
(iv) Give the mechanism for the following reaction.



(b) Identify **B** and **C** in the following transformations and suggest mechanisms for their formation.



(c) Give the mechanism for the following reaction.



4. Answer **all** of part (a) and **EITHER all** of part (b) **OR all** of part (c).
- (a) (i) Calculate the total valence-electron count for the following complexes using both covalent and ionic methods of electron counting where appropriate.
[Fe(CO)₅] [Mn(CO)₆]⁺ [HCo(CO)₄] **[5]**
- (ii) For the complex [Co(H₂O)₆]²⁺, give the oxidation state of Co, state the number of *d* electrons, explain whether the complex is high-spin or low-spin and calculate the spin-only magnetic moment. **[5]**
- (b) (i) Using suitable diagrams to illustrate your answer, describe the bonding interactions that take place between a transition-metal atom and carbon monoxide in a metal carbonyl complex. **[5]**
- (ii) Describe the effect each of the interactions you identify in part (b) (i) has on the strength of the C-O bond and the frequency of its stretching vibration (ν_{CO}). **[5]**
- (c) (i) Explain what is meant by a ligand *cone angle*. For trivalent phosphines, show with the aid of a diagram how the cone angle is defined. What are the main limitations in the use of cone angles to rationalise the behaviour of complexes? **[7]**
- (ii) Suggest reasons why trivalent phosphine ligands are very commonly used in transition-metal chemistry. **[3]**

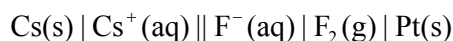
5. Answer **any TWO** of the following **three** parts, (a), (b) and (c).

- (a) (i) Give succinct accounts of the solvation of Na^+ and Cl^- ions by water, paying attention to how the water molecules are organised in the vicinities of the ions, and the molecular forces chiefly responsible for these types of ordering. [5]
- (ii) In a salt solution at low but finite concentration, the interaction energy between a Na^+ ion and a Cl^- ion separated by a large distance r is proportional to:

$$-\frac{1}{r} \times \exp(-r/\lambda_D),$$

where λ_D is the Debye length. Describe the physical mechanism responsible for the ' $\exp(-r/\lambda_D)$ ' factor that modifies the original Coulomb interaction energy. [5]

(b) Consider the following electrochemical cell at $T = 298 \text{ K}$:



- (i) For each half cell write down the potential determining equilibrium as a one-electron reduction, and hence derive the formal cell reaction for the cell as specified. [3]
- (ii) From the data given below, calculate the standard cell potential, $E_{\text{cell}}^\ominus$, and the standard Gibbs free energy change, $\Delta G^\ominus$, for the formal cell reaction. [3]
- (iii) Upon raising (lowering) the temperature by 5 K, the standard cell potential decreases (increases) by 0.003 V. Estimate the standard enthalpy and entropy changes for the formal cell reaction. [4]

$$[\text{At } T = 298 \text{ K: } E^\ominus(\text{Cs} \mid \text{Cs}^+) = -2.92 \text{ V; } E^\ominus(\text{F}^- \mid \text{F}_2) = +2.87 \text{ V.}]$$

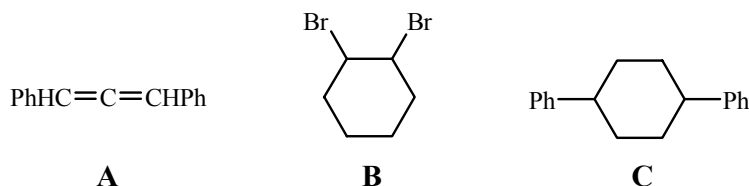
(c) The limiting molar conductivities of some simple electrolytes in aqueous solutions are given in the Table below.

Electrolyte	LiNO_3	HF	HNO_3
$\Lambda_m^0 / \text{S cm}^2 \text{ mol}^{-1}$	110	405	421

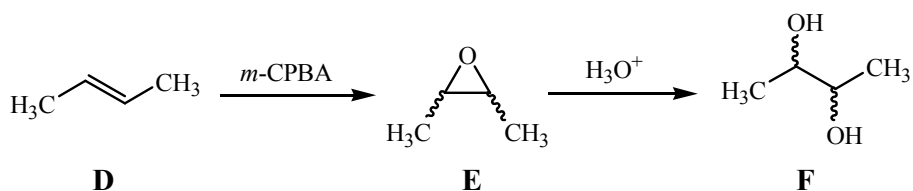
- (i) Calculate the limiting molar conductivity of LiF . [2]
- (ii) Explain why $\Lambda_m^0(\text{LiNO}_3) \ll \Lambda_m^0(\text{HNO}_3)$. [2]
- (iii) Explain why $\Lambda_m^0(\text{HF}) < \Lambda_m^0(\text{HNO}_3)$. [2]
- (iv) Explain why the molar conductivities of weak-electrolyte solutions and strong-electrolyte solutions decrease with increasing electrolyte concentration. [4]

6. Answer **all** of part (a) **and EITHER all** of part (b) **OR all** of part (c).

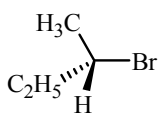
- (a) (i) Define the terms *enantiomer* and *diastereomer*. [2]
- (ii) For **each** of the following molecules, **A - C**, draw **all** possible stereoisomers, and indicate whether the structures you have drawn are related as enantiomers or diastereomers. [9]

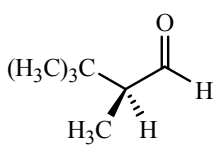


- (b) Consider the following reaction sequence:



(*m*-CPBA = *meta*-chloroperbenzoic acid = *m*-ClC₆H₄CO₃H)

- (i) Provide a mechanism for the conversion of the alkene **D** into the epoxide **E**, and draw **all** of the possible stereoisomers of **E** that can result. (Bear in mind the stereochemistry of the starting alkene **D**.) [3]
- (ii) Provide a mechanism for the conversion of the epoxide **E** into the diol **F**, and draw **all** of the possible stereoisomers of **F** that can result. (Bear in mind the stereochemistry of the epoxide **E**.) [3]
- (iii) Use appropriate examples from the reaction sequence depicted above to illustrate the terms *chiral*, *racemic*, and *meso*. [3]
- (c) For the reactions in part (c) (i) and part (c) (ii), give the structures of the unknown products and provide detailed mechanisms to account for the stereochemical outcomes.
- (i)
- 
 $\xrightarrow{\text{NaSEt}}$

G
- [3]
- (ii)
- 
 $\xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{PhMgBr}}$

H
- [4]
- (iii) Use the appropriate example(s) from part (c) (i) and/or part (c) (ii) above to illustrate the terms *stereoselective* and *stereospecific*. [2]