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

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CHEMISTRY 2

PAPER 1

Monday, 1st May 2006, 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.

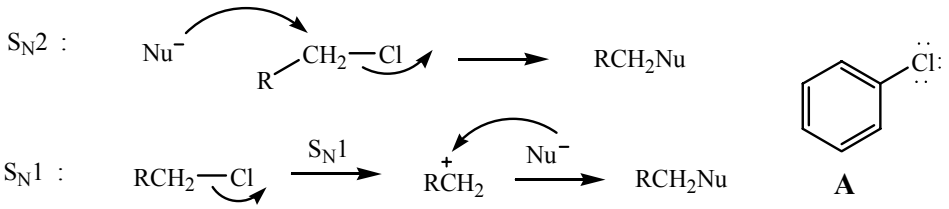
A data sheet is provided with this examination paper.

Unassembled molecular model kits may be used in this examination.

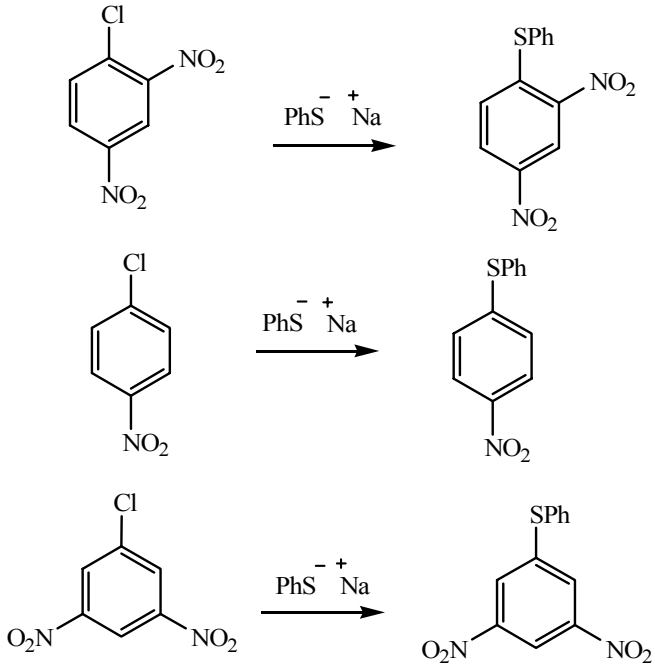
Only the calculator provided may be used in this examination.

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

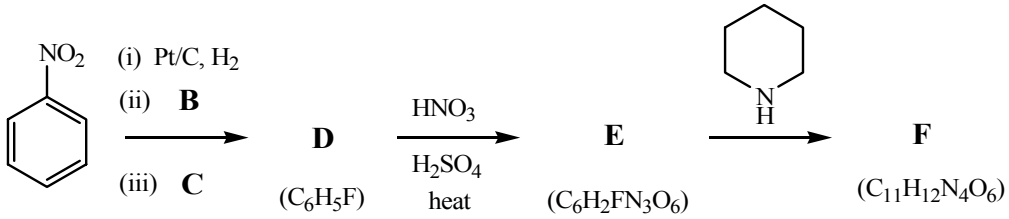
(a) Alkyl chlorides (R-Cl) typically undergo S_N1/S_N2 nucleophilic substitution reactions as shown below. These mechanisms are not possible with aromatic halides. Illustrate the reasons for this difference in the case of chlorobenzene **A**. **[10]**



(b) Draw the mechanism for each of the reactions below. Using resonance structures, predict which of the following nucleophilic aromatic substitution reactions will proceed the quickest. Give your reasons. **[10]**



(c) In the scheme below, suggest structures for the reagents and products **B**-**F**. **[10]**



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

(a) Draw a fully labelled molecular-orbital diagram for the molecule O_2, showing all valence-shell molecular orbitals and the atomic orbitals from which they are derived, and indicate how the electrons are distributed among the molecular orbitals. **[8]**

(b) (i) Explain the meaning of the term *degenerate orbitals*. Illustrate your answer with an appropriate diagram for the molecule O_2.

(ii) Explain what is meant by a σ_u orbital. Illustrate your answer with an appropriate diagram for the molecule O_2.

(iii) Explain, giving reasons, what would happen to the length of the O-O bond when two electrons are added, one at a time, to the O_2 molecule. **[6]**

(c) (i) Explain the *Born-Oppenheimer approximation*.

(ii) Describe the stages in the procedure for computing molecular-orbital wavefunctions of an equilibrium molecular structure, starting with wavefunctions for the atomic orbitals of the individual atoms. **[6]**

(d) (i) Explain how and why the molecular-orbital diagram for N_2 would differ from that for O_2 in part (a).

(ii) Explain how and why the molecular-orbital diagram for NF would differ from that for O_2 in part (a). **[6]**

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

(a) For the complex $[Co(H_2O)_6]^{2+}$:

(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) Describe the geometry of the complex $[Cu(H_2O)_6]^{2+}$ and explain why it deviates from ideal octahedral geometry. **[5]**

(ii) Explain what is meant by the term *spectrochemical series*. **[3]**

(c) (i) Explain why the following reaction takes a long time to reach equilibrium:

$$[Co(NH_3)_5Cl]^{2+} + H_2O \approx [Co(NH_3)_5(H_2O)]^{3+} + Cl^-$$

[3]

(ii) The pK_a of the species $[R_3PH]^+$ is sometimes used as a measure of the ligand strength of the corresponding species R_3P as R is varied. Give two reasons why this provides only a limited assessment of ligand properties. **[3]**

(iii) State the highest oxidation state observed for the metal vanadium and explain your answer. **[2]**

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

(a) The de Broglie relation is $\lambda = h/mv$, and the Compton formula is $p = h/\lambda$.

(i) Describe one experimental observation that can be explained using the de Broglie relation. **[3]**

(ii) Calculate the wavelength of a buckminsterfullerene molecule (C_{60}) travelling at a velocity v = 120 m s^{-1}, and comment on the likely significance of quantum mechanical effects in this case. **[3]**

(iii) Describe one experimental observation that can be explained using the Compton formula. **[2]**

(iv) Calculate the difference in momentum between a 'violet' photon ($\nu = 7.1\times10^{14}$ Hz) and a 'red' photon ($\nu = 4.5\times10^{14}$ Hz). **[2]**

(b) For a particle of mass m moving in one dimension, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\Psi_n}{\mathrm{d}x^2} = E_n\Psi_n .$$

(i) When the particle is trapped in a one-dimensional box of length L, the wavefunctions are $\Psi_n(x) = \sqrt{2/L}\sin(n\pi x/L)$. Show that these functions satisfy the Schrödinger equation, and hence determine a formula for the energy levels. **[4]**

(ii) Explain how the quantum numbers $n = 1, 2, 3, \ldots$ arise in the case of the trapped particle. (Mathematical details are not required.) **[3]**

(iii) In contrast to the trapped particle, a free particle travelling in the x-direction with momentum p has a wavefunction proportional to $\exp(-ipx/\hbar)$, where $i = \sqrt{-1}$. Obtain a formula for the energy of the particle, and compare this with the prediction of classical mechanics. **[3]**

(c) The wavefunction for an electron in the 1s orbital of a hydrogen atom is

$$\Psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}}\exp(-r/a_0)$$

where r is the distance from the nucleus, and $a_0 = 5.292\times10^{-11}$ m is the Bohr radius.

(i) Provide a concise statement of the *Born interpretation*. **[2]**

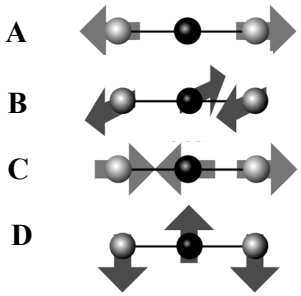
(ii) Derive an expression for the radial distribution function, $P_{1s}(r)\mathrm{d}r$, which represents the probability that the 1s electron in the hydrogen atom is at a distance between r and $r + \mathrm{d}r$ from the nucleus. Hence, show that the 'diameter' of the hydrogen atom is roughly equal to one angstrom. **[6]**

(iii) Explain why $\Psi_{1s}(r)$ has the prefactor $1/\sqrt{\pi a_0^3}$. (A mathematical derivation is not required.) **[2]**

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

(a) (i) A sample of hydrogen chloride, $^{1}H^{35}Cl$, absorbs radiation of wavenumber 2988.9 cm^{-1}. Calculate the vibrational frequency of the $^{1}H^{35}Cl$ molecule. **[2]**

(ii) The normal vibrational modes of CO_2, labelled **A – D**, are shown below. Which of these modes are degenerate? **[2]**



(iii) Which of the normal modes of CO_2, shown in part (a)(ii), are active in the infrared spectrum of the molecule? Explain your answer. **[3]**

(iv) Which of the following transitions are observed in the Balmer series of the emission spectrum of atomic hydrogen: 2*p* to 1*s*; 3*d* to 2*p*; 4*d* to 2*s*; 4*p* to 2*s*; 5*p* to 4*s*? Justify your answer. **[3]**

(b) The rotational spectrum of a diatomic molecule consists of a series of equally spaced lines with an interval of 22.66 cm^{-1}. The most intense line in the spectrum occurs at 135.96 cm^{-1}.

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

(ii) Between which two rotational levels does the most intense transition occur? **[4]**

(iii) Calculate the term value (wavenumber) of the $J = 2$ energy level. **[3]**

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

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

Define the terms γ, B_0 and σ in this equation. **[3]**

(ii) Using the equation in part (c)(i), explain what is meant by *nuclear shielding* and why this effect is so important in NMR spectroscopy. **[4]**

(iii) Using the method of successive splitting, draw to scale on graph paper the line positions and intensities for the multiplet expected for a proton showing simple (first-order) coupling to three other protons with coupling constants 8 Hz, 4 Hz and 4 Hz. **[3]**