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

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Senior Internal Examiners: Professor D A Leigh and Drs A C Jones and R M Paton

CHEMISTRY 2

PAPER 1

Tuesday, 24th 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 **all** of part (a) and **EITHER all** of part (b) **OR all** of part (c).

(a) In the photoelectric effect, electrons are emitted from a clean metal surface when the frequency (ν) of incident light exceeds a threshold value (ν_0). The kinetic energy of the electrons (*KE*) increases linearly with increasing ν.

(i) With the help of a simple energy-level diagram, explain the basic features of the photoelectric effect, and show that the kinetic energy of a photoemitted electron is $KE = h\nu - \Phi$, where Φ is the work function of the metal surface. **[4]**

(ii) Sketch a graph of *KE* as a function of ν, and indicate the positions of ν_0 and Φ on the graph. **[2]**

(iii) The work function of selenium is $\Phi = 5.11\,\text{eV}$. Calculate the threshold frequency (ν_0) required for photoemission. **[2]**

(iv) The work function of sodium is $\Phi = 2.28\,\text{eV}$. Calculate the de Broglie wavelength of electrons emitted from a sodium surface illuminated by monochromatic red light with wavelength $\lambda = 450\,\text{nm}$. **[4]**

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

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi \qquad (0 \le x \le L).$$

(i) Confirm that the wavefunctions $\psi_n(x) = \sqrt{2/L}\,\sin(n\pi x/L)$ satisfy the Schrödinger equation, and hence show that the energy of the n^{th} state is $E_n = n^2h^2/8mL^2$. **[4]**

(ii) Sketch the wavefunctions of the first three states (corresponding to n = 1, 2, 3). **[2]**

(iii) Sketch the probability densities [$P_n(x)$] for the first three states. **[2]**

(c) Solving the Schrödinger equation for an electron in a hydrogen atom yields a series of wavefunctions (ψ_{nlm_l}), each labelled by a set of quantum numbers n, l and m_l. The energy levels are determined by the formula $E_n = -R_H/n^2$ where $R_H = 13.6\,\text{eV}$ is the Rydberg constant.

(i) Outline briefly the connection between atomic orbitals and wavefunctions. **[2]**

(ii) Sketch the atomic orbital corresponding to the state with $n = 1$, $l = 0$, and $m_l = 0$. **[1]**

(iii) Sketch the atomic orbitals corresponding to the states with $n = 2$, $l = 1$, and m_l = -1, 0, 1. **[2]**

(iv) List the sets of quantum numbers that correspond to the five 3*d* orbitals. **[2]**

(v) Calculate the ionisation energy of atomic hydrogen in its electronic ground state. **[1]**

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

(a) For the complex $[FeCl_4]^{2-}$:

(i) draw a diagram to show the energy splitting of the 3*d* orbitals, including 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]**

(iii) calculate the spin-only magnetic moment. **[2]**

(b) (i) Give an example of a ligand that is good at stabilising a transition metal in a low oxidation state. Describe with the aid of a diagram the nature of the bonding between the ligand and the metal and explain why this leads to stabilisation of the metal in a low oxidation state. **[6]**

(ii) Give the highest oxidation state observed for chromium and explain your answer. **[2]**

(c) Account for **each** of the following observations.

(i) For the complex $[Ir(CO)Cl(PPh_3)_2]$, the PPh_3 ligands can be readily substituted by $PMePh_2$. **[2]**

(ii) Salts of the complex $[Cu(H_2O)_6]^{2+}$ are attracted towards a magnetic field. **[2]**

(iii) Substitution reactions involving complexes of Cr(III) are usually very slow. **[2]**

(iv) The salt $K[Ag(CN)_2]$ is colourless. **[2]**

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

(a) Explain what is meant by the terms:

(i) bonding orbital,

(ii) π orbital,

(iii) core orbital. **[6]**

(b) For $[O_2]^{2-}$:

(i) draw an energy-level diagram, showing all valence shell molecular orbitals and the atomic orbitals from which they are derived, **[6]**

(ii) label all the orbitals, **[4]**

(iii) indicate the electrons present in each orbital, **[2]**

(iv) label the HOMO and LUMO. **[2]**

(c) Valence bond theory proposes that the central B atom in the molecule BF_3 is sp^2 hybridised.

(i) What is orbital hybridisation? **[2]**

(ii) Show how the sp^2 orbitals on the B atom are formed. **[6]**

(iii) Sketch a diagram of BF_3 to show the geometry of the molecule. Indicate clearly all orbitals on B and F that overlap, and assign the symmetry of the resulting bonds as σ or π. **[6]**

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

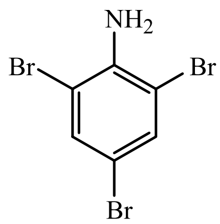
(a) Compare and contrast the chemistries of aniline ($C_6H_5NH_2$) and phenol (C_6H_5OH) using the following headings:

(i) acidity and basicity,

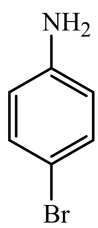
(ii) reactions with electrophiles,

(iii) reactions with acyl chlorides (RCOCl) or anhydrides [$(RCO)_2O$]. **[8]**

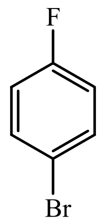
(b) Using aniline as the starting material, in conjunction with any suitable reagents, suggest synthetic routes to each of the compounds **A** - **C**. Assume that *ortho* and *para* isomers can be separated. **[12]**



A

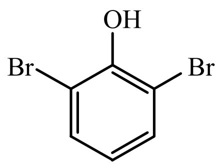


B

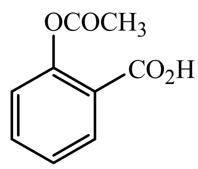


C

(c) Using phenol as the starting material, in combination with any appropriate reagents, suggest synthetic routes to each of the compounds **D** and **E**. Assume that *ortho* and *para* isomers can be separated. **[12]**



D



E

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 8.757 mm. Calculate the wavenumber (in cm^{-1}) of the radiation that is absorbed. **[2]**

(ii) The spacing between lines in the rotational spectrum of ICl is 0.2284 cm^{-1}. Calculate the rotational constant of ICl. **[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 = 2? Justify your answer. **[2]**

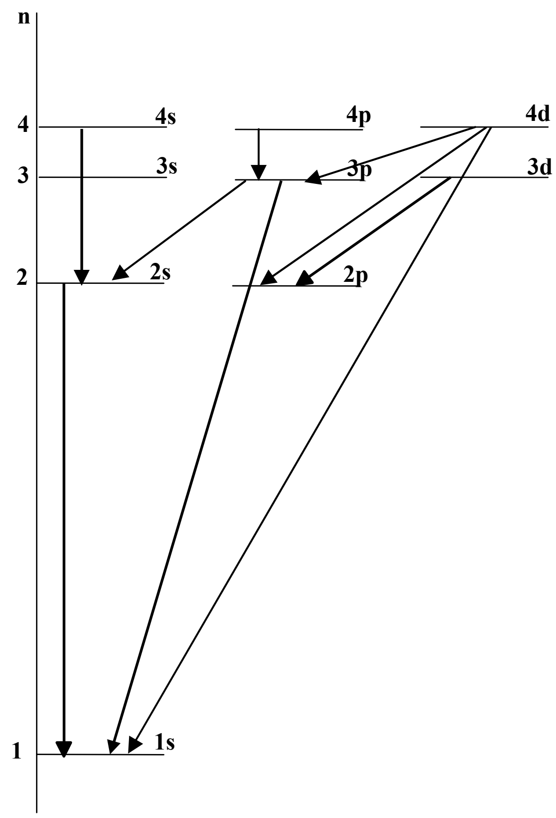
(iv) Hydrogen iodide ($^{1}H^{127}I$) absorbs infrared radiation of frequency 6.924×10^{13} s^{-1}. Calculate the force constant of the $^{1}H^{127}I$ bond. (The molar masses of ^{1}H and ^{127}I are 1.008 g mol^{-1}, and 126.904 g mol^{-1}, respectively.) **[4]**

(b) With reference to the energy-level diagram of the hydrogen atom shown below, answer parts (i) to (iii) below.

(i) Identify which of the transitions shown are forbidden. Explain your reasoning. **[3]**

(ii) Identify which of the transitions belong to the Balmer series, observed in the emission spectrum of hydrogen. Explain your answer. **[2]**

(iii) In the emission spectrum of hydrogen, the first three lines in the Lyman Series are observed at 82259 cm^{-1}, 97492 cm^{-1} and 102824 cm^{-1}. Using this information, determine the wavenumbers of **all** the transitions that are shown. **[5]**



Question 5 is continued on the following page.

Question 5 continued.

5. (c) (i) In NMR spectroscopy, the resonance frequency of a proton is given by the following equation.

$$\nu = \frac{\gamma B_0 (1-\sigma)}{2\pi}$$

Using this equation, explain why the resonance frequency depends on the chemical environment of the proton. **[4]**

(ii) Using the method of successive splitting, predict the multiplet patterns of the proton resonances in 1,2,4-trinitrobenzene, given the following coupling constants:

$^3J_{\mathrm{ortho}} = 10$ Hz $^4J_{\mathrm{meta}} = 4$ Hz $^5J_{\mathrm{para}} = 0$ **[6]**