

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



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CHEMISTRY 2 CLASS EXAMINATION

Tuesday, 5th December 2006, 2.30 – 5.30

St Leonard's Land Games Hall

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 Schrödinger equation for a single particle is $\hat{H}\psi = E\psi$, where $\hat{H}$ is the Hamiltonian, ψ is the wavefunction of the particle, and E is the energy of the particle.

(i) Identify the *operator*, *eigenfunction*, and *eigenvalue* in the Schrödinger equation. [2]

(ii) The Born interpretation is stated mathematically as $P(x) = |\psi(x)|^2$. Explain what is represented by $P(x)$. [2]

(iii) The de Broglie relation is $\lambda = h/p$, where h is Planck's constant. State what are represented by λ and p , and briefly outline an experimental observation that can be explained using the relation. [4]

(iv) Heisenberg's uncertainty principle is stated mathematically as $\Delta x \Delta p_x \geq h/4\pi$. What are represented by Δx and Δp_x ? [2]

(b) For a particle of mass m trapped in a one-dimensional box of length L , the Hamiltonian, wavefunctions, energy levels, and quantum numbers are:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad \psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad E_n = \frac{n^2 \hbar^2}{8mL^2} \quad n = 1, 2, 3, \dots$$

(i) Suggest a chemical situation for which the 'particle in a one-dimensional box' is a realistic model. [2]

(ii) Show that the wavefunctions are eigenfunctions of the Hamiltonian operator, and hence confirm the formula for the energy levels. [3]

(iii) Explain why ψ_n has a prefactor of $\sqrt{2/L}$. [2]

(iv) An electron is trapped in a one-dimensional box of length $L = 5 \times 10^{-9}$ m. Calculate the frequency of light required to promote a transition from the $n = 1$ level to the $n = 2$ level. [3]

(c) For an electron in a hydrogen atom, the energy levels, principal quantum numbers, and 1s-orbital wavefunction are:

$$E_n = -\frac{R_H}{n^2} \quad n = 1, 2, 3, \dots \quad \psi_{1s}(r) \propto e^{-r/a_0}$$

where R_H is Rydberg's constant and $a_0 = 0.529$ ångströms.

(i) Sketch an energy-level diagram for the electron, taking care to indicate the zero of energy, the first three energy levels (corresponding to $n = 1, 2, 3$), all of the quantum states belonging to each energy level, and the degeneracy of each energy level. [5]

(ii) Give the ionisation energy of a hydrogen atom in its ground state. [1]

(iii) Show that the diameter of a hydrogen atom in its ground state is approximately one ångström. [4]

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

(a) Consider the square-planar complex $[\text{Ni}(\text{CN})_4]^{2-}$.

(i) Give the oxidation state of the metal and state the number of d electrons. [2]

(ii) Draw a diagram to show the energy splitting of the $3d$ orbitals showing appropriate labels for the orbitals, and the occupancies of the orbitals with electrons. [6]

(iii) Explain why the complex is square-planar rather than tetrahedral. [2]

(iv) Give one example of a four-coordinate complex of nickel that is tetrahedral and explain why its geometry differs from that of $[\text{Ni}(\text{CN})_4]^{2-}$. [2]

(b) (i) Calculate the spin-only magnetic moment of $[\text{FeCl}_4]^-$. [4]

(ii) State the highest oxidation state observed for complexes of vanadium and explain your answer. [2]

(iii) State the most common oxidation state observed for complexes of zinc and explain your answer. [2]

(c) (i) Calculate the crystal-field stabilisation energy of $[\text{CrCl}_6]^{3-}$ in units of Δ_o . [2]

(ii) Give an example of a ligand that is good at stabilising an electron-rich transition metal. Explain with the aid of a diagram the nature of the bonding between the ligand and the metal and explain why this leads to stabilisation. [6]

[6]

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

(a) Draw a fully labelled molecular-orbital energy level diagram for the molecule B_2 , showing all valence-shell molecular orbitals and the atomic orbitals from which they are derived. Indicate how the electrons are distributed among the molecular orbitals and state the net number of bonding pairs. Hence conclude whether or not B_2 is a stable molecular species. [10]

(b) (i) Explain the meanings of the terms *HOMO* and *LUMO*.

(ii) Explain what is meant by a $2\sigma_u^*$ orbital. Illustrate your answer with an appropriate diagram for the molecule B_2 .

(iii) Explain, giving reasons, what would happen to the length of the B-B bond if two electrons were added to the B_2 molecule. [5]

(c) Summarise briefly three sources of experimental evidence that can be used to verify molecular-orbital energy-level diagrams. [5]

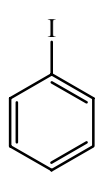
(d) State briefly the different approaches to constructing the molecular wavefunction, Ψ , under *valence bond theory* and *molecular orbital theory* conditions. State which method is the more successful, and justify your answer. [5]

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

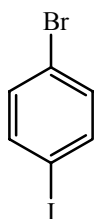
- (a) (i) A line in the emission spectrum of atomic hydrogen occurs at 97492 cm^{-1} . Calculate the wavelength of the radiation emitted, in nanometres. [2]
- (ii) Determine the number of modes of vibration of each of the following molecules:
water; carbon dioxide; butane. [3]
- (iii) Define the term *chemical shift* and explain why it is a more useful quantity than frequency for defining the position of lines in NMR spectra. [2]
- (iv) Using the method of successive splitting, draw to scale on graph paper the line positions and intensities of the multiplet expected for a proton showing simple (first order) coupling to three other protons with coupling constants 4 Hz, 2 Hz, 2 Hz. [3]
- (b) A sample of hydrogen iodide, $^1\text{H}^{127}\text{I}$, absorbs infrared radiation of wavenumber 2309.5 cm^{-1} .
- (i) Calculate the vibrational frequency of the $^1\text{H}^{127}\text{I}$ molecule. [3]
- (ii) Would you expect the vibrational frequency of $^2\text{H}^{127}\text{I}$ to be different from that of $^1\text{H}^{127}\text{I}$? Justify your answer. [4]
- (iii) Explain why the transition from $v = 1$ to $v = 2$ is not observed in the infrared spectrum of $^1\text{H}^{127}\text{I}$ at a temperature of 298 K, even though it is allowed by the selection rules. [3]
- (c) In the rotational spectrum of a diatomic molecule, the first three transitions are observed at 17.68 cm^{-1} , 35.36 cm^{-1} , and 53.04 cm^{-1} .
- (i) Calculate the rotational constant, B , of the molecule. [3]
- (ii) Predict the wavenumber of the transition from $J = 7$ to $J = 8$. [4]
- (iii) What other information would you need to be able to calculate the bond length of the molecule? Explain your answer. [3]

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

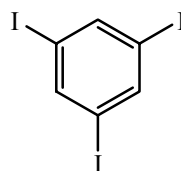
- (a) (i) Describe a synthetic route to aniline, $\text{C}_6\text{H}_5\text{NH}_2$, utilising benzene as starting material. Show how aniline can be transformed into benzenediazonium chloride, $\text{C}_6\text{H}_5\text{N}_2^+ \text{Cl}^-$. [6]
- (ii) Diazonium salts react with good nucleophiles without the need for catalysts. What is the driving force behind these reactions? [2]
- (b) Using the chemistry of diazonium salts, suggest reasonable synthetic routes to compounds **A** - **C** below. You may use benzene or toluene ($\text{C}_6\text{H}_5\text{CH}_3$) as starting materials in conjunction with any suitable reagents. Recall that iodine (I_2) does not undergo Friedel-Crafts halogenations. [12]



A



B



C

- (c) Suggest structures for the reagents and products, **D** - **H**, in the scheme below. [12]

