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

CHEMISTRY 2

PAPER 1

Thursday 28th April 2005, 09.30 - 12.30

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

(a) Incident monochromatic radiation causes electrons to be photoemitted from a clean surface of rubidium, provided that the frequency of the radiation is greater than $\nu_0 = 5.056 \times 10^{14}$ Hz.

(i) With the help of an energy-level diagram show that $\text{K.E.} = h\nu - \Phi$, where K.E. is the kinetic energy of the photoemitted electrons, ν is the frequency of the incident radiation, and Φ is the work function of the metal surface. Hence, explain why electrons can only be emitted when the frequency of the incident radiation exceeds some threshold value. **[6]**

(ii) Calculate the work function of the rubidium surface, giving your answer in electron volts (eV). **[2]**

(iii) The work functions of the Group I metals decrease down the group. Suggest a possible cause of this effect. **[2]**

(b) Schrödinger's equation for a particle of mass m in a one-dimensional box of length L is

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = E\Psi$$

(i) Prove that the functions $\Psi_n(x) = \sqrt{\tfrac{2}{L}}\sin\left(n\pi x/L\right)$ (n = 1,2,3…) satisfy the Schrödinger equation, and hence show that the energy levels are given by the formula $E_n = n^2h^2/(8mL^2)$. **[5]**

(ii) The average thermal energy of the particle is given by $\tfrac{1}{2}k_BT$, where k_B is Boltzmann's constant, and T is the temperature. Calculate the value of n that most closely corresponds to the average thermal energy of an electron trapped in a one-dimensional box of length L = 20 nm at a temperature T = 300 K. **[2]**

(iii) Calculate the wavelength of radiation emitted when the electron in part (b) (ii) undergoes a transition from the n = 4 level to the n = 3 level. **[3]**

(c) Write concise accounts of the following topics in quantum mechanics, including diagrams where appropriate.

(i) The *Born interpretation*, and distinctions between *wavefunctions* and *orbitals*. **[4]**

(ii) *Energy levels*, *quantum states*, and *degeneracy* in the context of the electron in a hydrogen atom. **[6]**

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

(a) For the complex $[MnCl_4]^{2-}$:

(i) draw a diagram to show the energy splitting of the 3*d* orbitals, indicating appropriate symmetry labels for the orbitals, the occupancies of the orbitals with electrons, and the crystal-field splitting parameter, **[7]**

(ii) calculate the crystal-field stabilisation energy in multiples of the crystal-field splitting parameter. **[3]**

(b) Suggest the likely outcomes of each of the following reactions and explain your answers.

(i) $[Cr(H_2O)_6]^{2+} + [Co(H_2O)_6]^{3+} \longrightarrow$ **[2]**

(ii) W + excess $F_2 \longrightarrow$ **[2]**

(iii) $FeCl_2$ + excess H_2O + air $\longrightarrow$ **[2]**

(iv) $[Ni(H_2O)_6]^{2+}$ + mild oxidising agent $\longrightarrow$ **[2]**

(v) $[Ni(CO)_3(PPh_3)] + PMe_3 \longrightarrow$ **[2]**

(c) (i) Explain what is meant by the *Jahn-Teller effect* and illustrate your answer with an appropriate example. **[4]**

(ii) Explain the main factors that affect the magnitude of the ligand-field splitting parameter in transition-metal complexes. **[6]**

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

(a) The HOMO in F_2 is labelled $1\pi_g{}^*$. Explain what is meant by the term HOMO and the symbols 1, π, g and *. **[10]**

(b) Draw a fully labelled molecular-orbital diagram for the molecule B_2, showing clearly all valence-shell molecular orbitals and the atomic orbitals from which they are derived. Use it to explain why B_2 is paramagnetic. **[10]**

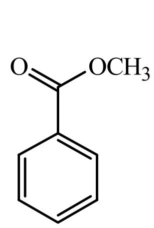
(c) Explain fully how valence-bond theory accounts for the planar geometry of benzene, C_6H_6. Your answer should include a description of atomic orbital hybridisation, and also account for the formation of σ and π bonds. **[10]**

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

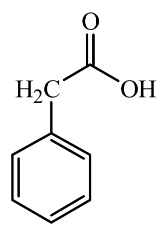
(a) (i) Discuss briefly the factors that govern the activating and directing effects of a substituent in electrophilic substitution reactions of aromatic compounds. **[4]**

(ii) Using resonance structures, write down the mechanism for the monobromination of benzene with bromine (Br_2) and iron tribromide ($FeBr_3$) (Friedel-Crafts conditions). **[6]**

(b) Predict the structure(s) of the major product(s) formed by electrophilic monobromination of each of the compounds **A - D**. Justify your predictions in each case. **[10]**



A



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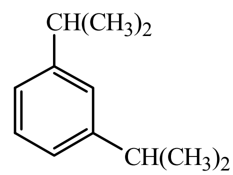

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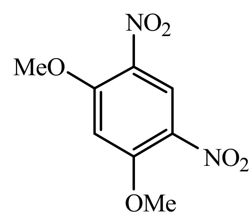
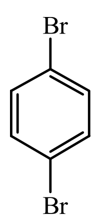
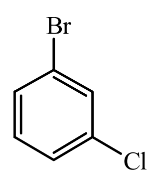


D

(c) Using either benzene (C_6H_6) or toluene ($C_6H_5CH_3$) as the starting material as appropriate, outline synthetic routes to each of the compounds **E - H**. Assume that any other necessary reagents are available and that *ortho* and *para* isomers can be separated if required. **[10]**



E



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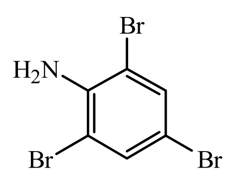

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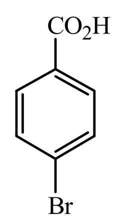

H

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

(a) (i) An absorption line is observed in the rotational spectrum of iodine monochloride, ICl, at a wavelength of 2.189 mm. Calculate the wavenumber (in cm^{-1}) of the radiation that is absorbed. **[2]**

(ii) Calculate the energy of the photons absorbed by the ICl molecule in part (a) (i). **[2]**

(iii) Which of the following transitions will be observed in the infrared spectrum of HCl at room temperature: v = 0 to v = 2, v = 2 to v = 3, v = 0 to v = 1, v = 1 to v = 0? Justify your answer. **[3]**

(iv) Which of the following transitions will be observed in the emission spectrum of Li^{2+}: 2*p* to 1*s*, 3*d* to 2*s*, 4*d* to 3*p*, 2*s* to 3*p*? Justify your answer. **[3]**

(b) In the emission spectrum of atomic hydrogen, the first three lines in the Lyman series are observed at 82259 cm^{-1}, 97492 cm^{-1} and 102824 cm^{-1}.

(i) Draw an energy-level diagram showing these transitions. **[4]**

(ii) Calculate the energy difference between the $n = 1$ and $n = 2$ energy levels. **[3]**

(iii) Predict the wavenumber of the first line in the Balmer series. **[3]**

(c) In the rotational spectrum of a diatomic molecule, lines are observed at 35.36 cm^{-1}, 53.04 cm^{-1}, 70.72 cm^{-1} and 88.40 cm^{-1}.

(i) Calculate the rotational constant, *B*, of the molecule. **[3]**

(ii) Determine which of the lines corresponds to the transition from $J = 3$ to $J = 4$. **[4]**

(iii) Calculate the relative populations of the $J = 3$ and $J = 4$ energy levels at 298 K. **[3]**

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

(a) (i) Explain clearly what is meant by *diamagnetic shielding* and how this affects proton resonance frequencies when the applied magnetic field remains constant. **[4]**

(ii) Define the term *chemical shift* as used in NMR spectroscopy. **[2]**

(iii) Explain why chemical shifts are used instead of absolute frequency units for defining resonance positions in NMR spectra. **[2]**

(iv) Explain why the chemical shift ($\delta = -1.8$) of the protons inside the carbon skeleton of 18-annulene is so different from the chemical shift ($\delta = +8.9$) of the protons outside the carbon skeleton. **[4]**

(b) The ^{1}H NMR spectrum of a molecule of molecular formula $C_4H_{10}O_2$ shows signals at δ = 4.5, 3.2, and 1.2 with corresponding areas in the ratio 1:6:3. The signals at δ = 4.5 and 1.2 show mutual spin-spin coupling (J = 7 Hz). The signal at δ = 3.2 is a single line.

(i) Explaining your reasoning, predict the appearance of the signals at δ = 4.5 and 1.2, and draw the structure of the hydrocarbon fragment from which these proton signals arise. **[4]**

(ii) Hence deduce the structure of the entire molecule. Explain your deduction. **[4]**

(c) By predicting the appearance of their proton NMR spectra show how each member of the following pairs of isomers may be distinguished. Sketch the spectrum of each molecule. (Hint: draw the molecular structures and think about their symmetry.)

(i) 1,1-dichloroethane and 1,2-dichloroethane. **[4]**

(ii) 1,3,5-tribromobenzene and 1,2,3-tribromobenzene. **[4]**