Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SUMMER EXAMINATIONS 1999

THIRD UNIVERSITY B. Sc. EXAMINATION IN SCIENCE
(INCLUDING DENOMINATED DEGREES)
CHEMISTRY — CH303

CHEMISTRY: *First Paper*

All questions carry equal marks.

(For a question with a choice between parts all parts of that question carry equal marks)

Answer *five* (5) questions.

Professor R J Donovan
Professor R N Butler
Professor B Ó Cochláin
Dr J M Simmie
Dr W M Carroll

Time allowed : *Three* hours

Gas Constant, $R = 8.314\ J\ K^{-1}\ mol^{-1}$	Avogadro constant, $N_A = 6.022 \times 10^{23}\ mol^{-1}$
Planck's constant, $h = 6.626 \times 10^{-34}\ J\ s$	Velocity of light, $c = 2.998 \times 10^{8}\ m\ s^{-1}$
Electronic mass, $m_e = 9.109 \times 10^{-31}\ kg$	Boltzmann constant, $k = 1.381 \times 10^{-23}\ J\ K^{-1}$
Electronic charge, $e = 1.602 \times 10^{-19}\ C$	Bohr magneton, $\mu_B = 9.274 \times 10^{-24}\ J\ T^{-1}$
Faraday constant, $F = 96485\ C\ mol^{-1}$	Atmosphere $= 101325\ N\ m^{-2}$

1. Derive the Clapeyron equation and use it to solve the following problem.

Sulphur is to be pumped from underground deposits at 6 bar total pressure. What must be the minimum temperature?
Sulphur melts at 115.2 °C and its ΔH_{fusion} is 53.67 kJ mol^{-1}; the densities (g cm^{-3}) of liquid and solid sulphur are 1.811 and 2.050 respectively.

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2. **Answer EITHER (a) OR (b).**

(a) The standard Gibbs free energies of graphite and diamond are zero and 2.866 kJ mol^{-1} respectively; the respective densities are 2.25 and 3.5 g cm^{-3}. At what pressure will the two forms be in equilibrium at room temperature? What assumptions are necessary?

(b) Derive a relationship between osmotic pressure and mole fraction and use it to calculate the osmotic pressure of a 0.010 molal solution at 298 K

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3. **Answer EITHER (a) OR (b).**

(a) What are the fundamental statistical mechanical assumptions and the main steps in obtaining the formula

$$E = NkT^2\left(\frac{\partial \ln f}{\partial T}\right)_V$$

relating the molar energy E to the partition function f for a monatomic gas?

(b) The data in the table are for the adsorption of a gas (molecular area = 16.2×10^{-20} m^2) on 3.022g of charcoal at 273K. Find the surface area of the charcoal.

P/mm Hg	100	200	300	400	500	600	700
V/cm^3 stp	10.2	18.6	25.5	31.4	36.9	41.6	46.1

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4. **Answer (a) and (b).**

(a) Describe the interfacial changes which occur when a copper electrode is initially immersed in a Cu^{2+} solution.

(b) The data in the following table refer to the anodic current through a platinum electrode of area 2.0 cm^2 in contact with an Fe^{3+}, Fe^{2+} aqueous solution at 298K.

η/mV	50	100	150	200	250	350
I/mA	8.8	25.0	58.0	131	298	300

Estimate the exchange current density (i_0), the transfer coefficient (α) and the limiting current (i_L) for the electrode process.

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5. Answer (a) and (b).

(e) Because synthetic polymers are **polydisperse,** the various techniques that are used to measure their molar masses result in different types of mean values. Discuss this statement.

(f) The following viscosities were measured for solutions of cellulose acetate in acetone of concentration 0.5g/100cm^3:

M_w	100,000	200,000	300,000
$\eta/10^{-4}$ kg m^{-1} s^{-1}	5.6	7.4	9.0

The viscosity of acetone at the temperature of these measurements is 3.2 x 10^{-4} kg m^{-1} s^{-1} Derive an expression from these data which could be used for routine determinations of the relative molar masses of cellulose acetate samples from viscosity measurements.

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6. Write down the Schrödinger wave equation for a particle of mass m confined to movement along a one-dimensional coordinate, x.

What information does this equation yield?

What restrictions are placed on ψ?

The energy of a particle of mass, m, confined to a region along the x-axis of zero potential energy between $x=0$ and $x=L$ is given by:

$$E_n = n^2h^2/8mL^2$$

Calculate the difference in energy between the levels $n=2$ and $n=1$ in joules of an electron in a box of length 1.0 nm.

What are the most likely locations of a particle in a box of length L in the state $n=3$?

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7. Outline the basic features of Raman spectroscopy with the aid of a labelled diagram.

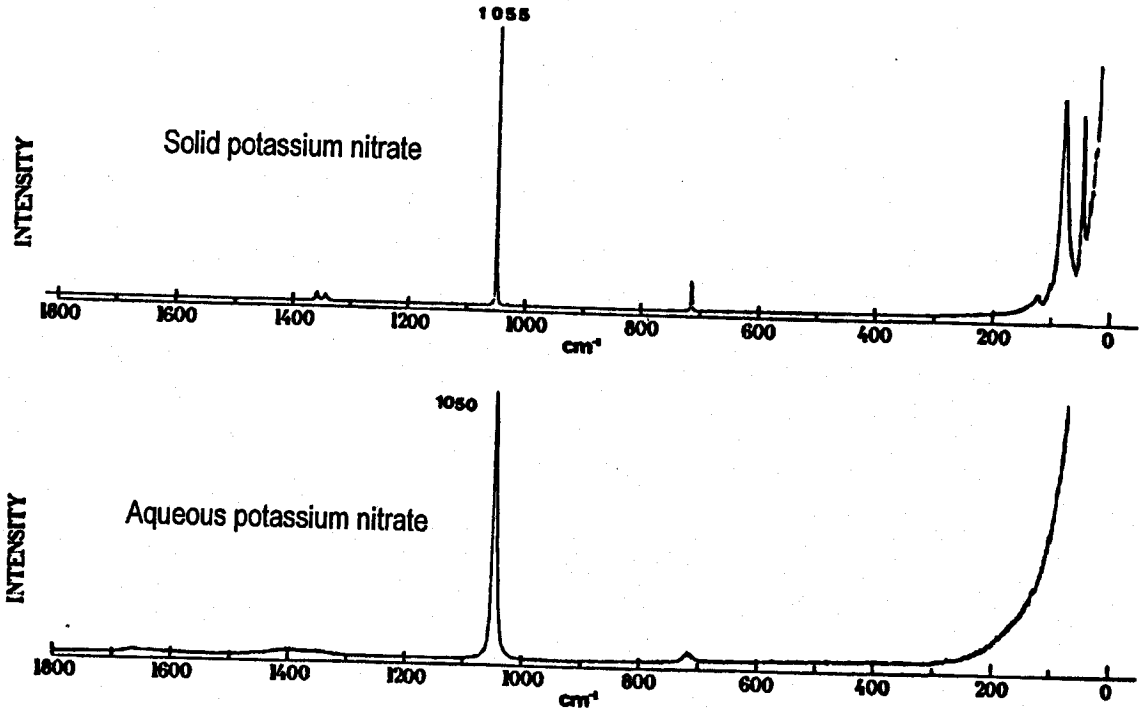
Describe the light sources that are used?

If the sample is a fluid what type of cell is required?

Why are the Raman frequencies essentially symmetrical about the excitation line? Sketch a molecular energy-level diagram to explain your answer.

What governs whether a particular molecular vibration will show up in a Raman spectrum?

Comment on the quality and appearance of the Raman spectra shown below for the nitrate anion, NO_3^-, in comparison to similar infrared spectra.



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8. The kinetics of a first-order reaction in a plug-flow reactor are given by:

$$[A]_o = [A]_i \,.\, \exp\left(-k\,V / v\right)$$

Briefly, explain the meaning of each term.

An aqueous 0.068 mol dm^{-3} solution of cyanamide, $NCNH_2$, flows at 2.4×10^{-4} $dm^3\ s^{-1}$ through a 6.0 cm diameter cylindrical reactor at a temperature of 323K and must exit the reactor with a concentration of ≤ 0.010 mol dm^{-3}.

What is the minimum length of reactor required if the reaction which destroys cyanamide:

$$NCNH_2 + H_2O \rightarrow OC(NH_2)_2$$

proceeds with first-order kinetics and with a rate constant of 9.72×10^{-6} s^{-1} at 323 K?