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

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CHEMISTRY 2

PAPER 1

Monday 15th August, 2005
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 **ANY TWO** of the following **three** parts, (a), (b) and (c).

(a) In 1937, G. P. Thomson (working in Aberdeen) and C. J. Davisson (working in New York) were awarded a Nobel Prize for their respective studies of electron diffraction by metals. You are given the de Broglie relation, $\lambda = h/p$, and the formula for kinetic energy, $E = p^2/2m$.

(i) Thomson used electrons with kinetic energies in the region of 10^4 eV, whereas Davisson opted for 50 eV electrons. Calculate the wavelengths of the two sets of electrons (1 eV = 1.602×10^{-19} J). **[5]**

(ii) Diffraction is most pronounced when the wavelength of the electrons is comparable to the spacing between the atoms in the metal. In whose experiment - Thomson's or Davisson's - would the electron diffraction be most pronounced? Explain your reasoning. **[3]**

(iii) Calculate the speed of a neutron with wavelength $\lambda = 10^{-10}$ m. [$m_N = 1.675 \times 10^{-27}$ kg.] **[2]**

(b) The energy levels, E_n, for a particle in a one-dimensional box are $E_n = n^2h^2/(8mL^2)$, and those for a harmonic oscillator are $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$.

(i) Sketch energy-level diagrams for the two systems including the respective zeroes of energy, the zero-point energies, and the spacings between the energy levels. **[6]**

(ii) Carbon monoxide can be modelled by a harmonic oscillator with vibrational angular frequency $\omega = \sqrt{k/\mu}$, force constant $k = 1860\ \mathrm{N\,m^{-1}}$, and reduced mass $\mu = m_C m_O/(m_C + m_O)$. Calculate the frequency of radiation absorbed by CO as a result of vibration, and state in which region of the electromagnetic spectrum such an absorption should appear. **[4]**

(c) The energy levels of the electron in a hydrogen atom are given by the formula $E_n = -R_H/n^2$, where $R_H = 13.60\ \mathrm{eV}$, and n = 1,2,3... is the principal quantum number.

(i) Sketch an energy-level diagram for the electron, including the zero of energy, the spacings between the energy levels, and the first ionisation energy of the hydrogen atom. **[4]**

(ii) List the principal quantum number, the orbital angular momentum quantum number, l, and the magnetic quantum number, m_l, of each of the distinct quantum states (or orbitals) in the first three energy levels. **[5]**

(iii) Suggest a formula for the degeneracy of the n^{th} energy level. **[1]**

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

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

(i) draw a diagram to show the energy splitting of the 3*d* orbitals, indicating appropriate symmetry labels for the orbitals, the occupancies of the orbitals with electrons and the crystal-field splitting parameter, **[7]**

(ii) draw a diagram to illustrate the changes in energies that occur to the 3*d* orbitals of a transition-metal atom upon changing from octahedral to square-planar geometry, and explain why complexes with eight *d* electrons are the most likely to show square-planar geometry. **[3]**

(b) (i) Give an example of a ligand that is good at stabilising transition metals in high oxidation states. With the aid of a diagram describe 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. **[7]**

(ii) State the highest oxidation state observed for each of the metals Mn and Fe and explain your answer. **[3]**

(c) (i) Write down an expression that defines the formation constant for the complex $[Fe(NH_3)_6]^{3+}$. **[2]**

(ii) Explain why $[Fe(en)_3]^{3+}$ has a much higher formation constant than $[Fe(NH_3)_6]^{3+}$ (en = $NH_2CH_2CH_2NH_2$). **[4]**

(iii) Explain why formation constants for transition-metal complexes with a given ligand typically vary as:

Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II). **[4]**

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

(a) 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. Explain why the ordering of the molecular orbitals is different from O_2. **[10]**

(b) Explain in turn how valence-bond theory and molecular-orbital theory describe the bonding in the molecule H_2. **[10]**

(c) The predictions made by molecular-orbital theory have been rigorously investigated by experimental methods. Discuss briefly three sources of experimental data that have lent support to the theory. **[10]**

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

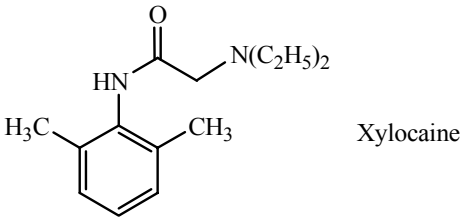
(a) Discuss the chemistry of aniline ($C_6H_5NH_2$) under each of the following headings.

(i) Industrial synthesis.

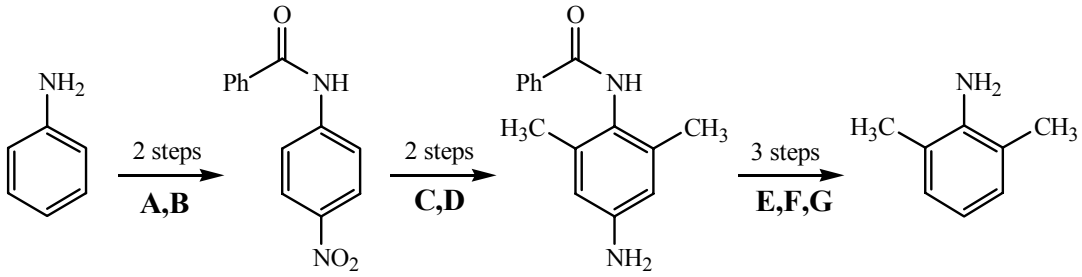
(ii) Basicity.

(iii) Bromination reactions. **[10]**

(b) 2,6-Dimethylaniline is a key intermediate in the synthesis of Xylocaine™, a local anaesthetic. Starting with aniline ($C_6H_5NH_2$), provide appropriate reagents for steps **A** to **G** to enable the transformation into 2,6-dimethylaniline. You may assume that any isomers can be separated.

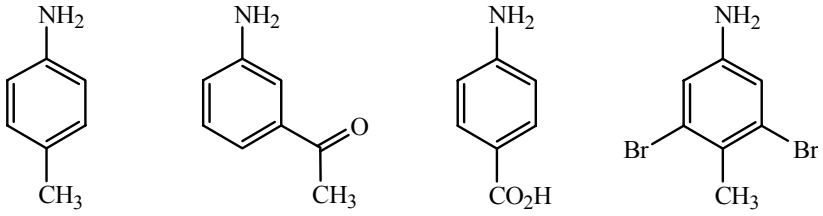


Xylocaine



[10]

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



H **I** **J** **K**

[10]

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

(a) (i) A transition is observed in the vibrational spectrum of hydrogen chloride at 2988.9 cm^{-1}. Calculate the wavelength of the radiation that is absorbed. Give your answer in μm. **[2]**

(ii) Determine the number of normal vibrational modes of each of the following molecules: carbon monoxide, hydrogen cyanide, butane. **[4]**

(iii) Which of the following transitions in atomic hydrogen correspond to the first line in the Paschen series: 4*p* to 3*s*, 4*p* to 2*s*, 3*d* to 2*p*, 4*d* to 3*p*, 3*p* to 1*s*, 4*d* to 3*s*? Justify your answer. **[4]**

(b) The rotational spectrum of a diatomic molecule consists of a series of equally spaced lines with an interval of 32.6 cm^{-1}.

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

(ii) Predict the wavenumbers of the first three lines in the rotational spectrum of the molecule. **[4]**

(iii) Would you expect this molecule to show an infrared (vibrational) spectrum? Explain your answer. **[3]**

(c) Hydrogen iodide ($^{1}H^{127}I$) absorbs infrared radiation of wavenumber 2309.5 cm^{-1}.

(i) Calculate the energy difference between the v = 0 and v = 1 vibrational levels of hydrogen iodide. **[3]**

(ii) Calculate the ratio of hydrogen iodide molecules in the v = 1 and v = 0 levels at 25 ^{o}C. **[3]**

(iii) The force constant, *k*, of hydrogen fluoride ($^{1}H^{19}F$) is approximately three times that of hydrogen iodide. Would you expect the population of hydrogen fluoride molecules in v = 1 at 25 ^{o}C to be greater or less than the population of hydrogen iodide molecules in v = 1? Explain your answer. **[4]**

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

(a) (i) How is the magnitude of spin angular momentum, P, of a nucleus defined in terms of the spin quantum number I? How is the magnetic moment, μ, defined in terms of P? Hence define the magnitude of μ in terms of I. **[3]**

(ii) Describe what happens when a collection of identical nuclei of spin $I = 1/2$ is placed in a magnetic field of strength B_0. **[4]**

(iii) Show that the resulting energy (E) of such a nucleus is given by $E = -m_I \gamma B_0 h/2\pi$ where m_I is the magnetic quantum number and γ is the magnetogyric (gyromagnetic) ratio. **[3]**

(iv) Use the result from part (a) (iii) above to derive an expression relating the resonance frequency, ν, the magnetogyric ratio and the magnetic field strength. **[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) 9 Hz, 5 Hz, 2 Hz **[2]**

(ii) 8 Hz, 5 Hz, 3 Hz **[2]**

(iii) 8 Hz, 4 Hz, 4 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 their proton NMR spectra show how each member of the following pairs of isomers may be distinguished. Sketch the spectrum of each molecule. (Hint: draw the molecular structures and think about their symmetry.)

(i) 1,3,5-trinitrobenzene and 1,2,3-trinitrobenzene. **[4]**

(ii) 1,3-dichloropropanone and 2,3-dichloropropanal. **[4]**