

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SUMMER EXAMINATIONS 2002

**FIRST EXAMINATION IN SCIENCE INCLUDING APPLIED PHYSICS AND
ELECTRONICS/EXPERIMENTAL PHYSICS, CHEMISTRY AND APPLIED
CHEMISTRY, EARTH SCIENCES**

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CHEMISTRY (CH101)

Time allowed: Three Hours

Answer Five questions and include at least one from each Section.

Use a separate answer book for each Section.

Leave the first page of the Answer Book blank and list on it clearly the numbers of the questions attempted.

All questions carry 20 marks distributed as shown.

Universal Gas Constant: $R = 8.31 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ ($\text{JK}^{-1} \text{ mol}^{-1}$)

Standard Temperature: 273K

Atomic Masses (a.m.u.): H, 1.0; C, 12.0; N, 14.0; O, 16.0; F, 19.0; Mg, 24.3; S, 32.0; Cl, 35.5; Ar 40.0.

Charge of the electron: $-1.6 \times 10^{-19} \text{ C}$; mass of the electron: $9.109 \times 10^{-31} \text{ kg}$.

Faraday: 96500 C

Avogadro Number: 6.022×10^{23}

Planck Constant: $h = 6.626 \times 10^{-34} \text{ Js.}$; ($\text{kg m}^2 \text{ s}^{-2}$)

Velocity of light: $c = 2.997 \times 10^8 \text{ ms}^{-1}$

Section A (Atomic and Molecular Structure)

1. Answer each of the following: [5 marks each]

- (i) Two electrons occupying an atomic orbital have the following quantum numbers:
 $n = 3, \ell = 1, m_\ell = 0, m_s = +\frac{1}{2}$ and $-\frac{1}{2}$. Explain the term “orbital” and indicate which atomic orbital these electrons occupy.
- (ii) Determine the wavelength of an electron moving at a velocity of 90% of the speed of light.
- (iii) Qualitatively explain the Balmer series of lines in the emission spectrum of excited H atoms and derive an expression for the radius of the Bohr electron orbits.
- (iv) Write and explain the electronic configuration of the nitrogen atom (Atomic number, 7) and briefly explain how this influences the valency of Nitrogen. Show one compound in each case where the oxidation number of Nitrogen is -3 , $+3$ and $+5$.

2. Answer any two of the following:

- (i) Show the molecular orbital diagram of the dioxygen molecule (O_2). Use it:
 - (a) to explain why O_2 is paramagnetic and why O_2^- , the superoxide ion, is a stable entity and
 - (b) to determine the bond order in the peroxide anion, O_2^{2-} . Comment on the biological importance, if any, of the molecular species mentioned. [10 marks]
- (ii) Explain the central points of the Valence Domain (Shell) Electron Pair Repulsion Theory (VSEPR) and use it to describe the structures of the following molecules:
 H_2SO_4 ; HNO_3 ; PCl_5 [10 marks]
- (iii) Explain the structures and bond angles of the molecules H_2O , H_2S and CH_4 . Show how H_2O molecules aggregate on freezing to give a unit cell for Ice I_h consisting of 12 water molecules. Explain the anomalous properties of water that you are aware of. [10 marks]

3. Answer any three of the following: [6.67 marks each]

- (i) Explain Daltons Law of Partial Pressures.
A mixture of gases in a closed container at $25^\circ C$ showing a total pressure of 103kPa is made up of N_2 (10.0g), O_2 (3.0g) and Ar (1.0g). Calculate the partial pressure of each gas in the container. (atomic masses, N, 14.0; O, 16.0; Ar, 39.95 amu).
- (ii) Explain the term solubility product (K_{sp}). If the solubility of $BaSO_4$ in water at $25^\circ C$ is 9.1mg per litre calculate K_{sp} for $BaSO_4$ at $25^\circ C$ (atomic masses, Ba, 137.34; S, 32.06; O, 16.0 amu).
- (iii) Explain the terms “resonance hybrid”, “resonance energy”, “resonance contributing (canonical) form”. Draw the resonance contributing forms for the species CH_3COO^- (ethanoate or acetate anion) and CO (carbon monoxide) and comment on any physical properties which illustrate the hybrid picture of these molecules.
- (iv) Show and explain the trends in the first ionization potentials of the 18 elements from H to Ar.
- (v) Define the term “electronegativity”. Indicate the positive and negative ends of the dipole and the bond length for the polar covalent bond in Br-F. Estimate the ionic character of the bond and determine the dipole moment of the molecule (*electronegativities*: Br, 2.8; F, 4.0. *covalent radii* Br, 0.116nm; F, 0.064nm).

Section B
(Organic Chemistry)

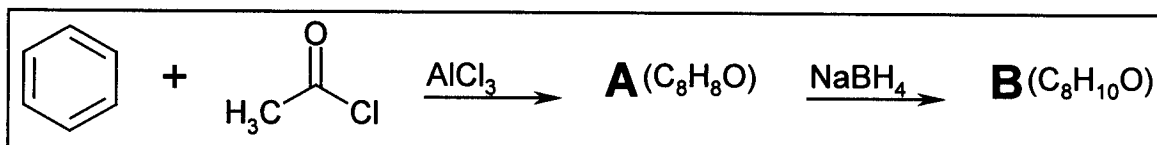
4. Answer any three of the following: [6.67 marks each]

- (i) Draw butane and 2-methylpropane. Label each carbon atom as primary, secondary or tertiary.
- (ii) Describe the preparation of methylmagnesium iodide from iodomethane including any experimental precautions that must be observed. What would be the product of reaction of this Grignard reagent with carbon dioxide (CO_2)?
- (iii) Draw and explain the existence of two isomers of but-2-ene (C_4H_8). Label each isomer as *Z* or *E* indicating the reasoning behind your assignment.
- (iv) Give the definition of a chiral compound, and draw the structures of any pair of enantiomers. What interaction of each of these enantiomers would you expect with plane polarised light?

5. Answer any two of the following:

- (i) Discuss the $\text{S}_{\text{N}}2$ mechanism for the nucleophilic substitution of an alkyl halide using the reaction of iodoethane ($\text{CH}_3\text{CH}_2\text{I}$) with hydroxide (HO^-) as an example [7 Marks]
Draw and label a free energy diagram for this reaction [3 Marks]
- (ii) The addition of HCl to 2-methylpropene ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2$) gives two isomeric chloroalkanes of molecular formula ($\text{C}_4\text{H}_9\text{Cl}$).
 - (a) Draw the structure of these two isomeric chloroalkanes [4 Marks]
 - (b) Indicate which would be the major product [2 Marks]
 - (c) Give a mechanistic explanation of the product distribution [4 Marks]
- (iii) Discuss, with the use of appropriate chemical equations, the reactions of carbonyl containing compounds under the following headings:
 - (a) Reduction to alcohols (including the different types of alcohols (primary, secondary or tertiary) formed from aldehydes or ketones) [4 Marks]
 - (b) Reduction to alkanes [4 Marks]
 - (c) Addition of Grignard reagents (e.g. CH_3MgI) [2 Marks]
- (iv) Discuss, with the use of appropriate chemical equations, the synthesis and properties of carboxylic acids under the following headings:
 - (a) Acidity in water and higher than expected boiling point [4 Marks]
 - (b) Preparation by hydrolysis [4 Marks]
 - (c) Preparation by oxidation [2 Marks]

6. Describe in detail the structure, and account for the extra stability of benzene [10 Marks]
Explain why benzene undergoes substitution and not addition reactions [3 Marks]
Deduce structures for **A** and **B** [6 Marks]
How does the AlCl_3 participate in the first reaction? [1 Mark]



Section C
(Inorganic Chemistry)

7. Answer each of the following:

- (i) Give the electronic configuration and write Lewis (electron dot) pictures for the elements; calcium, sulphur, and boron. **[5marks]**
- (ii) Write chemical equations that show the reaction of lithium hydroxide with carbon dioxide. **[5marks]**
- (iii) Describe some uses of lithium. **[5marks]**
- (iv) Write briefly on acidity and hardness in water. **[5marks]**

8. Answer each of the following:

- (i) Give the most common oxidation states for the elements, magnesium, carbon, and sulphur. Write molecular formulae for; magnesium carbide, carbon sulphide, and magnesium sulphide. **[5marks]**
- (ii) Write a balanced chemical equation for the reaction of chlorine with sodium bromide. Assign oxidation states and write oxidation and reduction half reactions. **[5marks]**
- (iii) Describe some uses of chlorine compounds. **[5marks]**
- (iv) Write briefly on the chemistry of the atmosphere. **[5marks]**

9. Answer each of the following:

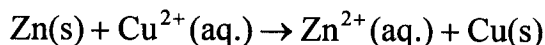
- (i) Explain the term ionisation energy and relate it to the chemical properties of metals. Place the following elements in order of increasing ionisation energy; sodium, caesium, fluorine, aluminium. **[5marks]**
- (ii) Write equations for the extraction of lead, Pb, from its ore, lead sulphide. **[5marks]**
- (iii) Describe the structures and uses of carbon. **[5marks]**
- (iv) Write briefly on sources of energy. **[5marks]**

Section D
(Physical Chemistry)

10. Answer any two of the following:

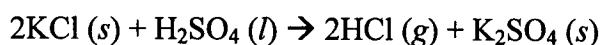
- (i) Describe some of the properties of liquids and solids that are dependent, to some extent, on the strength of intermolecular forces. **[10 Marks]**

- (ii) In a certain zinc-copper Galvanic cell,

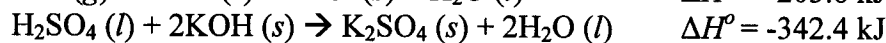
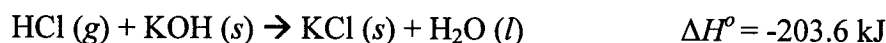


the ion concentrations are $[\text{Cu}^{2+}] = 0.10 \text{ mol L}^{-1}$ and $[\text{Zn}^{2+}] = 1.0 \text{ mol L}^{-1}$. What is the cell potential at 25°C? $E^\circ_{\text{Cu/Cu}^{2+}} = +0.34\text{V}$ and $E^\circ_{\text{Zn/Zn}^{2+}} = -0.76\text{V}$ **[10 Marks]**

- (iii) We can generate hydrogen chloride by heating a mixture of sulphuric acid and potassium chloride according to the equation



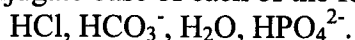
Calculate ΔH° in kilojoules for this reaction from the following thermochemical equations.



[10 Marks]

11. Answer all parts:

- (i) Give the formula for the conjugate base of each of the following Bronsted acids:



[4 Marks]

Which of these substances above are amphoteric?

[3 Marks]

- (ii) Calculate the pH and pOH of a 0.10 mol L^{-1} aqueous solution of ethanoic acid, CH_3COOH , given that the pK_a is 4.75. **[7 Marks]**

- (iii) Describe why ice melts spontaneously at 0°C even though it is an **endothermic** process. **[6 Marks]**

12. Answer both (i) and (ii):

- (i) Explain and compare the phase diagrams for CO_2 and H_2O . **[10 Marks]**

- (ii) The concentration of a drug in the body is often expressed in units of milligrams per kilogram of body weight. The initial dose of a drug in an animal was 25.0 mg/kg body weight. After 120 min., this concentration had dropped to 15.0 mg/kg body weight. If the drug is eliminated metabolically by a first-order process, what is the rate constant for the process (in units of min^{-1})? **[10 Marks]**