

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



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CHEMISTRY 2

PAPER 2

Friday, 27th April 2007

2.30 p.m. – 5.30 p.m.

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) Describe how the first ionisation potentials of the elements vary along the first period (Li to Ne) and account for these variations. [5]
- (b) Using D₂O as a source of deuterium, suggest routes for the preparation of:
- (i) D₂
 - (ii) DBr
 - (iii) ND₃
 - (iv) LiD
 - (v) CD₄
- [5]
- (c) Use the following bond dissociation energies to explain why PCl₃ is more stable than NCl₃ with respect to decomposition in the gas phase to Cl₂ and either N₂ or P₄. [5]

Bond	D/kJ mol ⁻¹	Bond	D/kJ mol ⁻¹
P-Cl	289	N-Cl	190
N≡N	946	P-P	200
Cl-Cl	243		

- [5]
- (d) Polonium, Po, is a short-lived radioactive element. Use your knowledge of periodicity to predict:
- (i) the types of structures (ionic, covalent, or polymeric) adopted by Cs₂Po and PoF₄ under normal conditions, and,
 - (ii) the products formed if each of these compounds were treated with dilute aqueous acid.
- [5]
- (e) Explain why multiple bonding is more common for elements of the first period than for elements of the second and subsequent periods. [5]
- (f) State the formal oxidation state of iodine in **each** of the following compounds and draw the shape of each molecule.
- (i) SnI₄
 - (ii) IF₅
 - (iii) IO₃⁻
- [5]

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

(a) One mole of an ideal gas initially at 298 K is allowed to expand irreversibly from an initial volume of 1 dm³ to a final volume of 2 dm³ under adiabatic conditions against a constant pressure of 10⁵ Pa. (1 Pa m³ = 1 J)

- (i) Calculate the work, w , done on the system. [1]
- (ii) Determine the internal energy change, ΔU , for the system. [2]
- (iii) Estimate the enthalpy change, ΔH , for the system. [3]
- (iv) Calculate the entropy change, ΔS , for the system. [3]
- (v) Is this a spontaneous process? Give reasons for your answer. [1]

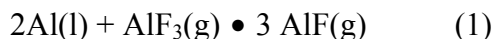
Hint: $C_{v,m} = 12.47 \text{ J K}^{-1} \text{ mol}^{-1}$ and $C_{p,m} = 20.78 \text{ J K}^{-1} \text{ mol}^{-1}$

- (b)
- (i) Explain whether graphite can be converted spontaneously into diamond at 298 K and 10⁵ Pa (1 atm) of pressure given that $\Delta G_{298}^{\ominus}$ for the process is 2.84 kJ mol⁻¹. [2]
 - (ii) The standard entropies $S_{298}^{\ominus}$ for graphite and diamond are 5.7 and 2.4 J K⁻¹ mol⁻¹, respectively. Calculate the changes in the standard entropy $\Delta S_{298}^{\ominus}$ and the standard enthalpy $\Delta H_{298}^{\ominus}$ for the transformation of graphite into diamond at 298 K and constant pressure. [3]
 - (iii) The molar volume, V_m , of carbon changes from $5.333 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ to $3.419 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ as it transforms from graphite to diamond. Calculate the pressure required to allow spontaneous conversion of graphite to diamond at 298 K. V_m for each material can be assumed to be independent of pressure. [5]

Question 2 is continued on the following page.

Question 2 continued.

2. (c) Aluminium(I) fluoride is formed in low concentrations when aluminium(III) fluoride vapour is passed over liquid aluminium at high temperatures.



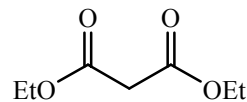
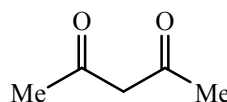
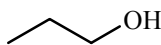
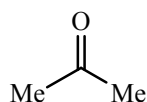
The enthalpy and entropy changes of this process were investigated by measuring the gas pressure above the container of liquid aluminium. By assuming that the vapour pressure of the liquid is negligible, it is possible to determine the partial pressures of the two gaseous compounds as a function of temperature, as recorded in the Table.

T/K	$p(\text{AlF})/\text{atm}$	$p(\text{AlF}_3)/\text{atm}$
1199	0.0189	0.0171
1223	0.0254	0.0188
1261	0.0301	0.0107
1298	0.0290	0.0075
1323	0.0559	0.0121

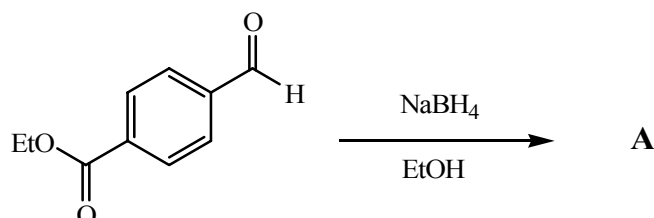
- (i) Write down an expression for the equilibrium constant for reaction (1) in terms of the concentrations of the species involved. You may assume that the liquid metal has unit activity in all cases. **[1]**
- (ii) Calculate the equilibrium constant for reaction (1) for each of the temperatures recorded in the Table. **[2]**
- (iii) The van't Hoff equation relates the equilibrium constant for a reaction to its standard enthalpy, $\Delta H_r^\ominus$, as follows: $\ln K = -\Delta H_r^\ominus / RT + \text{constant}$. Use this expression to determine the enthalpy change for reaction (1), applying a suitable graphical technique to the data in the Table. You may assume that the enthalpy change of the reaction is constant over the temperature range of these measurements. **[4]**
- (iv) Using your value for the equilibrium constant at 1261 K, calculate the free-energy change and hence the entropy change for reaction (1) at this temperature. **[3]**

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

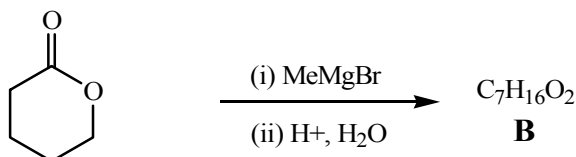
(a) (i) Place the following compounds in order of acidity (most acidic first). [3]



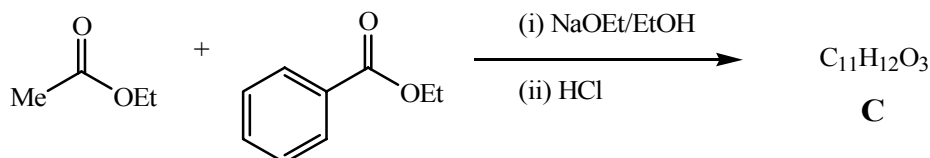
(ii) What is the product **A** from the following reaction? Show the mechanism by which it is produced. [3]



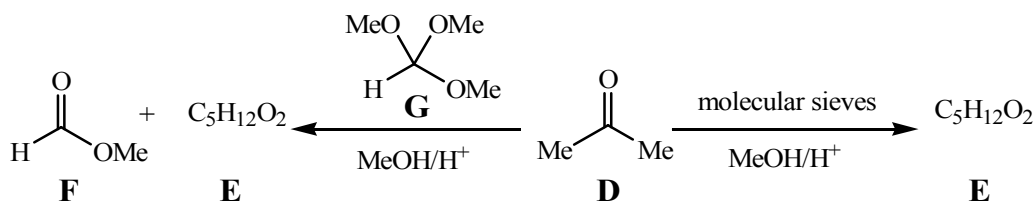
(iii) What is the product **B** from the following reaction? Show the mechanism by which it is produced. [4]



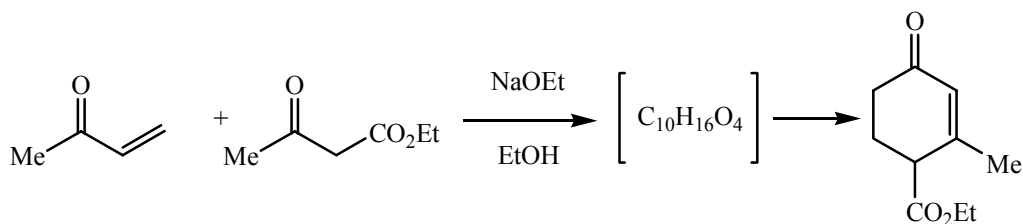
(iv) What is the product **C** from the following reaction? Show the mechanism by which it is produced. [3]



(b) What is the product **E** in the reaction scheme below? Provide a mechanism for the transformation from **D** to **E**. Provide a mechanism for the formation of **F**. What is the function of the molecular sieves in the reaction shown below? [7]



(c) Give the mechanism for the following transformation. [7]



4. Answer **all** of part (a) and **either** part (b) or part (c).

- (a) (i) Using appropriate diagrams, describe the bonding that occurs between a transition metal and carbon monoxide. [3]
- (ii) Why is the M-CO bonding described as synergistic? [2]
- (iii) For the complex $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]$, 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) Explain in simple terms why the metal atoms in many organometallic complexes contain a total of 18 valence electrons. [2]
- (ii) Determine the number of valence electrons for each metal in the following complexes using both the covalent and ionic methods of electron counting:
 $[\text{H}_2\text{Fe}(\text{CO})_4]$ $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\mu\text{-Cl})_2]$ [4]
- (iii) Classify each of the following complexes as either an oxidising agent or a reducing agent. Justify your answers.
 $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]^+$ $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]$ [4]
- (c) (i) Transition-metal ions and ligands can be classified into the categories hard, soft and borderline. Explain how these categories can be used to predict the stabilities of metal-ligand complexes and outline the theoretical rationalisation for this effect. Illustrate your answer with one example **each** of a soft transition-metal ion, a hard transition-metal ion, a soft ligand and hard ligand. Explain your choices. [8]
- (ii) Explain why $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is a strong oxidising agent when dissolved in an organic solvent such as CH_3CN , but is not a strong oxidising agent when dissolved in H_2O . [2]

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

- (a) (i) Sketch typical structures of the hydration shells around Na^+ and Cl^- ions in aqueous solution. Identify the principal interactions that stabilise these structures. [3]
- (ii) The Debye-Hückel limiting law (DHLL) is an expression for the mean activity coefficient $\gamma_{\pm}$ of ions in solution at low concentration. List the main approximations made in obtaining the DHLL, and identify the main reasons why it fails at high ionic strengths. [3]
- (iii) For singly-charged ions in aqueous solution at room temperature, the DHLL is

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

where I is the ionic strength and $I^{\ominus} = 1 \text{ mol dm}^{-3}$. The solubility product of copper (I) iodide (CuI) is $K_{sp} = 5.1 \times 10^{-12}$. Calculate the solubilities of CuI in pure water and in 0.1 M NaCl(aq) , and explain any difference between your answers. [4]

- (b) Consider the electrochemical cell



at $T = 298 \text{ K}$ for which the standard electrode potentials of the left-hand and right-hand electrodes are -2.92 V and $+1.36 \text{ V}$, respectively.

- (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. [3]
- (ii) Calculate the standard cell potential ($E^{\ominus}$), the standard Gibbs free energy change ($\Delta G^{\ominus}$), and the equilibrium constant (K) for the formal cell reaction at $T = 298 \text{ K}$. [4]
- (iii) The formal cell reaction is strongly exothermic. If the temperature of the cell were raised, would the standard cell potential increase or decrease? Justify your answer. [3]
- (c) (i) Explain why in an aqueous solution of a strong electrolyte, the ionic conductivity decreases with increasing electrolyte concentration. [4]
- (ii) The law of independent ion migration states that $\Lambda_0 = \lambda_0^+ + \lambda_0^-$, where Λ_0 is the limiting ionic conductivity of an electrolyte, and λ_0^+ and λ_0^- are the limiting single-ion conductivities of the constituent cations and anions, respectively. Explain why this law is accurate. [2]
- (iii) The limiting single-ion conductivities (in units of $\text{S cm}^2 \text{ mol}^{-1}$) of H^+ , Li^+ , and Cs^+ in aqueous solution are 349.8, 38.6, and 77.2, respectively. Account for the differences between these values. [4]

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

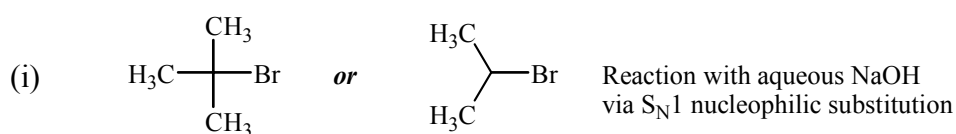
(a) Define **all** of the following stereochemical terms, using isomers of $C_4H_8Cl_2$ to illustrate your answer:

- (i) enantiomers,
- (ii) diastereomers,
- (iii) meso compound,
- (iv) *R*-configuration.

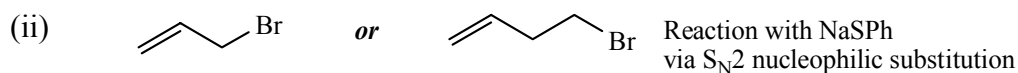
[12]

[For some terms, there is more than one possible correct answer. Only one example is required for each term.]

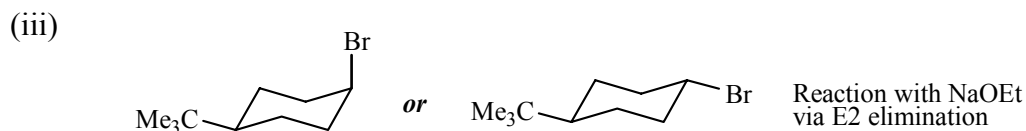
(b) For each of the following pairs of compounds, state with reasons (and/or diagrams if necessary) which compound of each pair will react faster via the indicated mechanism.



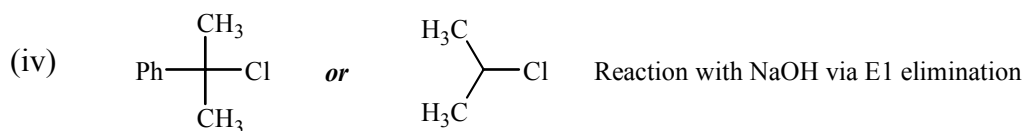
[2]



[2]



[2]



[2]

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

