OLLSCOIL NA hÉIREANN, GAILLIMH

THE NATIONAL UNIVERSITY OF IRELAND, GALWAY

SUMMER EXAMINATIONS 1999

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

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CHEMISTRY

Time Allowed: Three Hours

Answer <u>Five</u> questions and include <u>at least one from each Section</u>.
<u>Use a separate answer book for each Section.</u>
Leave the first page of the Answer Book blank and list on it clearly the numbers of the questions attempted.
All questions carry equal marks. (For a question with a choice between parts, all parts of that question carry equal marks).

Universal Gas Constant: R = 8.31 $kPadm^3K^{-1}mol^{-1}$ ($J\,K^{-1}mol^{-1}$)
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: -1.6×10^{-19}C; Mass of the electron: 9.109×10^{-31}kg.
Faraday: 96500C
Avogadro Number: 6.022×10^{23}
Planck Constant: h: 6.626×10^{-34} J.s.; ($kg.m^2.s^{-2}$);
Velocity of light, c:2.997×10^8 $m.s.^{-1}$

Section A (Atomic and Molecular Structure)

1. Answer <u>each</u> of the following:

(a) Explain the main points of the Bohr theory of atomic structure and use it to derive an expression for the energy levels of the electron in the H atom and to explain the emission spectra of excited gaseous H atoms.

(b) In the context of atomic structure explain the following terms:
orbit, orbital, Pauli exclusion principle, Hund's Rule.
Explain the electronic structure of the N atom (atomic number 7) and write the quantum numbers for each electron in the atom.

(c) Briefly explain the meaning of the equations $E=h\nu$ (Planck) and $E=mc^2$ (Einstein) and use them to derive the de Broglie equation for the wavelength of a particle of mass m and velocity v and comment on the significance of the de Broglie equation for atomic structure.

2. Answer any <u>three</u> of the following:

(a) Explain the kinetic theory of ideal gases and use it to derive Graham's Law of Diffusion. Determine the relative rate of diffusion of the gases SO_2 and N_2. (Atomic masses, N, 14.0; O, 16.0; S, 32.0 amu).

(b) Explain the origin of the electronegativity scale of the elements. Use the electronegativities of H(2.1) and O(3.5) to determine the ionic character of the O-H bond in water. Use the electronegativities of carbon (2.5) and chlorine (3.0) to determine the ionic character of the C-Cl bond in CCl_4 and then explain why CCl_4 is a non-polar molecule with no dipole moment.

(c) Discuss and explain the phenomenon of the hydrogen bond (bridge). Explain the structure of normal crystalline ice (Ih) and why water has a maximum density at 3.98°C and a boiling point of 100°C.

(d) Comment on the factors which control the solubility of ionic salts in water. If the solubility of MgF_2 in water at 20°C is 0.075g per litre, determine K_{sp} for MgF_2 at 20°C. (Atomic masses, Mg, 24.3, F, 19.0 amu).

3. Answer any <u>two</u> of the following:

(a) Comment on the main points of the VSEPR theory of molecular structure and use the theory to describe the structures of the following molecules: H_2SO_4, HNO_3, PCl_5, PCl_3.

(b) Briefly explain the theory of resonance to describe the electronic structures of molecules and discuss the electronic structures of the following species: $HCO_2^- Na^+$; CO; C_6H_6.

(c) Explain the electronic structure and bonding in the molecules N_2 and O_2. One of these is paramagnetic. Explain which one and determine its magnetic moment in superoxide ion.

Section B (Organic Chemistry)

4. Answer <u>each</u> of the following:

(1) Explain the electronic basis for the tetrahedral structure of methane [CH_4]. Draw the structures and give the systematic names for the isomeric alkanes C_4H_{10}.

(2) Explain the electronic structure of the alkene functional group [$R_2C{=}CR_2$]. Draw and explain the existence of two stereoisomeric forms of 2-butene [C_4H_8].

(3) Give a short account of the properties, preparation and reactions of organolithium reagents.

5. Answer <u>any two</u> of the following:

(a) In the free radical addition of chlorine to propane two isomeric chloropropanes can result. Draw the structure of each, give a mechanistic explanation for their formation and indicate which you think should be the major product.

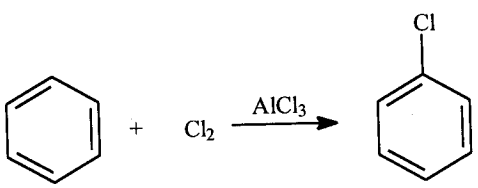
(b) Using the following reaction as a typical example, explain the S_N1 mechanism for the nucleophilic substitution of an alkyl halide. Include in your answer the free energy diagram describing the course of the reaction.

$$(CH_3)_3C\text{-}Cl + I^- \rightarrow (CH_3)_3C\text{-}I + Cl^-$$

(c) Give an account of the structure and reactivity of the carbonyl functional group - illustrate your answer with appropriate chemical equations.

(d) Draw the structure of a primary, a secondary and a tertiary aliphatic amine. Explain the origin of amine basicity and write the equations for the reaction of a primary aliphatic amine with H_2O and with HCl. How does the basicity of aniline compare with that of a primary aliphatic amine.

6. Give an account of the structure of benzene and explain why it undergoes substitution and not addition reactions. Describe the mechanism for the following transformation.



Section C (Inorganic Chemistry)

7. Answer <u>each</u> of the following:

a) Sketch structures for the allotropes of carbon.

b) Give some of the uses for elemental carbon.

c) Describe how carbon black, coke and carbon fibres are made.

d) Give Lewis (electron dot) pictures for the oxides of carbon and compare their structures with that for silicon dioxide.

8. With respect to the oxyacids of chlorine answer <u>each</u> of the following:

a) Name and give molecular formulae for each oxyacid

b) Write Lewis (electron dot) pictures for each oxyacid.

c) Assign an oxidation state to chlorine in each oxyacid

d) Rank the oxyacids in order of increasing acid strength, explain your ranking.

9. Answer <u>each</u> of the following:

a) Write a chemical equation which shows sodium acting as a reducing agent.

b) Discuss briefly three industrial uses of compounds of sodium.

c) Identify and assign oxidation states to the products obtained when the alkali metals react with oxygen.

d) Briefly describe the chemistry of the 'Solvay Process'.

Section D (Physical Chemistry)

10. Answer <u>any two</u> of the following:

(a) Methanol, a potential replacement for petrol as a fuel, can be made from H_2 and CO by the reaction below, which has a ΔH^o of –18kJ. List the kind of changes that would alter the amount of methanol present in the system at equilibrium. If the equilibrium constant (Kp) for this

$$2H_2(g) + CO(g) \Leftrightarrow CH_3OH(g)$$

reaction at 500K is 6.25×10^{-3} calculate ΔG^o_{500} for this reaction in units of kJ.

(b) Describe the process of reverse osmosis for the desalination of water.

(c) Explain why deviations from the ideal equation of state PV=nRT occur. How does Van der Waal's equation improve matters?

11. Answer <u>both</u> (a) and (b)

(a) Write the thermochemical equation for the formation of methanol, $CH_3OH(g)$, from its elements and evaluate its standard enthalpy of formation given that the heat of sublimation of carbon (graphite) is 716.7 $kJmol^{-1}$. Selected mean bond enthalpies are given in the table.

Bond	Mean Bond Enthalpies ($kJmol^{-1}$)
C-C	348
C-O	463
O=O	497
H-H	436
O-H	463

(b) Describe some of the properties of liquids and solids that are dependent, to some extent, on the strength of intermolecular forces.

12. Answer <u>each</u> of the following:

(a) Describe why ice melts spontaneously at 0°C even though it is an exothermic process.

(b) Explain the term conjugate acid-base pair and select out the conjugate pairs among the following:

$$HPO_4^{2-},\ NH_3,\ HS^-,\ NH_4^+,\ H_2PO_4^-,\ PO_4^{3-},\ H_2S$$

(c) The age of wine can be determined by measuring the trace amount of radioactive tritium, the concentration of which dimishes by a first-order radioactive decay with a half-life of 12.5 years once the wine is bottled. If a bottle of wine is found to have a tritium concentration that is 0.100 that of freshly bottled wine, what is the age of the wine?

(d) Illustrate the difference between Galvanic and electrolytic electrochemical cells, giving examples of each.