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

CHEMISTRY 2

PAPER 2

Thursday 18th August 2005
9:30 a.m. – 12:30 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) Outline synthetic routes to each of the following compounds.

(i) Anhydrous KCl

(ii) Anhydrous $BeCl_2$

(iii) LiD

(iv) D_2S

(v) CD_4 **[5]**

(b) Use the following bond-dissociation energies (in kJ mol^{-1}) to explain why under normal conditions phosphorus can adopt a structure based on P_4 units, but nitrogen exists as N_2.

D(N–N) = 167 D(P-P) = 200

D(N≡N) = 946 D(P≡P) = 490 **[5]**

(c) Explain why the bond-dissociation energies of the halogens vary in the order,

F-F < Cl-Cl > Br-Br > I-I. **[5]**

(d) Give reasons why IF_5 may be prepared, but all attempts to prepare ICl_5 have been unsuccessful. **[5]**

(e) Explain how the concept of electronegativity may be used to rationalise trends in:

(i) bond energies,

(ii) structures of the halides of the elements. **[5]**

(f) State the formal oxidation state of chlorine in **each** of the following compounds and draw the shape of each molecule.

(i) $SiCl_4$

(ii) ClF_3

(iii) Cl_2O **[5]**

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

(a) Give a brief account of the first law of thermodynamics describing *heat*, *work*, *internal energy changes* and *enthalpy changes* that accompany a chemical process. **[8]**

(b) Thermodynamic data, at 298 K, for the reagents and products of the gas phase reaction:

$$2HNO_2(g) \equiv H_2O(g) + NO(g) + NO_2(g)$$

are given below.

	$\Delta H_f^{\ominus}$ / **kJ mol^{-1}**	$S^{\ominus}$ / **J K^{-1} mol^{-1}**
$HNO_2(g)$	-79.5	254.0
$H_2O(g)$	-241.8	188.7
$NO(g)$	90.2	210.7
$NO_2(g)$	33.2	240.0

(i) Calculate $\Delta H_r^{\ominus}$, $\Delta S_r^{\ominus}$ and $\Delta G_r^{\ominus}$ for the above reaction at 298 K. **[6]**

(ii) At 548 K the values of $\Delta H_r^{\ominus}$ and $\Delta S_r^{\ominus}$ are 42.95 kJ mol^{-1} and 137.1 J K^{-1} mol^{-1}, respectively. Calculate $\Delta G_r^{\ominus}$ at 548 K. **[2]**

(iii) Assuming that the values of $\Delta H_r^{\ominus}$ and $\Delta S_r^{\ominus}$ at 548 K are the same as those at 298 K, calculate $\Delta G_r^{\ominus}$ at 548 K. Compare your value with the more precise value you obtained in part (b) (ii). For this reaction, what is the major source of the temperature variation of $\Delta G_r^{\ominus}$? **[4]**

(c) Thermodynamic data, at 298 K, for the reagents and products of the gas phase reaction:

$$SO_2(g) + ½\ O_2(g) \equiv SO_3(g)$$

are given below.

	$\Delta H_f^{\ominus}$ / **kJ mol^{-1}**	$S^{\ominus}$ / **J K^{-1} mol^{-1}**
$SO_2(g)$	-300	250
$SO_3(g)$	-395	258
$O_2(g)$	0	205

(i) Calculate $\Delta S_r^{\ominus}$ for the above reaction and comment on the sign of the result. **[4]**

(ii) Write down an expression for the equilibrium constant, K_p, of the reaction above in terms of the partial pressures of the species involved. **[2]**

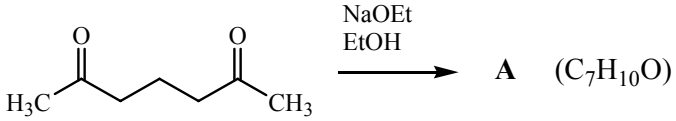
(iii) Calculate $\Delta G_r^{\ominus}$ and hence K_p of the reaction. **[6]**

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).

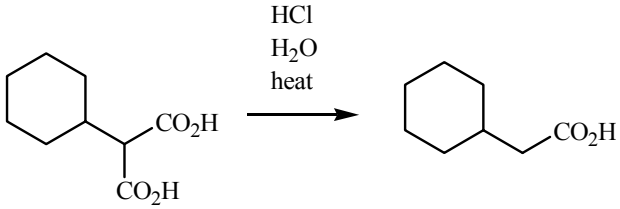
[3]

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



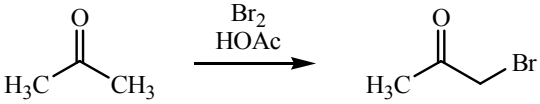
[4]

(iii) Give the mechanism for the following transformation.



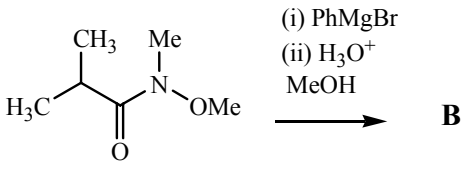
[4]

(iv) Give the mechanism for the following transformation.



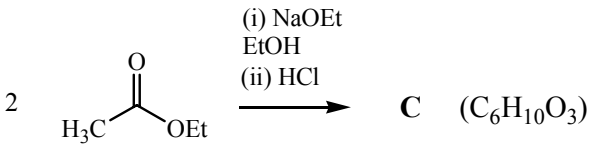
[4]

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



[5]

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



[5]

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.

$[Ni(CO)_4]$ $[Cr(CO)_5]^{2-}$ $[Br_2Fe(CO)_4]$ **[5]**

(ii) For the complex $[FeBr_4]^{2-}$, give the oxidation state of the metal, state the number of *d* electrons, explain whether the complex is high-spin or low-spin and calculate the spin-only magnetic moment. **[5]**

(b) (i) Explain why the 17-electron complex $[Mn(CO)_5]$ spontaneously forms a dimer containing a Mn-Mn bond whereas the 17-electron complex $[V(CO)_6]$ exists as a monomer. **[4]**

(ii) Identify the manganese complexes **A** – **D** in the following reactions.

$[Mn_2(CO)_{10}] + Br_2 \rightarrow 2\ \mathbf{A}$

$\mathbf{A} + CH_3MgCl \rightarrow \mathbf{B}$

$[Mn_2(CO)_{10}] + Na/Hg \rightarrow 2\ \mathbf{C}$

$\mathbf{C} + CH_3CH_2I \rightarrow \mathbf{D}$ **[6]**

(c) (i) Explain why substitution reactions of the complex $[Cr(NH_3)_6]^{3+}$ proceed very slowly. **[3]**

(ii) Explain the relative rates of complexation expected for a given transition-metal ion with a macrocyclic ligand and for an analogous open-chain ligand. **[2]**

(iii) Explain why the stabilities of halide complexes with Ti(IV) increase in the order $I^- < Br^- < Cl^- < F^-$. **[3]**

(iv) Give one example of a transition-metal ion that would form a more stable complex with I^- than with F^- and explain your answer. **[2]**

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

(a) The mean activity coefficient, $\gamma_{\pm}$, of an electrolyte solution can be estimated using the Debye-Hückel limiting law,

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

where $I = \frac{1}{2}\sum_i c_i z_i^2$, $I^{\ominus} = 1\,\text{mol dm}^{-3}$, c_i and z_i are the concentration and charge number, respectively, of species *i*, and for aqueous solutions at 298 K $A = 0.509$.

(i) Calculate the mean activity coefficient of a 0.1 M aqueous solution of KNO_3. **[2]**

(ii) Calculate the mean activity coefficient of a 0.1 M aqueous solution of $CaCl_2$. **[2]**

(iii) The solubility product of AgI is $K_{sp} = 9 \times 10^{-17}$. Calculate the solubility of AgI in pure water. **[2]**

(iv) Calculate the solubility of AgI in 0.1 M KNO_3(aq). Compare your answer to that in part (a) (iii) and describe the cause of any difference. **[4]**

(b) Consider the following electrochemical cell involving uranium at $T = 298$ K:

$$\text{U(s)} \,|\, \text{U}^{3+}\text{(aq)} \,||\, \text{Cl}^{-}\text{(aq)} \,|\, \text{Cl}_2\text{(g)} \,|\, \text{Pt(s)}$$

(i) For each half cell write down the potential determining equilibrium as a one-electron reduction, and hence determine the formal cell reaction for the cell as specified. **[3]**

(ii) Using the data given below, calculate the standard cell potential, $E^{\ominus}_{\text{cell}}$, and standard Gibbs free energy change, $\Delta G^{\ominus}$, for the formal cell reaction. **[3]**

(iii) Calculate the cell potential for the electrochemical cell when the activity of the chloride ions is $a_{\text{Cl}^-} = 0.68$, and all other activities are equal to unity. **[2]**

(iv) State whether the dissolution of solid uranium by reaction with atmospheric chlorine is a likely route for the radioactive contamination of water, and justify your answer on thermodynamic grounds. **[2]**

[At $T = 298\,\text{K}$: $E^{\ominus}(\text{U} \,|\, \text{U}^{3+}) = -1.79\,\text{V}$; $E^{\ominus}(\text{Cl}^- \,|\, \text{Cl}_2) = +1.36\,\text{V}$.]

(c) The limiting molar conductivities of some simple electrolytes are summarised below.

Electrolyte	**HBr**	**NaBr**	**RbBr**	**RbF**
$\Lambda_m^0 / \text{S cm}^2\ \text{mol}^{-1}$	428	128	156	133

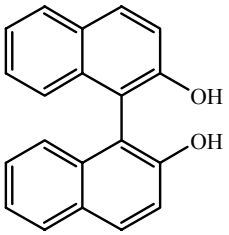
(i) The limiting ionic conductivity of Br^- is $\lambda^0 = 78\,\text{S cm}^2\ \text{mol}^{-1}$. Calculate the limiting ionic conductivities of H^+, Na^+, and Rb^+, and explain the variation. **[6]**

(ii) Calculate the limiting molar conductivity of HF. **[2]**

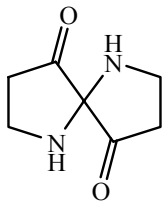
(iii) Explain why the limiting ionic conductivities of Rb^+ and Br^- are so similar. **[2]**

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

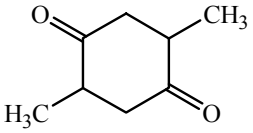
(a) (i) For **each** of the following molecules, **A** - **C**, draw **all** possible stereoisomers, and indicate whether the structures you have drawn are related as enantiomers or diastereomers. **[8]**



A

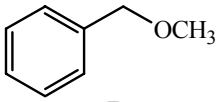


B



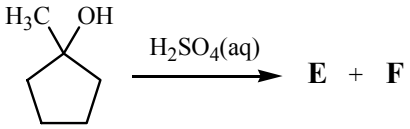
C

(ii) Illustrate the meaning of the term *prochiral* by reference to appropriate atoms/groups in the molecule **D** below, and assign the prochiralities of these atoms/groups. **[4]**

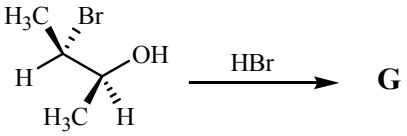


D

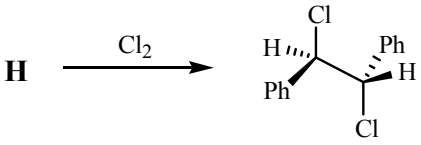
(b) (i) Give the structures of the isomeric products **E** and **F** (C_6H_{10}) below, and provide mechanisms to illustrate their formation. Indicate which isomer you expect to be predominant and explain your reasoning. **[4]**



(ii) Give the structure of the product **G** ($C_4H_8Br_2$) below, and provide a detailed mechanism to account for the stereochemical outcome. **[4]**



(c) (i) Work out the structure of the substrate **H** below, and provide a detailed mechanism for the overall conversion of **H** into **I**. **[4]**



I

(ii) Provide a detailed mechanism for the following transformation. What is the name given to this type of elimination and why? **[4]**