

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



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CHEMISTRY 2

PAPER 2

Thursday 23rd August 2007, 2.30 pm – 5.30 pm

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 BeCl_2
 - (iii) PD_3
 - (iv) DCl
 - (v) $\text{DC}\equiv\text{CD}$ [5]
- (b) Explain the concept of electronegativity. How does electronegativity affect heteronuclear bond-dissociation energies? [5]
- (c) Explain why the bond-dissociation energies of the halogens vary in the order $\text{F-F} < \text{Cl-Cl} > \text{Br-Br} > \text{I-I}$. [5]
- (d) State the formal oxidation state of chlorine in **each** of the following compounds and draw the shape of each molecule or ion.
- (i) GeCl_4
 - (ii) ClF_3
 - (iii) $[\text{ClO}_4]^-$ [5]
- (e) Give reasons why IF_5 may be prepared, but all attempts to prepare ICl_5 have been unsuccessful. [5]
- (f) (i) Explain why there are two different types of B-H bond in B_2H_6 .
- (ii) Give two experimental techniques that would confirm the presence of two different types of B-H bond in B_2H_6 . [5]

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

- (a) The shells of marine organisms contain CaCO_3 mostly in the crystalline form known as calcite. Another crystalline form of CaCO_3 is known as aragonite. Some thermodynamic data for each of these substances at 298 K are given in the following table.

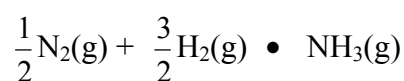
	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	$\Delta G_f^\ominus / \text{kJ mol}^{-1}$	Density / g cm^{-3}
CaCO_3 (calcite)	-1206.87	-1128.76	2.71
CaCO_3 (aragonite)	-1207.04	-1127.71	2.93

- (i) Use the thermodynamic data in the table to determine the standard enthalpy change, $\Delta H_r^\ominus$, for the reaction: calcite $\rightarrow$ aragonite. [2]
- (ii) Based on the thermodynamic data in the table, would calcite convert spontaneously to aragonite given time? Justify your answer. [3]
- (iii) Calculate the pressure required to make the process spontaneous, at a constant temperature of 298 K. The relative molar mass of CaCO_3 is 80 g mol^{-1} . [5]
- (b) (i) The heat capacity at constant pressure, C_p , for ammonia gas varies with temperature T as follows:

$$C_p = a + bT + cT^{-2}$$

The coefficients a , b and c have the values $29.75 \text{ J K}^{-1} \text{ mol}^{-1}$, $25.10 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}$ and $1.55 \times 10^5 \text{ J K mol}^{-1}$, respectively. If the standard entropy $S_{298}^\ominus$ for NH_3 at 298 K is $192.45 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate the standard entropy for NH_3 at 773 K. [5]

- (ii) The reaction between hydrogen and nitrogen on heating over an iron catalyst is an important industrial route to ammonia, which is known as the Haber Process and which may be represented by the equation :



This reaction runs efficiently at 773 K, at which temperature the standard entropies of nitrogen and hydrogen are 222.1 and $149.1 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively, and the standard enthalpy of the reaction is $-51.8 \text{ kJ mol}^{-1}$. Calculate the free-energy change for the Haber Process at 773 K and predict whether the equilibrium concentration of ammonia will increase or decrease if the temperature of the reaction is reduced at constant pressure. [5]

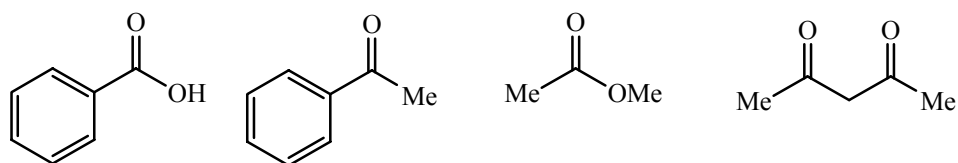
Question 2 is continued on the following page.

Question 2 continued.

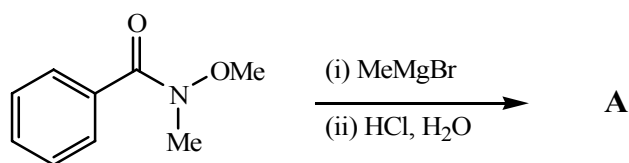
2. (c) (i) One mole of an ideal gas, initially at 298 K, is compressed adiabatically and irreversibly to half its initial volume. State whether each of the thermodynamic quantities, q , w , ΔU and ΔS , for the system is greater than, equal to or less than zero. Calculations are not necessary but you must explain your reasoning. [4]
- (ii) Two identical flasks, each of volume V , are connected via a tap. Initially, one flask contains one mole of an ideal gas at 298 K, while the other flask is completely empty (i.e. it is under vacuum). The flasks are immersed in an ice/water bath at atmospheric pressure. At some point the tap is opened and sufficient time is allowed for the system to reach equilibrium. The entire experiment, consisting of the flasks and the ice/water bath are thermally isolated from the rest of the laboratory. Calculate, w , ΔU , q , and ΔS as a result of the process that the system (the ideal gas) undergoes. [6]

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

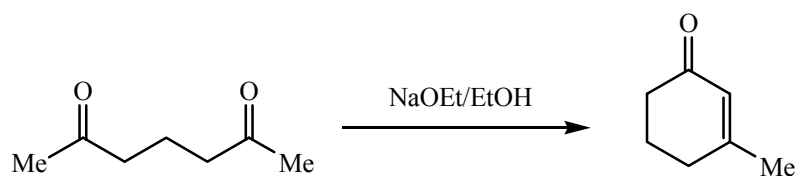
(a) (i) Place the following compounds in order of acidity (most acidic first). [3]



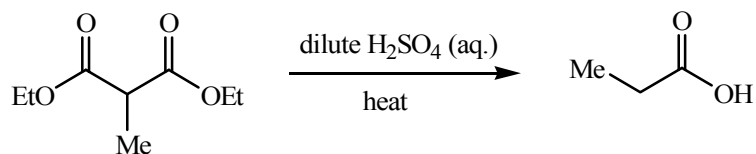
(ii) What is the product **A** from the following reaction? Show the mechanism by which it is produced. [3]



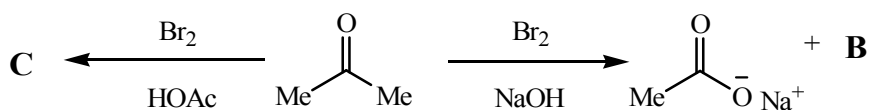
(iii) Give the mechanism for the following transformation. [3]



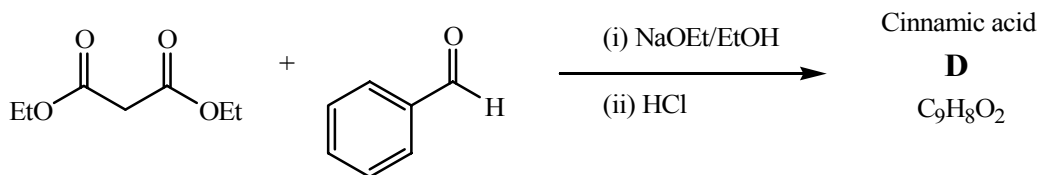
(iv) Provide the mechanism for the following transformation.



(b) What are the products **B** and **C** from the following reactions? Provide mechanisms for the formation of **B** and **C** from propanone. [7]



(c) Show the mechanism by which cinnamic acid (**D**) is produced from diethyl malonate and benzaldehyde: [7]



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

- (a) (i) Cobalt forms a cluster complex with the formula $[\text{Co}_3(\text{CO})_{10}]^-$, which displays absorptions due to CO stretching vibrations in the following three regions of its IR spectrum: 2030, 1850, 1740 cm^{-1} . Using this information and the 18-electron rule, deduce the number of metal-metal bonds in the cluster and the coordination modes of the CO ligands, and thus predict its structure. [5]
- (ii) For the complex $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3]$, give the oxidation state of the metal, state the number of d electrons, explain whether the complex is expected to be high-spin or low-spin and draw clearly the isomers for this complex. [5]
- (b) (i) In terms of the characteristics of the metal-ligand bonding, explain how the electronegativity of carbon accounts for the typical properties of ligands that bond to transition metals through carbon [4]
- (ii) Predict the formula of each of the products **A** and **B** in the following reactions.
- $$\text{Mn}_2(\text{CO})_{10} + 2\text{Na} \rightarrow \text{A}$$
- $$\text{Mn}_2(\text{CO})_{10} + \text{Br}_2 \rightarrow \text{B} \quad [2]$$
- (iii) Explain why the energy of the CO stretching vibrations is higher in **B** than in **A**. [4]
- (c) Explain the following observations.
- (i) In the complex $[\text{Cr}(\text{NCS})_6]^{3-}$, the ligand NCS^- coordinates to the metal through the nitrogen atom rather than through the sulfur atom. [2]
- (ii) $[\text{Ni}(\text{PR}_3)_4]$ is much more stable when $\text{R} = \text{CH}_3$ than when $\text{R} = \text{C}(\text{CH}_3)_3$. [2]
- (iii) Substitution reactions of the complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ are very slow. [3]
- (iv) The formation constant for $[\text{Ni}(\text{en})_3]^{2+}$ is over 10^{10} times larger than for $[\text{Ni}(\text{NH}_3)_6]^{2+}$. ($\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) [3]

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

- (a) You are given standard electrode potentials (at $T = 298\text{ K}$) for the left-hand-side and right-hand-side electrodes of an electrochemical cell.

Electrode		$E^\ominus/\text{V}$
Left-hand side	$\text{Ag(s)} \mid \text{Ag}^+(\text{aq})$	+ 0.80
Right-hand side	$\text{AgCl(s)} \mid \text{Ag(s)} \mid \text{Cl}^-(\text{aq})$	+ 0.22

- (i) Write down the potential-determining equilibria for the left-hand-side and right-hand-side electrodes as one-electron reductions, and hence determine the formal cell reaction for the electrochemical cell. [3]
- (ii) Calculate the standard cell potential ($E_{\text{cell}}^\ominus$), the Gibbs free energy change ($\Delta G^\ominus$) for the formal cell reaction, and the solubility product (K_{sp}) for silver chloride. [4]
- (iii) Starting from familiar thermodynamic relationships, show that the standard entropy change ($\Delta S^\ominus$) for a formal cell reaction is given by $\Delta S^\ominus = F(dE_{\text{cell}}^\ominus/dT)$ and state any assumptions made. [2]
- (iv) When the temperature is raised by 5 K, the standard cell potential increases by 0.0017 V. Calculate the standard entropy change and standard enthalpy change ($\Delta H^\ominus$) for the formal cell reaction. [3]
- (b) The Debye-Hückel limiting law (DHLL) for an aqueous solution of singly-charged ions in water at $T = 298\text{ K}$ is

$$\log_{10} \gamma_{\pm} = -0.509 \sqrt{I/I^\ominus}$$

where I is the ionic strength and $I^\ominus = 1\text{ mol dm}^{-3}$.

- (i) On a single sketch, indicate how the logarithm of the mean activity coefficient ($\log_{10} \gamma_{\pm}$) varies with ionic strength in an ideal solution, a real electrolyte solution, and according to the DHLL. [4]
- (ii) The solubility product of CuBr is $K_{\text{sp}} = 4.2 \times 10^{-8}$. Calculate the solubilities of CuBr in pure water and in 0.01 M NaCl(aq), and explain any difference between your answers. [4]

Question 5 is continued on the following page.

Question 5 continued.

5. (c) The limiting single-ion conductivities of $\text{H}^+(\text{aq})$ and $\text{CH}_3\text{CO}_2^-(\text{aq})$ are $349.8 \text{ S cm}^2 \text{ mol}^{-1}$ and $40.9 \text{ S cm}^2 \text{ mol}^{-1}$, respectively.

(i) Calculate the limiting conductivity (Λ_0) of $\text{CH}_3\text{CO}_2\text{H}(\text{aq})$. [2]

(ii) Explain why the molar conductivity (Λ_m) of $\text{CH}_3\text{CO}_2\text{H}(\text{aq})$ (a weak electrolyte) decreases with increasing concentration, c . [2]

(iii) If α denotes the degree of dissociation of a weak electrolyte then the molar conductivity is $\Lambda_m = \alpha \Lambda_0$. Calculate the degree of dissociation in $0.005912 \text{ M CH}_3\text{CO}_2\text{H}(\text{aq})$, for which $\Lambda_m = 21.0 \text{ S cm}^2 \text{ mol}^{-1}$. [1]

(iv) Show that the acidity (or dissociation) constant is related to α and c by $K_a = \alpha^2 c / [(1 - \alpha)c^+]$, and calculate its value from your answer to part (c)(iii). [3]

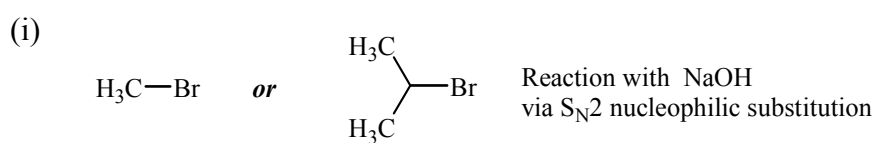
6. Answer **all** of part (a) **and EITHER all** of part (b) **OR all** of part (c).

(a) Describe in detail **each** of the following terms, giving an appropriate example to illustrate your answer:

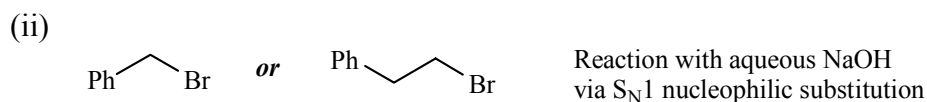
- (i) racemisation,
- (ii) diastereomerism,
- (iii) neighbouring-group participation.

[12]

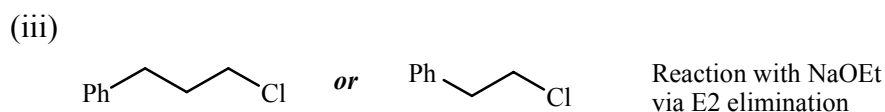
(b) For each of the following pairs of compounds, state with reasons (and/or diagrams if necessary) which compound of each pair will react faster via the indicated mechanism.



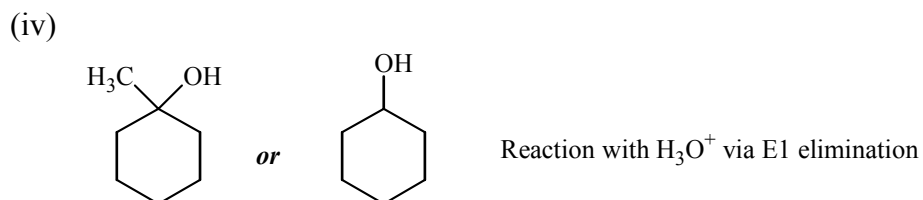
[2]



[2]

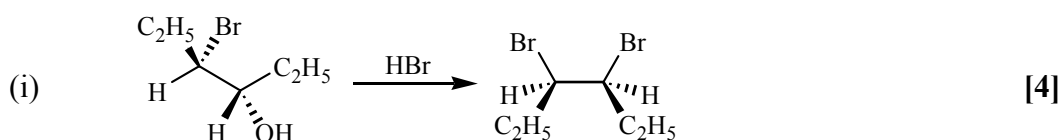


[2]

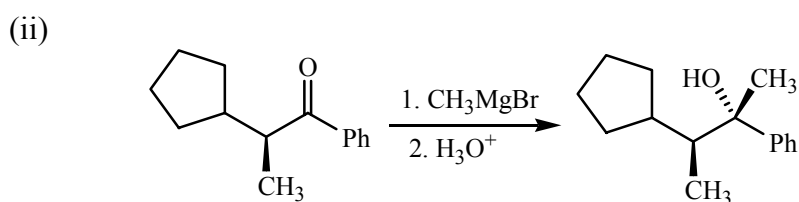


[2]

(c) For **each** of the following reactions, draw mechanisms that are consistent with the formation of the products shown.



[4]



[4]