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



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CHEMISTRY 2

PAPER 2

Thursday 24th August 2006, 9.30 am – 12.30 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) Explain why compounds containing an element in its highest oxidation state usually have fluorine bonded to the element. Give an example to illustrate this.
 [5]
- (b) (i) Explain the concept of *effective nuclear charge* and account for its variation along a row of the periodic table.
 - (ii) Explain why Al and Ga have similar ionic radii. [5]
- (c) Describe the structures of LiCl, BeCl₂, and BCl₃ under conditions of normal temperature and pressure. Account for the differences between these structures.
 [5]
- (d) Explain why the bond dissociation energies of the halogens vary as follows: F-F < Cl-Cl > Br-Br > I-I [5]
- (e) Use the following bond dissociation energies (in kJ mol⁻¹) to explain why under normal conditions phosphorus can adopt a structure based on P₄ units, but nitrogen exists as N₂.

Bond	D/kJ mol ⁻¹
N–N	167
P-P	200
N≡N	946
P≡P	490

- (f) State the formal oxidation state of nitrogen in **each** of the following species and draw the shape of each molecule or ion.
 - (i) $[NH_4]^+$
 - (ii) [NO₃]⁻
 - (iii) N_2H_4

[5]

- 2. Answer **all** of part (a) and **EITHER all** of part (b) **OR all** of part (c).
 - (a) (i) Explain why the vibration of the C-O bond in transition-metal carbonyl complexes almost always occurs at a lower energy than that in free carbon monoxide gas.
 [3]
 - (ii) Use both the covalent and ionic methods of electron counting to determine the number of valence electrons in the anion $[HFe(CO)_4]$. [2]
 - (iii) For the complex $[Mn(CN)_5(NCS)]^{4-}$, give the oxidation state of the metal, state the number of *d* electrons, explain whether the complex is high-spin or low-spin, and explain whether the complex can exist in more than one isomeric form. [5]
 - (b) (i) Explain why carbon monoxide is a good ligand for transition metals even though the carbon lone pair has no detectable Brönsted or Lewis acidity.
 [3]
 - (ii) One of the few examples of a carbon monoxide complex with a main group element is H₃B-CO. Explain why the energy of the C-O vibration in this complex is higher than that in free carbon monoxide gas. [3]
 - (iii) The reaction of $[(\eta-C_5H_5)Fe(CO)_2]_2$ with X_2 (X = Br, I) results in the formation of the monomeric complexes $[(\eta-C_5H_5)Fe(CO)_2X]$. The stretching vibrations of the CO ligands in the bromide and iodide complexes absorb at 2053 and 2044 cm⁻¹ respectively. Explain why the vibration in the Br complex is at a higher energy. [4]
 - (c) The following diagram shows the variation in the hydration energies of the first-row, divalent transition metal ions plotted against the number of *d* electrons.



- (i) Explain the trends illustrated within the diagram. [6]
- (ii) Explain what is meant by the term *spectrochemical series*, and use information provided by the diagram to suggest the position of H_2O within the series. [4]

- 3. Answer all of part (a) and EITHER all of part (b) OR all of part (c).
 - (a) (i) State the sign of the entropy change in each of the following processes and briefly explain your answers. [6]

 $CaCO_{3}(s) \rightarrow CaO(s) + CO_{2}(g)$ $2SO_{2}(g) + O_{2}(g) \rightarrow 2SO_{3}(g)$ $AgCl(s) + \frac{1}{2}H_{2}(g) \rightarrow Ag(s) + H^{+}(aq) + Cl^{-}(aq)$

- (ii) 1 mole of N₂, which may be considered to be an ideal gas, is expanded isothermally at 273 K from a volume of 1 dm³ to a volume of 10 dm³. Write down the value of ΔU for this change, and briefly explain your answer. [2]
- (iii) Calculate the value of the entropy change, ΔS , for the expansion in part (a)(ii). [4]
- (b) Consider the following reaction.

$$CINO(g) \approx NO(g) + \frac{1}{2}Cl_2(g).$$

- (i) Write down an expression for the equilibrium constant, K_p , of this reaction in terms of the partial pressures of the three gases, assuming that they behave ideally. [2]
- (ii) 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 at 298 K. [6]

	ΔH_f^{\bullet} / kJ mol ⁻¹	S^{\leftrightarrow} / J K⁻¹ mol⁻¹
ClNO(g)	52.29	263.6
NO(g)	90.37	210.6
$Cl_2(g)$	0	222.9

- (c) (i) What is the thermodynamic criterion for a chemical reaction to proceed spontaneously in a closed system at constant temperature and pressure? [2]
 - (ii) The standard heats of vaporisation and the boiling points at standard pressure of five compounds are given below. Calculate the standard molar entropy changes associated with the phase transitions and comment on their values.

	$\Delta H_{vap}^{\leftrightarrow}$ / kJ mol ⁻¹	Boiling point / °C
CCl ₄	30.00	76.1
C ₆ H ₁₂	30.1	80.7
NH ₃	23.35	-33.0
H ₂ O	40.6	100
H_2S	18.7	-60.4

- 4. Answer **all** of part (a) and **EITHER all** of part (b) **OR all** of part (c).
 - (a) The solubility of copper(I) chloride (CuCl) in water can be investigated using the following electrochemical cell.

 $\operatorname{Cu}(s) | \operatorname{Cu}^+(\operatorname{aq}) || \operatorname{Cl}^-(\operatorname{aq}) | \operatorname{Cu}\operatorname{Cl}(s) | \operatorname{Cu}(s)$

At T = 298 K the standard half-cell potentials for the left-hand side (LHS) and right-hand side (RHS) are $E_{\text{LHS}}^{\phi} = +0.518$ V and $E_{\text{RHS}}^{\phi} = +0.163$ V, respectively.

- Write down the potential-determining equilibria for the two half cells as one-electron reductions, and hence determine the formal cell reaction for the cell as specified.
- (ii) Calculate the standard cell potential, E_{cell}^{\bullet} . [1]
- (iii) Calculate the solubility product, K_{sp} , of CuCl at T = 298 K. [3]
- (iv) The Nernst equation for the cell is $E_{cell} = E_{cell}^{-+} \frac{RT}{F} \ln(a_{Cu^+} a_{Cl^-})$. Why doesn't the activity of CuCl(s) appear in this equation? [2]
- (v) When the concentrations of both Cu⁺(aq) and Cl⁻(aq) are equal to 0.001 M, the measured cell potential at T = 298 K is $E_{cell} = +0.002$ V. Calculate the mean activity coefficient, γ_{\pm} , for a 0.001 M aqueous solution of CuCl. You are reminded that activity $a_i = \gamma_i c_i / c^{\oplus}$. [3]
- (b) The Debye-Hückel limiting law (DHLL) for an electrolyte solution is expressed by the formula

$$\log_{10} \gamma_{\pm} = -A |z_{+}z_{-}| \sqrt{I/I^{\div}}$$

where $I = \frac{1}{2} \sum_{i} c_i z_i^2$ is the ionic strength. For aqueous solutions at T = 298 K, the dimensionless constant A is equal to 0.509.

- (i) List the primary causes of non-ideal behaviour in aqueous electrolyte solutions. [3]
- (ii) Define the symbols z_+ , z_- , and I° in the DHLL. [3]
- (iii) Using the DHLL, calculate the mean activity coefficient, γ_{\pm} , of a 0.001 M aqueous solution of copper(I) chloride. Compare your answer to that from part (a)(v), and comment on the accuracy of the DHLL. [2]
- (c) Provide concise explanations for the following trends and observations concerning the conductivities of ions in aqueous solution.
 - (i) The limiting single-ion conductivity increases down Group 17. [2]
 - (ii) The limiting molar conductivity of HCl is far greater than that of LiCl. [2]
 - (iii) The molar conductivities of strong electrolytes decrease with increasing electrolyte concentration. [2]
 - (iv) The molar conductivities of weak electrolytes decrease with increasing electrolyte concentration. [2]

5. Answer **all** of part (a) and **ANY TWO** from parts (b), (c) and (d).

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

$$H_{3C} \rightarrow OCH_{3} H_{3C} \rightarrow CH_{3} EtOH H_{3C} \rightarrow H$$

(ii) Give a mechanism for the following transformation:



(iii) Give a mechanism for the following transformation: [4]



(b) What is the product **A** from the following reaction? Show the mechanism by which it is produced. [5]



(c) What is the product **B** from the following reaction? Show the mechanism by which it is produced. [5]



(d) What is the product C from the following reaction? Show the mechanism by which it is produced. [5]



[3]

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

(a) (i) For each of the following molecules A and B draw all possible stereoisomers, and indicate whether the structures you have drawn are related as *enantiomers* or *diastereomers*. [8]



(ii) Suggest reaction conditions that could be used to *racemise* the enantiomerically pure compound C. Provide a mechanism to explain how racemisation takes place. [4]



enantiomerically pure

(b) For each of the following reactions, give the structures of the unknown products and provide detailed mechanisms to account for the stereochemical and/or regiochemical outcomes.



(c) For each of the following reactions, give the structures of the unknown products and provide detailed mechanisms to account for the stereochemical and/or regiochemical outcomes.

(i)
$$HBr \to F$$

(ii) HPh¹ Br Aqueous NaOH $G(C_8H_{10}O)$ (racemic) H_3C