

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



Chairman of the Board of Examiners: Professor D W H Rankin
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Senior Internal Examiners: Professor D A Leigh and Drs A C Jones and R M Paton

CHEMISTRY 2

PAPER 1

Thursday 16th August 2007, 2.30 pm – 5.30 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 **all** of part (a) and **EITHER all** of part (b) **OR all** of part (c).

- (a) The energy levels of an electron in a hydrogen atom are given by $E_n = -R_H/n^2$, where $R_H = 13.6 \text{ eV}$ is the Rydberg constant, and n is the principal quantum number.
- (i) The energy levels are the eigenvalues of the Schrödinger equation for the hydrogen atom, which is solved using the *Born-Oppenheimer approximation*. Describe this approximation, and indicate why it is reliable in the case of the hydrogen atom. [3]
 - (ii) Sketch an energy-level diagram for the electron showing the zero of energy, the first three energy levels, the distinct quantum states belonging to each energy level, and the degeneracy of each energy level. [4]
 - (iii) Outline the relationship between a wavefunction (an eigenfunction of the Schrödinger equation) and the associated atomic orbital. [2]
 - (iv) The hydrogen 1s wavefunction is $\psi_{1s}(r) = A \exp(-r/a_0)$ where A is the normalisation constant, and $a_0 = 5.29 \times 10^{-11} \text{ m}$ is the Bohr radius. Show that the hydrogen atom has a diameter of about $1 \text{ \AA}$. [3]
- (b) The harmonic oscillator (HO) is an approximate model of the vibrations in molecules. For an oscillator with reduced mass μ and spring constant k , the angular frequency is $\omega = \sqrt{k/\mu}$ and the allowed energy levels are $E_n = (n + \frac{1}{2})\hbar\omega$, where $n = 0, 1, 2, \dots$ is the quantum number.
- (i) For a pair of bonded atoms with equilibrium bond length r_e , sketch the potential energy as a function of bond length r as modelled in the HO. [You are given the relation $V(r) = \frac{1}{2}k(r - r_e)^2$.] [3]
 - (ii) Predict the average bond length, within the HO approximation. [1]
 - (iii) The N-H stretch typically gives rise to a peak in the infrared spectrum at a wavenumber in the region of $\bar{\nu} = 3300 \text{ cm}^{-1}$. Calculate the spring constant for the N-H bond. [4]
- (c) The Hamiltonian operator for a particle of mass m travelling through free space in the x direction is $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$.
- (i) Confirm that the wavefunction $\psi(x) = A \exp(-2\pi i x/\lambda)$ is an eigenfunction of $\hat{H}$, and hence show that the kinetic energy of the particle (E) is given by the formula $E = \hbar^2/2m\lambda^2$. [Recall that $\hat{H}\psi = E\psi$ and that $i^2 = -1$.] [4]
 - (ii) The classical formula for the kinetic energy is $E = p^2/2m$, where p is the momentum in the x direction. By comparison with the results of part (c)(i), derive a relationship between p and λ . [2]
 - (iii) Calculate the wavelength of an electron travelling with a velocity $1 \times 10^5 \text{ m s}^{-1}$. [2]

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

(a) For the complex $[\text{V}(\text{CO})_6]$:

- (i) draw a diagram to show the energy splitting of the $3d$ 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) Explain the principal factors that influence the magnitude of the crystal-field splitting parameter in transition-metal complexes. [8]

(c) Suggest the most likely outcomes for **each** of the following reactions and explain your answers.

- (i) $\text{V} + \text{excess F}_2$ [2]
- (ii) $\text{Fe} + \text{excess CO}$ [2]
- (iii) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + \text{air}$ [2]
- (iv) $\text{Ni}(\text{s}) + \text{HCl}(\text{aq})$ [2]

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

(a) (i) One of the molecular orbitals in F_2 is labelled $1\pi_g^*$. Explain what is meant by the symbols 1 , π , g and $*$. Sketch this molecular orbital. [8]

(ii) For which second-row homonuclear diatomic molecule is $1\pi_g^*$ the highest energy orbital that is completely filled? [2]

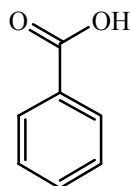
(b) The first three bands (those corresponding to the lowest ionisation potentials) in the photoelectron spectrum of F_2 all consist of progressions of relatively sharp lines. Explain the origin of this fine structure, and predict qualitatively the relative spacings of the lines in the three bands. [10]

(c) Assuming that each carbon atom has three sp^2 -hybridised orbitals, draw sketches to illustrate:

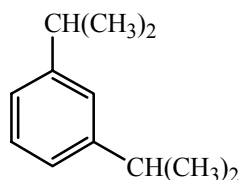
- (i) the formation of C-H bonding and antibonding orbitals in ethene,
- (ii) the formation of the C=C bonding orbitals in ethene. [10]

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

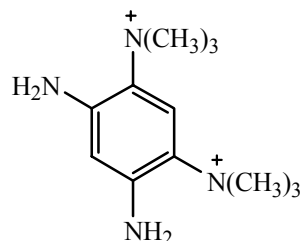
- (a) (i) Discuss briefly the factors that control the activating and directing effects of a substituent in electrophilic substitution reactions of aromatic compounds. [4]
- (ii) Predict the structure(s) of the major product(s) formed by electrophilic monobromination of each of the compounds **A** - **C**. Justify your predictions in each case. [6]



A

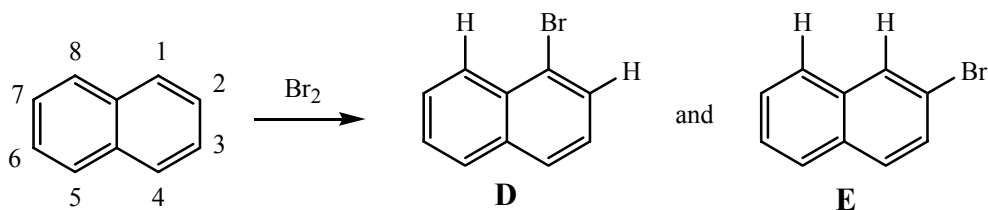


B

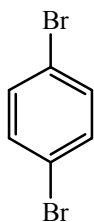


C

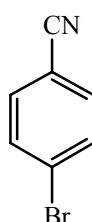
- (b) Draw resonance structures of the intermediate carbocations in the bromination of naphthalene and account for the fact that naphthalene undergoes electrophilic attack at C1 to give 1-bromonaphthalene (**D**) rather than at C2 to give 2-bromonaphthalene (**E**). [10]



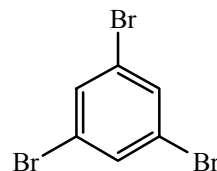
- (c) Using either benzene (C_6H_6) or toluene ($C_6H_5CH_3$) as the starting material as appropriate, outline synthetic routes to **all** of the compounds **F** - **H**. Assume that any other necessary reagents are available and that *ortho* and *para* isomers can be separated if required. [10]



F



G



H

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

- (a) (i) A line in the emission spectrum of atomic hydrogen occurs at 15238 cm^{-1} . Calculate the wavelength of the radiation emitted and give your answer in nanometres. [2]
- (ii) State which of the following molecules will show an infrared (vibrational) spectrum: H_2 , CO , Cl_2 , ICl . Justify your answer. [3]
- (iii) Sketch the multiplet structure of the aldehyde CH resonance in the ^1H NMR spectrum of ethanal (CH_3CHO). Explain your answer. [5]
- (b) A sample of hydrogen fluoride, $^1\text{H}^{19}\text{F}$, absorbs infrared radiation of wavelength $2.4147\text{ }\mu\text{m}$. (The molar masses of ^1H and ^{19}F are 1.008 g mol^{-1} and 18.998 g mol^{-1} , respectively.)
- (i) Calculate the vibrational frequency of $^1\text{H}^{19}\text{F}$. [2]
- (ii) Calculate the force constant of the $^1\text{H}^{19}\text{F}$ bond. [4]
- (iii) The vibrational frequency of an unknown hydrogen halide, HX , was found to be $8.9607 \times 10^{13}\text{ s}^{-1}$. Estimate the force constant of the HX bond, justifying any assumptions that you make. [4]
- (c) The rotational spectrum of $^{63}\text{Cu}^{79}\text{Br}$ vapour was recorded at high temperature. The $J = 13$ to 14 , 14 to 15 , 15 to 16 and 16 to 17 transitions were observed at 2.8160 , 3.0170 , 3.2180 and 3.4190 cm^{-1} , respectively. The molar masses of ^{63}Cu and ^{79}Br are 62.929 g mol^{-1} and 78.918 g mol^{-1} , respectively.
- (i) Calculate the rotational constant, B , of $^{63}\text{Cu}^{79}\text{Br}$. [2]
- (ii) Calculate the bond length of $^{63}\text{Cu}^{79}\text{Br}$. [4]
- (iii) The ratio of the intensities of the $J = 16$ to 17 and the $J = 13$ to 14 transitions was 1.2143 . Determine the temperature at which the spectrum was measured. [4]