

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

AUTUMN 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:

- (i) Briefly explain the terms “orbital”, the “Pauli Exclusion Principle” and “Hund’s Rule” in connection with atomic structure. Write the electronic structure of the carbon atom (atomic number, 6) and list the four quantum numbers for each electron in this atom. [7 marks]
- (ii) Use the Bohr theory to explain the emission spectra of excited hydrogen atoms and show qualitatively how the Lyman and Balmer series of emission lines arise. [7 marks]
- (iii) Explain the term Ionisation Potential and briefly discuss the trends in the first ionisation potentials of the 18 elements from Hydrogen to Argon. [6 marks]

2. Answer (i) and (ii).

- (i) Briefly explain the main points of the Valence Shell (Domain) Electron Pair Repulsion Theory and derive the structures of the following molecules:

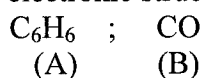


- (ii) Dioxygen (O_2) is a para magnetic gas with a magnetic moment of 2.84 bohr magnetons. Using molecular orbital theory explain this and assess the relative stabilities of the following gaseous molecules using bond orders:



3. Answer any three of the following: [6.7 marks each]

- (i) Describe the kinetic theory of ideal gases and use it to explain Graham’s Law of Diffusion.
- (ii) Explain what happens when an ionic crystalline salt dissolves in water; The solubility product of BaSO_4 is 4×10^{-11} at 25°C ; determine the solubility of this salt in pure water and in a $0.1\text{M Na}_2\text{SO}_4$ solution.
- (iii) Describe the phenomenon of hydrogen bonding and show how it controls the physical properties and structure of water and ice.
- (iv) The dipole moment of $\text{CH}_3\text{-Br}$ is $5.96 \times 10^{-30}\text{Cm}$ and the per cent ionic character of the C-Br bond is 19.6%. Calculate the bond length of the C-Br bond in this molecule. (Assume that the dipole moment of each CH bond is zero).
- (v) Explain the theory of resonance in the electronic structure of molecules and comment on the electronic structures of the species (A) and (B).



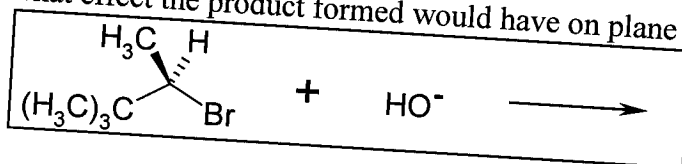
Section B
(Organic Chemistry)

4. Answer any three of the following:

- (i) Briefly account for the three dimensional structure of methane. Draw the structure of all isomers of the alkane with molecular formula C_5H_{12} . [6.67 Marks]
- (ii) Give a brief account of the preparation of ethers. Explain why ethers are generally regarded as good solvents for a variety of reactions [6.67 Marks]
- (iii) Explain the origin of amine basicity in water. What is the product of reaction of diethylamine with hydrochloric acid? [6.67 Marks]
- (iv) Draw the structure of methyl benzoate and describe how this compound may be prepared from benzoic acid and methanol. [6.67 Marks]

5. Answer any two of the following:

- (i) The reaction rate for the following nucleophilic substitution reaction has been shown to be proportional to the concentration of the alkyl bromide only when the reaction is carried out in water. Can you:
 - (a) Draw the product of the reaction [3 Marks]
 - (b) Explain in detail why the above information proves the reaction proceeds via a S_N1 and not a S_N2 mechanism. [4 Marks]
 - (c) Explain what effect the product formed would have on plane polarised light [3 Marks]



- (ii) Discuss using appropriate chemical equations the preparation of alcohols under the following headings (ensure at least one example of a primary, secondary and tertiary alcohol is indicated in your answer):
 - (a) Reduction of carbonyl containing compounds. [4 Marks]
 - (b) Grignard reagent addition to carbonyl containing compounds [4 Marks]
 - (c) Alkene hydration [2 Marks]

- (iii) In the light initiated free radical reaction of chlorine (Cl_2) with propane ($CH_3CH_2CH_3$) two isomeric chloroalkanes of molecular formula C_3H_7Cl are formed:
 - (a) Draw the structure of these two chloroalkanes. [4 Marks]
 - (b) Indicate which would be the major product. [2 Marks]
 - (c) Give a mechanistic explanation of your answer to part (b) [4 Marks]

- (iv) Discuss, using chemical equations, the reactions of alkenes under the following headings:
 - (a) Addition of HCl , Br_2 and H_2O [6 Marks]
 - (b) Oxidation by $KMnO_4$ and ozone (O_3) [4 Marks]

Briefly describe the structure of benzene

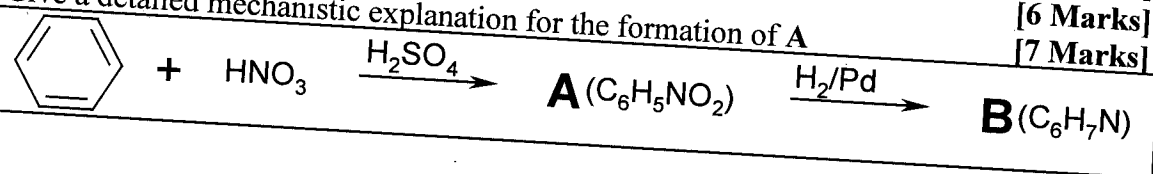
Deduce structures for **A** and **B**

Give a detailed mechanistic explanation for the formation of **A**

[7 Marks]

[6 Marks]

[7 Marks]



Section C
(Inorganic Chemistry)

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

- (i) Give the electronic configuration and write Lewis (electron dot) pictures for the elements; phosphorus, aluminium, and bromine.
- (ii) Write a balanced chemical equation that shows the preparation of synthesis gas from methane (CH_4) and oxygen (O_2).
- (iii) Describe some uses of chemicals in the household.
- (iv) Write briefly on nuclear energy.

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

- (i) Give the most common oxidation states for the elements, potassium, silicon, and sulphur. Predict the molecular formulae for; potassium sulphide, silicon sulphide, and potassium silicide.
- (ii) Write a balanced chemical equation that shows the preparation of bleach from chlorine and water.
- (iii) Describe some uses of chemicals in health.
- (iv) Write briefly on pollution.

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

- (i) Explain the term electronegativity and describe its role in predicting the polarity of chemical bonds. Place the following elements in order of increasing electronegativity; oxygen, nitrogen, fluorine, chlorine.
- (ii) Write equations for the extraction of any element from its ore.
- (iii) Describe the structure and uses of silicon and its compounds.
- (iv) Write briefly on 'the air we breath'.

Section D
(Physical Chemistry)

10. Answer any two of the following:

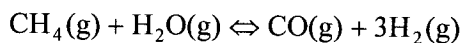
- (i) Write an explanatory note on “like dissolves like”. [10 marks]
- (ii) Describe the process and advantages of freeze-drying. [10 marks]
- (iii) Benzene and toluene help achieve good engine performance from lead-free petrol. At 40°C, the vapour pressure of benzene is 180 torr and that of toluene is 60 torr. To prepare a solution of these that will have a total vapour pressure of 96 torr at 40°C requires what mole percent concentration of each? [10 marks]

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

- (i) Explain the origin and limits of the pH scale. [5 marks]
Calculate the pH of a 0.15 mol L⁻¹ aqueous solution of CH₃COOH given that the pK_a is 4.75. [5 marks]
- (ii) Describe a practical application of a galvanic cell. [10 marks]

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

- (i) The reversible reaction



has been used as a commercial source of hydrogen. At 1500°C, an equilibrium mixture of these gases was found to have the following concentrations: [CO] = 0.300 M, [H₂] = 0.800 M, and [CH₄] = 0.400 M. At 1500°C, K_c = 5.67 for this reaction. What was the equilibrium concentration of H₂O (g) in this mixture? [5 marks]

What is K_p for this reaction at 1500°C? [5 marks]

- (ii) Carbon-14 is a radioactive isotope that decays to form Nitrogen-14 by a first-order process with a half-life of 5770 years.

What is the rate constant for the decay? [5 marks]

How many years will it take for 1/100 of the ¹⁴C in a sample of naturally occurring carbon (a mixture of carbon isotopes including ¹⁴C) to decay? [5 marks]