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

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CHEMISTRY 2

CLASS EXAMINATION

Friday, 21st January 2005, 2.00 p.m. - 5.00 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 TWO** of the following **three** parts, (a), (b) and (c).

(a) In a famous paper, Werner Heisenberg proposed the construction of a microscope that works on γ-rays (very high frequency electromagnetic radiation) in order to 'see' electrons. For this question you are given the relations $p = h/\lambda$ and $\Delta x \cdot \Delta p \geq h/4\pi$.

(i) Calculate the frequency and momentum of a photon with wavelength $\lambda = 5\times10^{-12}$ m. **[3]**

(ii) Assuming that such a photon imparts all of its momentum to an electron initially at rest, calculate the velocity of the electron after a collision. **[2]**

(iii) Upon collision with an electron, the photon can impart anywhere between none and all of its momentum to the electron. Hence, the uncertainty in the momentum of the electron is roughly equal to the momentum of the incident photon. Calculate the minimum uncertainty in the position of an electron that has just collided with the photon in part (a) (i), and comment on whether a γ-ray microscope could be used to 'see' atoms and molecules. **[5]**

(b) The energy levels of a harmonic oscillator with force constant k and reduced mass μ are given by the formula:

$$E_n = \left(n + \tfrac{1}{2}\right)\hbar\omega,$$

where $n = 0,1,2,\ldots$, $\hbar = h/2\pi$, and $\omega = \sqrt{k/\mu}$.

(i) Sketch an energy-level diagram for the harmonic oscillator, indicating the zero of energy, the zero-point energy, and the spacing between energy levels. **[3]**

(ii) Calculate the reduced mass, $\mu = m_1 m_2/(m_1 + m_2)$, of a single molecule of hydrogen iodide, $^{1}H^{127}I$, and comment on the significance of your answer. **[3]**

(iii) The vibrational wavenumber of $^{1}H^{127}I$ is $2308.09\,cm^{-1}$. Calculate the force constant of the interatomic bond. **[4]**

Question 1 is continued on the next page.

(c) A particle of mass m is confined to a three-dimensional cubic box of side L. The energy levels of the particle are given by:

$$E(n_x, n_y, n_z) = \frac{\left(n_x^2 + n_y^2 + n_z^2\right)h^2}{8mL^2},$$

where $n_x, n_y, n_z = 1,2,3,\ldots$.

(i) Sketch an energy-level diagram showing the first four energy levels, indicating the zero of energy, the zero-point energy, and the degeneracies of each of the levels. **[4]**

(ii) Explain why none of the quantum numbers (n_x, n_y, n_z) can be equal to zero. **[2]**

(iii) A single helium-4 (^{4}He) atom is trapped in cubic box of side $L = 10^{-8}$ m. Calculate the frequency of light required to excite the atom from the ground state ($n_x = n_y = n_z = 1$) to a first excited state with $n_x = 2, n_y = n_z = 1$. **[4]**

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

(a) Explain the meanings of **three** of the following terms.

(i) The *Born-Oppenheimer approximation.*

(ii) *Orbital hybridisation* in valence bond theory.

(iii) *Bonding* and *anti-bonding* orbitals.

(iv) *Self-consistent field* molecular orbitals. **[9]**

(b) Draw a fully labelled molecular orbital diagram for the molecule N_2, showing clearly all valence-shell molecular orbitals and the atomic orbitals from which they are derived. **[11]**

(c) Sketch clearly how the atomic orbitals combine to form molecular orbitals for the molecule H_2O. Hence construct a fully labelled molecular orbital diagram and use it to explain the origin of the two lone pairs located on oxygen. **[11]**

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

(a) For **both** of the metal complexes $[Fe(H_2O)_6]^{3+}$ and $[Cr(CO)_6]$:

(i) state the oxidation state of the metal, **[2]**

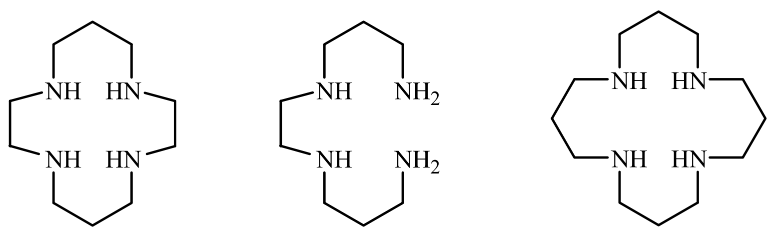
(ii) state the number of *d*-electrons, **[2]**

(iii) indicate whether the complex would be expected to be high spin or low spin and explain your assignment, **[4]**

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

(b) (i) Explain what is meant by the *chelate effect* and why this effect occurs. **[5]**

(ii) Place the following compounds in order of binding strength to a transition metal ion. Explain your answer. **[5]**



A **B** **C**

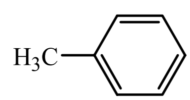
(c) (i) Give one example of a ligand that acts as a *π-donor* ligand to a transition metal and explain your choice. Draw a diagram to indicate the σ and π interactions between the ligand valence orbitals and the metal *d* orbitals. **[5]**

(ii) Explain why $[PtCl_2(NH_3)_2]$ has two isomers. **[3]**

(iii) Show with the aid of a diagram why $[Ni(en)_3]^{2+}$ has two enantiomers. (en = $NH_2CH_2CH_2NH_2$) **[2]**

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

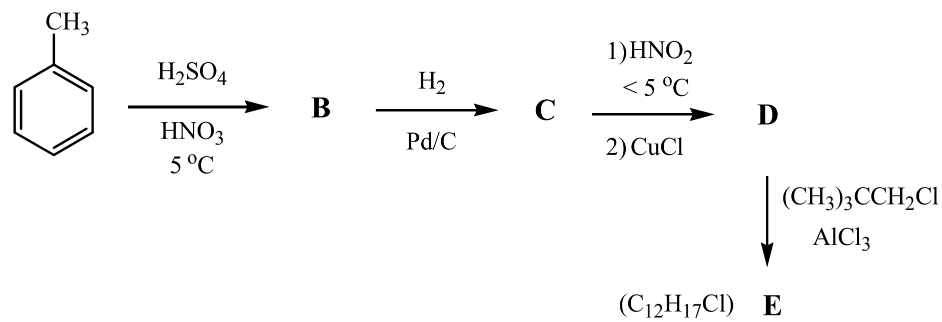
(a) Draw the resonance structures of the carbocation intermediates formed by reaction of an electrophile at the *ortho*, *meta* and *para* positions of toluene **A**. Hence predict whether the CH_3- group is *meta* or *ortho/para* directing in electrophilic substitution reactions. **[10]**



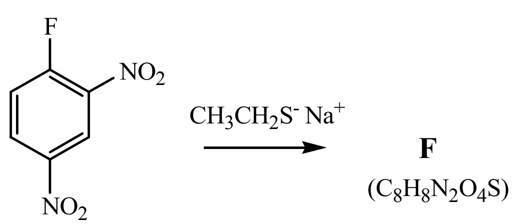
A

(b) Suggest structures for the products **B** - **F** in the schemes below. **[10]**

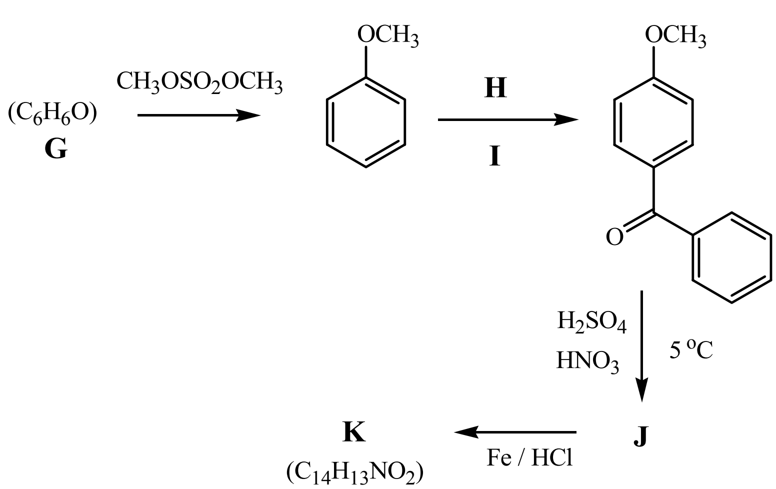
(i)



(ii)



(c) Suggest structures for the reagents and products **G - K** in the below. **[10]**



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 20565 cm^{-1}. Calculate the wavelength of the radiation emitted. Give your answer in nanometres. **[2]**

(ii) In which region of the electromagnetic spectrum does the transition in part (a) (i) occur? **[1]**

(iii) Deduce which of the following molecules will show an infrared (vibrational) spectrum: H_2, HBr, CO. Explain your answer. **[3]**

(iv) The energy difference between the v=0 and v=1 vibrational levels of hydrogen iodide is 4.588×10^{-20} J. Calculate the ratio of hydrogen iodide molecules in the v=1 and v=0 levels at 25 °C. **[4]**

(b) The wavenumbers of the lines observed in the emission spectrum of the Li^{2+} ion can be calculated using the following equation,

$$\bar{\nu} = Z^2 R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where Z is the atomic number, R= 109729 cm^{-1} is the Rydberg constant for Li^{2+}, and n_1 and n_2 are principal quantum numbers.

(i) Calculate the wavenumber of the first line in the Paschen series of transitions in the emission spectrum of Li^{2+}. **[4]**

(ii) Explain which of the following transitions will be observed in the emission spectrum of Li^{2+}: 4*p* to 3*d*; 3*d* to 1*s*; 3*p* to 2*s*; 4*p* to 3*s*. **[3]**

(iii) Identify the transition in part (b) (ii) that belongs to the Balmer series. **[1]**

(iv) Identify the transitions in part (b) (ii) that emit light of the same wavenumber. **[2]**

(c) In the microwave spectrum of $^{1}H^{35}Cl$, absorption lines are observed at 83.32 cm^{-1}, 103.84 cm^{-1} and 124.37 cm^{-1}.

(i) Determine the value of the rotational constant, B, of $^{1}H^{35}Cl$. **[3]**

(ii) Between which two rotational energy levels does the 83.32 cm^{-1} transition occur? **[4]**

(iii) Calculate the term value (wavenumber) of the rotational level from which the 83.32 cm^{-1} transition occurs. **[3]**

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

(a) (i) Explain concisely what is meant by *nuclear spin-spin coupling* using the ^{1}H NMR spectrum of $CHBr_2CHO$ as an example. Explain how spin-spin coupling arises in this example. **[8]**

(ii) What is meant by the term *coupling constant (J)*? **[2]**

(iii) State the number of lines expected for a proton that shows coupling to *n* other protons in the case where the coupling constants are identical, and in the case where the coupling constants are all different. **[2]**

(b) Using the method of successive splitting, draw on graph paper *to scale* the line positions and intensities for each of the multiplets expected for a proton showing first-order coupling to three other protons with the coupling constants given in (i) – (iii) below.

(i) 7 Hz, 4 Hz, 1 Hz **[2]**

(ii) 6 Hz, 4 Hz, 2 Hz **[2]**

(iii) 6 Hz, 3 Hz, 3 Hz **[2]**

(iv) State how the separation (Hz) of the first and last line of each multiplet is related to the corresponding coupling constants. **[2]**

(c) By predicting the appearance of its proton NMR spectrum show how each member of the following pairs of isomers may be distinguished. Sketch the spectrum for each molecule. Ignore *meta* and *para* couplings in part (c) (ii). (Hint: draw the molecular structure and think about the symmetry.)

(i) 1,3-dibromopropan-2-one and 2,3-dibromopropanal. **[4]**

(ii) 1,3,dichlorobenzene and 1, 4-dichlorobenzene. **[4]**

PTO