

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



Chairman of the Board of Examiners: Professor D W H Rankin
External Examiners: Professors M Schröder, R J K Taylor and B Vincent
Senior Internal Examiners: Professors R J Donovan, D A Leigh and Dr R M Paton

CHEMISTRY 2

CLASS EXAMINATION

Friday 20th January 2006, 1.00 p.m. – 4.00 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.

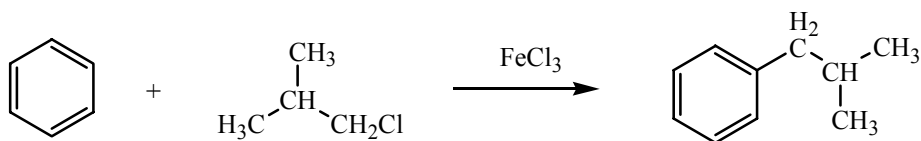
1. Answer part (a) **and EITHER all** of part (b) **OR** all of part (c).
 - (a) Draw a fully labelled orbital energy-level diagram for O_2 , showing all valence-shell molecular orbitals and the atomic orbitals from which they are derived. [8]
 - (b)
 - (i) Use the diagram you have drawn in part (a) to predict qualitatively how the bond length of O_2 would change on reduction to O_2^- . [3]
 - (ii) Use the diagram you have drawn in part (a) to predict qualitatively how the vibrational frequency of O_2 would change on oxidation to O_2^+ . [3]
 - (iii) Describe the first two (lowest ionisation potential) bands in the photo-electron spectrum of O_2 , and explain the origin of the vibrational fine structure in these bands. [6]
 - (c)
 - (i) Draw an orbital energy-level diagram for N_2 , and show clearly the ways in which it differs from that for O_2 . Explain why the diagram, particularly the order of the molecular orbitals, is different from that for O_2 . [8]
 - (ii) The vibrational structure of the first band in the photo-electron spectrum of N_2 is such that there is one intense, sharp peak, followed by one or two much weaker peaks. Explain why most of the intensity is concentrated in a single peak. [4]

2. Answer **all** of part (a) **and EITHER all** of part (b) **OR all** of part (c).
 - (a) For the square-planar complex $[Pt(NH_3)_2Cl_2]$:
 - (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) explain with the aid of a diagram why the complex exists in more than one isomeric form. [2]
 - (b)
 - (i) give an example of a ligand that is good at stabilising a transition metal in a high 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 high oxidation state, [6]
 - (ii) state the highest oxidation state observed for the metal W and explain your answer. [2]
 - (c)
 - (i) explain why substitution reactions of octahedral, low-spin $Co(III)$ complexes are typically very slow, [4]
 - (ii) calculate the spin-only magnetic moment for $[Cr(H_2O)_6]^{3+}$. [4]

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

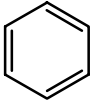
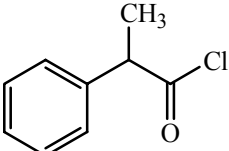
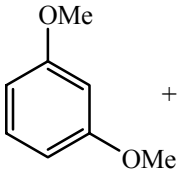
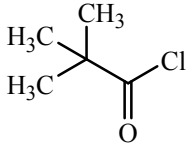
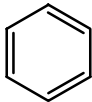
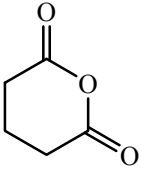
(a) (i) Provide a mechanism for the Friedel-Crafts acylation of benzene by an acyl chloride (RCOCl) in the presence of a suitable Lewis acid catalyst. **[5]**

(ii) Outline the problems with the Friedel-Crafts alkylation below. **[3]**

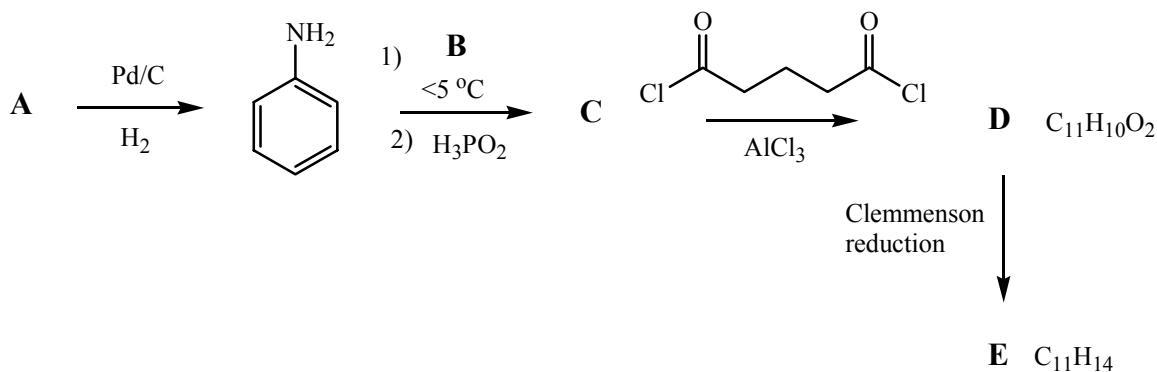


(iii) Propose a solution that overcomes the problems observed in part (a)(ii). **[2]**

(b) What products are formed from the following reactions under Friedel-Crafts conditions? Explain your reasoning in each case. **[10]**

Reactions	
	+ 
	+ 
	+ 
(From Haworth Synthesis)	

(c) Suggest structures for the reagents and products **A – E** in the scheme below. **[10]**



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

- (a) (i) Outline the principal ways in which classical mechanics is unable to explain the following physical effects: the *Davisson-Germer experiment* (the diffraction of electrons by a nickel crystal); the *Compton effect* (the scattering of electrons by incident light).

[4]

- (ii) The de Broglie relation is $\lambda = h/p$. Calculate the wavelength of a fluorinated-fullerene molecule ($C_{60}F_{48}$) travelling with velocity $v = 105 \text{ m s}^{-1}$. Comment on your answer in relation to the likely diameter of a fullerene molecule. [4]

- (iii) Red laser-pointers typically operate at a wavelength $\lambda = 650 \text{ nm}$ and emit about 4×10^{15} photons per second. Calculate the net momentum of a one-second light pulse from a red laser pointer. [2]

- (b) A particle of mass m is trapped in a cubic box with dimensions $L \times L \times L$. The allowed quantum states of the particle are labelled with the principal quantum numbers $n_x, n_y, n_z = 1, 2, 3, \dots$. The energy levels are given by

$$E_{n_x, n_y, n_z} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2).$$

- (i) Sketch an energy-level diagram for the particle showing the first four energy levels. Indicate the zero of energy, the zero-point energy, and all of the distinct quantum states belonging to each energy level. [4]

- (ii) Calculate the degeneracies of the first four energy levels. [2]

- (iii) An electron is trapped in a cubic box with $L = 1 \times 10^{-8} \text{ m}$. Calculate the wavelength of light required to promote the particle from the state with $(n_x = 1, n_y = 1, n_z = 1)$ to the state with $(n_x = 32, n_y = 1, n_z = 1)$. [4]

- (c) The electron in a hydrogen atom is restricted to the following energy levels labelled with the principal quantum numbers $n = 1, 2, 3, \dots$:

$$E_n = -\frac{R_H}{n^2}.$$

The wavefunction and radial distribution function for an electron in a $1s$ orbital are $\Psi_{1s}(r) = \text{constant} \times \exp(-r/a_0)$ and $P_{1s}(r) = 4\pi r^2 \Psi_{1s}^2(r)$, respectively, where $a_0 = 0.529 \text{ \AA}$ is the Bohr radius.

- (i) Sketch an energy-level diagram for the electron in a hydrogen atom, showing the first three energy levels. Indicate the zero of energy, and all of the distinct quantum states (orbitals) belonging to each energy level. [4]

- (ii) Justify the mathematical form of $P_{1s}(r)$. [2]

- (ii) Sketch $\Psi_{1s}(r)$ and $P_{1s}(r)$ on a single graph, and show – using calculus – that the corresponding most probable proton-electron distance is equal to a_0 . **[4]**

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

- (a) (i) Hydrogen bromide ($^1\text{H}^{81}\text{Br}$) absorbs infrared radiation of wavenumber 2649.7 cm^{-1} . Calculate the force constant of the $^1\text{H}^{81}\text{Br}$ bond. (The molar masses of ^1H and ^{81}Br are 1.008 g mol^{-1} , and 80.916 g mol^{-1} , respectively.) [4]
- (ii) Define the term *chemical shift* and explain why it is used to define the position of lines in NMR spectra. [2]
- (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 6 Hz, 4 Hz, 2 Hz. [4]
- (b) In the emission spectrum of atomic hydrogen, the first three lines in the Lyman Series are observed at 82259 cm^{-1} , 97492 cm^{-1} and 102824 cm^{-1} .
- (i) Draw an energy level diagram showing these transitions. [4]
- (ii) Calculate the value of the Rydberg constant of hydrogen. [3]
- (iii) Predict the wavenumber of the next line in the Lyman series. [3]
- (c) In the microwave spectrum of $^1\text{H}^{35}\text{Cl}$, absorption lines are observed at 83.32 cm^{-1} , 103.84 cm^{-1} and 124.37 cm^{-1} . The molar masses of ^1H and ^{35}Cl are 1.008 g mol^{-1} and 34.969 g mol^{-1} , respectively.
- (i) Determine the value of the rotational constant, B , of $^1\text{H}^{35}\text{Cl}$. [3]
- (ii) Calculate the moment of inertia of $^1\text{H}^{35}\text{Cl}$. [3]
- (iii) Between which two rotational energy levels does the 124.37 cm^{-1} transition occur? [4]