Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SUMMER EXAMINATIONS 2000

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.

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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.

The equilibrium constant for the reaction

$$A_2(g) + B_2(g) = 2AB$$

may be expressed as

$$\ln K_p = 8.57 + 985/(T/\mathrm{K}) + 0.9\ln(T/\mathrm{K})$$

Calculate ΔG^o, ΔH^o and ΔS^o at 400 K.

[100 marks]

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2. Derive the Planck equation:

$$\frac{d\Delta H}{dT} = \Delta C_p + \frac{\Delta H}{T} - \Delta H\left(\frac{\partial \ln \Delta V}{\partial T}\right)_P$$

for the variation of ΔH of a phase change with temperature

[50 marks]

Show that for solid→vapour and liquid→vapour transitions the equation becomes

$$\frac{d\Delta H}{dT} = \Delta C_p$$

to a very good approximation.

[50 marks]

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

(a) Using Boltzmann's statistics, give the principal steps in obtaining the formula

$$S = \frac{E}{T} + R\ln\left(\frac{f}{N}\right) + R$$

for the entropy of an ideal gas.

[60 marks]

(b) Write the corresponding formula for the entropy of a solid and explain any difference.

[40marks]

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

(i) Write an account of the use of the *Hertz - Knudsen equation* in surface chemistry.

(ii) Discuss the following concepts in catalysis: *active sites, metal dispersion.*

(iii) Write a concise account of the *use of zeolites* in heterogeneous catalysis.

(iv) Discuss the interpretation of *Arrhenius plots* in catalysis.

(v) Write an account of the Brunauer classification of sorption isotherms.

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

[4 @ 25 marks]

5. Answer (a) and (b)

(a) Mixed potential theory has proved to be useful in corrosion studies because it permits prediction of complex corrosion behaviour and has been used to develop new corrosion prevention methods. Discuss.

[50 Marks]

(b) Draw an Evans diagram for a metal M corroding in an acid solution under activation control. Label it carefully and indicate the corrosion rate of this system. Is the corrosion rate increased or decreased by the following changes? (Give reasons for your answers).

(i) Increasing i_0 of the $M \rightarrow M^+ + e^-$ reaction.

(ii) Increasing i_0 of the $H^+ + e^- \rightarrow 1/2H_2$ reaction.

(iii) Shifting the reversible potential of the $M \rightarrow M^+ + e^-$ to a more noble (+) value.

(iv) Increasing the value of the Tafel slope, b, for the oxidation reaction.

[50 Marks]

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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:

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

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

[20 marks]

(b) Set up the secular determinant for butadiene.

[20 marks]

(c) The MO energies for butadiene are x = –1.618, –0.618, +0.618 and +1.618; draw an energy level diagram and calculate the delocalisation energy of the neutral molecule.

[20 marks]

(d) The wavefunctions for butadiene are given by:

	Atom 1	Atom 2	Atom 3	Atom 4
#4	0.372	–0.602	0.602	–0.372
#3	–0.602	0.372	0.372	–0.602
#2	0.602	0.372	–0.372	–0.602
#1	0.372	0.602	0.602	0.372

Sketch and describe each molecular orbital.

[40 marks]

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7. Answer (a) and (a).

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

[40 marks]

(b) The ESR spectrum of triethylenediamine cation consists of 65 lines with just two coupling constants of 1.7 and 0.73 mT.

$$N(CH_2CH_2)_3N^+$$

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

[60 marks]

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8. Answer (a) and (b).

(a) A shock tube study was carried out of the reaction of carbon atoms with nitric oxide by heating a mixture of carbon suboxide, nitric oxide and argon. Following the shock, carbon suboxide, C_3O_2, is rapidly pyrolysed:

$$C_3O_2 \rightarrow C + 2\,CO_2$$

And the C atoms then react with an excess of NO.
The relative concentrations of carbon atoms, S_C, was determined mass spectroscopically. From the data in the Table below, confirm that the kinetics of reaction are first order and calculate the first order rate constant.

Time / μs	10	20	30	40	50	60
S_C	5.74	4.33	3.13	2.33	1.83	1.40

[80 marks]

(b) Why is the study being carried out in a shock tube? What is the advantage in having an excess of NO present?

[20 marks]
