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

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Senior Internal Examiners: Professors R J Donovan, D A Leigh and Dr R M Paton

CHEMISTRY 2
PAPER 2

Thursday, 4th May 2006, 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) Account for the variation in covalent radii

(i) across a period, and

(ii) down a group of the periodic table. **[5]**

(b) Using D_2O as a source of deuterium, suggest routes for the preparation of:

(i) D_2,

(ii) DCl,

(iii) ND_3,

(iv) NaD,

(v) DC≡CD. **[5]**

(c) Use the following bond dissociation energies to explain why NF_3 is more stable than NCl_3 with respect to decomposition to N_2 and the respective halogen. **[5]**

Bond	**D/kJ mol^{-1}**	**Bond**	**D/kJ mol^{-1}**
N-F	278	N-Cl	190
N≡N	946	F-F	158
Cl-Cl	243		

(d) Astatine, At, is a short-lived radioactive element. Use your knowledge of periodicity to predict:

(i) the types of structures adopted by CsAt and BAt_3 under normal conditions, and,

(ii) the products formed if these compounds were added to water. **[5]**

(e) (i) Explain why there are numerous compounds containing C=C double bonds, but only very few compounds containing Si=Si double bonds.

(ii) Suggest the type of functional group, R, that might stabilise a compound of the type $R_2Si{=}SiR_2$. **[5]**

(f) Explain why BCl_3 and $SiCl_4$ are readily hydrolysed but CCl_4 is not. **[5]**

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

(a) (i) Why are complexes of carbon monoxide with high oxidation state transition metals unknown? **[1]**

(ii) Why does the C-O stretching in transition-metal carbonyl complexes usually occur at lower energy than that in free CO gas? **[2]**

(iii) Use both the covalent and ionic methods of electron counting to determine the number of valence electrons in $[HMn(CO)_5]$. **[2]**

(iv) For the complex $[Co(H_2O)_4Cl_2]^+$, give the oxidation state of the metal, state the number of *d* electrons, explain whether the complex is high-spin or low-spin, and indicate whether the complex can exist in more than one isomeric form. **[5]**

(b) (i) Explain why cobaltocene $[Co(C_5H_5)_2]$ is a reducing agent while the ferrocenium cation $[Fe(C_5H_5)_2]^+$ is an oxidising agent. **[4]**

(ii) Use both the covalent and ionic methods of electron counting to determine the valence electron count for the Ru atoms in the complex $[(C_6H_6)ClRu(\mu_2\text{-}Cl)]_2$. **[4]**

(iii) Explain why the 18-electron carbonyl complexes $[M_x(CO)_y]$ of Mn and Co are dimeric with a M-M bond, but those of Cr and Fe are monomeric. **[2]**

(c) (i) Explain what is meant by the *chelate effect* and why this effect occurs. **[5]**

(ii) Give one example of a ligand with a soft donor atom, and give one example of a transition-metal centre to which it would be expected to bind strongly. **[3]**

(iii) Explain whether Mn(II) would be expected to bond to the $[NCS]^-$ ligand through the N or the S atom, and explain your answer. **[2]**

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

(a) (i) How is the standard reaction Gibbs free energy, $\Delta G_r^{\ominus}$, related to the equilibrium constant, K_p, for a gas-phase reaction? **[1]**

(ii) Write down an expression for K_p for the following reaction in terms of the partial pressures of the three gases, assuming that they behave ideally.

$$2NO(g) + N_2O_4(g) \approx 2N_2O_3(g)$$ **[2]**

(iii) Using the data in the table below (all values refer to T = 298 K) calculate the value of the equilibrium constant, K_p, for the reaction in part (a)(ii) at 298 K. **[6]**

	$\Delta H_f^{\ominus}$ / kJ mol^{-1}	**$S^{\ominus}$ / J K^{-1} mol^{-1}**
$NO(g)$	90.29	210.7
$N_2O_4(g)$	9.08	304.3
$N_2O_3(g)$	82.84	309.3

(b) (i) At T = 248 K the standard reaction entropy for the reaction in part (a)(ii) is 104.8 J K^{-1} mol^{-1}, and K_p = 0.279. Determine the standard reaction enthalpy, $\Delta H^{\ominus}$, at 248 K. **[4]**

(ii) Write down an expression for the temperature dependence of the standard reaction enthalpy of a chemical reaction. Hence, or otherwise, determine the value of ΔC_p for the reaction in part (a)(ii), assuming that the molar heat capacities (C_p) of all three components are independent of temperature over the range 248-298 K. **[7]**

(c) (i) Write an expression for K_p for the reaction in part (a)(ii) in terms of the mole fractions of the three components, and the total pressure. **[2]**

(ii) A sample of N_2O_3 in a reaction vessel is allowed to come to equilibrium at 248 K. Given that K_p = 0.279 at T = 248 K, what pressure would be needed to ensure that the mole fraction of N_2O_3 at equilibrium is equal to 0.1? **[9]**

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

(a) The mean activity coefficients ($\gamma_\pm$) for various aqueous electrolyte solutions at $T = 298\,\text{K}$ are given in the Table below.

0.001 M HCl	**2 M HCl**	**0.001 M $CaCl_2$**	**0.001 M $LaCl_3$**
0.966	1.011	0.888	0.790

(i) List the dominant reasons why, in aqueous ionic solutions, $\gamma_\pm \neq 1$. **[3]**

(ii) Using the Debye-Hückel limiting law, $\log_{10}\gamma_\pm = -0.509|z_+ z_-|\sqrt{I/I^{\ominus}}$, estimate $\gamma_\pm$ for each solution, and compare the results critically with the experimental data given above. **[5]**

(iii) Indicate the primary reasons why the limiting law ultimately fails at high electrolyte concentrations. **[2]**

(b) Consider the following electrochemical cell for which the standard electrode potentials at $T = 298\,\text{K}$ of the left-hand side (LHS) and right-hand side (RHS) are $E^{\ominus}_{\text{LHS}} = -1.66\,\text{V}$ and $E^{\ominus}_{\text{RHS}} = -0.76\,\text{V}$, respectively.

$$\text{Al(s)} \,|\, \text{Al}^{3+}\text{(aq)} \,||\, \text{Zn}^{2+}\text{(aq)} \,|\, \text{Zn(s)}$$

(i) Write down the potential-determining equilibria as one-electron reductions, and hence determine the formal cell reaction. **[3]**

(ii) Calculate the standard cell potential ($E^{\ominus}_{\text{cell}}$) and the Gibbs free energy change ($\Delta G^{\ominus}$) for the formal cell reaction at $T = 298$ K. **[3]**

(iii) When the temperature is raised to $T = 308$ K, the standard cell potential changes by –0.0046 V. Calculate the standard enthalpy change ($\Delta H^{\ominus}$) and standard entropy change ($\Delta S^{\ominus}$) for the formal cell reaction. **[4]**

(c) The molar conductivity (Λ_m) of 0.001 M HCl(aq) is 420.9 S cm^2 mol^{-1}, whereas that of 0.004 M HCl(aq) is 415.9 S cm^2 mol^{-1}. The limiting single-ion conductivities (λ^0_m) of H^+(aq) and Cl^-(aq) are 349.6 S cm^2 mol^{-1} and 76.3 S cm^2 mol^{-1}, respectively.

(i) State and justify the *law of independent ion migration*. Use the law to calculate the limiting molar conductivity (Λ^0_m) of HCl(aq). **[3]**

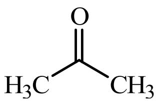
(ii) Explain why the single-ion conductivity of H^+ is so much larger than that of Cl^-. **[2]**

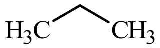
(iii) Explain briefly why the molar conductivity of a strong electrolyte decreases with increasing concentration. **[3]**

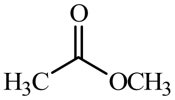
(iv) Show that the molar conductivity data at finite concentration are consistent with *Kohlrausch's law*, $\Lambda_m = \Lambda^0_m - k\sqrt{c}$. Hence, determine the value of the constant *k*. **[2]**

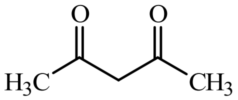
5. Answer **all** of part (a) and **EITHER** part (b) **OR** part (c).

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

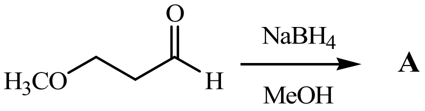




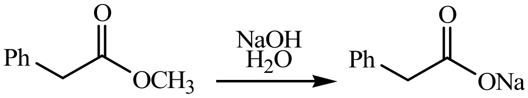




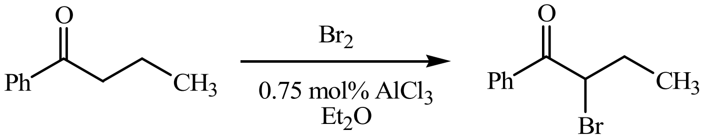
(ii) What is the product **A** from the following reaction? Show the mechanism by which it is produced. **[3]**



(iii) Write out the mechanism for the transformation: **[4]**

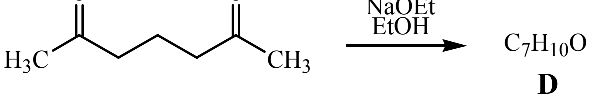


(iv) Give a mechanism for the following reaction: **[4]**



(b) Identify **B** and **C** in the following transformations and suggest mechanisms for their formation. **[6]**

(c) Identify **D** in the following reaction and give the mechanism for its formation. **[6]**

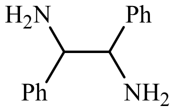


6. Answer **all** of part (a) and **EITHER all** of part (b) **OR all** of part (c).

(a) (i) Define the following terms: *chiral*; *enantiomer*; *racemic*. **[3]**

(ii) Briefly describe a physical property that may be used to distinguish between enantiomers of the same compound. **[2]**

(iii) For **each** of the molecules **A** and **B** draw **all** possible stereoisomers, and indicate whether the structures you have drawn are related as *enantiomers* or *diastereomers*. **[7]**

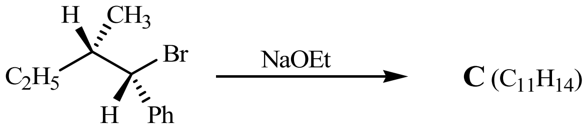


A

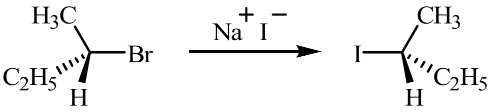
PhHC=C=CHPh

B

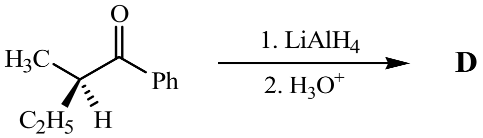
(b) (i) For the following reaction, give the structure of the product **C** and provide a detailed mechanism to account for the stereochemical outcome. **[4]**



(ii) By drawing diagrams of the frontier molecular orbitals involved, explain the course of the following S_N2 reaction. (Pay attention to the transition state of the reaction.) **[4]**



(c) (i) Predict the structure of the product **D** of the following reaction, and provide a detailed mechanism to account for the stereochemical outcome. **[4]**



(ii) Provide a detailed mechanism that explains the stereochemical outcome of the following reaction. **[4]**