Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SUMMER EXAMINATIONS 1999

FINAL EXAMINATION FOR THE DEGREE OF B Sc

HONOURS CHEMISTRY

First Paper

All questions carry 100 marks, distributed as shown where appropriate

Answer *five* (5) questions.

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

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

(a) Given $dE = TdS - PdV + \gamma da$ where a is surface area and γ is surface tension, show that

$$\left(\frac{\partial \gamma}{\partial T}\right)_{a,V} = -\left(\frac{\partial S}{\partial a}\right)_{T,V}$$

[20 marks]

(b) Using the Van der Waals equation of state with the constants a = 1.345 (litres mol^{-1})^{2}atm and b = 0.0322 litres mol^{-1} and C_V = 12.47 J K^{-1} mol^{-1} for Ar, calculate ΔE when 1 mole of Ar changes from

state (A): T = 511 K, V = 2.5 litres to state (B): T = 950 K, V = 5.0 litres

[80 marks]

---

2. **Answer (a), and (b).**

(a) Derive a general relationship which allows the calculation of the fugacity of a gas from compressibility data.

[50 marks]

(b) Explain why fugacity is important and show also that if the compressibility is given by $Z = 1 + BP/RT$ the fugacity is given by $f = Pe^{Z-1}$.

[50 marks]

---

3. **Answer (a), and (b).**

(a) Give the principal steps in obtaining the formula

$$S_{elect} = \frac{E}{T} + R\ln f = R\left[\frac{T}{f}\left(\frac{\partial f}{\partial T}\right) + \ln f\right]$$

where f is the electronic partition function and E is the electronic energy.

[50 marks]

(b) Use the above equation and the data in the table below to calculate the contribution from the electronic levels to the entropy of fluorine at 1000 K.

Term	$\bar{\nu}$ /cm^{-1}
$P_{3/2}$	0
$P_{1/2}$	404
$P_{5/2}$	102406.5

[50 marks]

---

4. Answer <u>four</u> of the following six items:

(i) Write an account of the *volcano effect* in heterogeneous catalysis.

(ii) Discuss the following concepts in catalysis: *selectivity, structure sensitivity* and *activity trends across the periodic table*.

(iii) Write a concise account of catalysis in the petroleum industry.

(iv) Discuss the interpretation of the kinetics of heterogeneous reactions.

(v) Write an account of the BET equation and its use in obtaining the surface area of solids.

(vi) Write an account of the Langmuir adsorption equation and its use in surface chemistry.

[4 @ 25 marks]

---

5. Answer (a), (b) and (c).

(a) The introduction of dimensionally stable anodes (DSA) in the 1960's and the use of catalytic coatings on cathodes have considerably improved energy consumption in the chlor-alkali industry. Discuss this statement.

[40 Marks]

(b) The cell voltage for the Hall-Heroult cell used in aluminium production is nearly four times the calculated reversible cell potential. What are the major factors which contribute to this overvoltage?

[40 Marks]

(c) Suggest reasons, why developments in the cell technology used in aluminium production have not kept pace with those used in the chlor-alkali industry?

[20 Marks]

---

6. Answer (a), (b), (c) and (d).

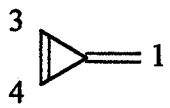
(a) In LCAO–MO theory the energies of a system can be easily obtained by solving the equation:

$$|\mathbf{H-ES}| = 0 \qquad (1)$$

What are the Hückel approximations for solving equation (1)?

[20 marks]

(b) Set up the secular determinant for methylenecyclopropane:



[20 marks]

(c) The MO energies are $x = -2.170, -0.311, +1.000$ and $+1.481$; draw an energy level diagram and calculate the delocalisation energy of the neutral molecule.

[20 marks]

(d) The wavefunctions are given by:

	Atom 1	Atom 2	Atom 3	Atom 4
#4	*0.506*	*–0.749*	*+0.302*	*+0.302*
#3	*0.000*	*+0.000*	*+0.707*	*–0.707*
#2	*0.815*	*+0.254*	*–0.368*	*–0.368*
#1	*0.282*	*+0.612*	*+0.523*	*+0.523*

Sketch and describe each molecular orbital.

[40 marks]

---

7. Answer (a) and (b).

(a) What is the origin of the interaction, *hyperfine coupling*, between an unpaired electron and a magnetic nucleus in a molecule?

[40 marks]

(a) Recently the species $Sc_3@C_{82}$, part of the fullerene family, has been prepared and its ESR spectrum (g-value of 1.999) obtained in a solution of toluene at 220K; only one hyperfine coupling constant of 64 mT is observed, each of the 22 lines has a linewidth of 4mT, see *Figure 1*.

Interpret the spectrum and use the information to deduce the structure.

[60 marks]

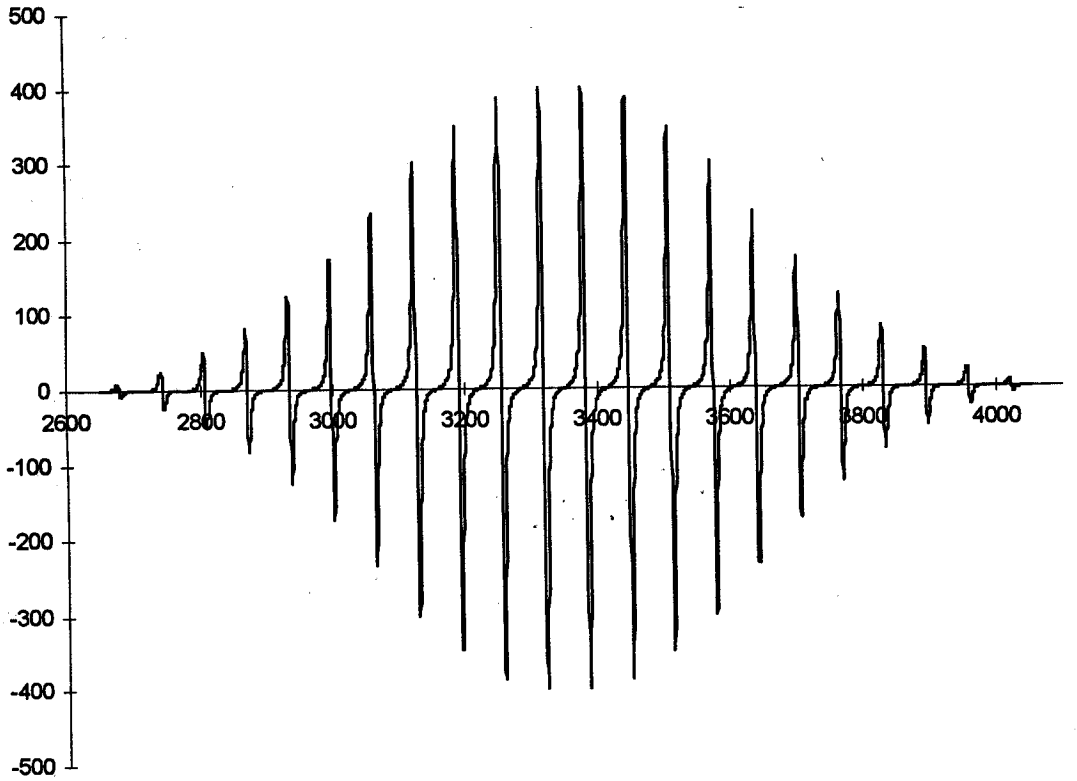


Figure 1: ESR spectrum of $Sc_3@C_{82}$

---

8. Answer (a) and (b).

(a) Calculate the concentration of iodine atoms when an excimer laser pulse of 10 mJ at 248 nm is incident on a $1cm^3$ cubical cell containing 3×10^{15} molecules of ethyl iodide. What assumptions must you make to answer this question?

[50 marks]

(b) In order to use collision theory to calculate rates of reactions one needs to know the fraction of molecular collisions with an energy greater than or equal to some critical value, E_C. What is this fraction when (i) E_C = 10 kJ mol^{-1}, (ii) E_C = 100 kJ mol^{-1} for a temperature of 300K?
Calculate the percentage increase in the fractions when the temperature is increased by 10 K. Comment on your answers.

[50 marks]
