GX351

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SEMESTER 2 2002

THIRD YEAR CHEMISTRY

Physical Chemistry (CH 313)

All questions carry equal marks distributed as shown.

Answer *four* (4) questions.

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

Time allowed : *Two* 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 vapour pressure of a liquid between 15°C and 35°C fits the expression:

$$\log(P/\text{mm Hg}) = -\frac{1625}{(T/K)} + 8.750$$

Calculate **(a)** the enthalpy of vaporisation

[13 marks]

(b) the normal boiling point.

[12 marks]

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2. Answer **Three** of the following:

(i) Derive two of Maxwell's relations.

[8 marks]

(ii) Show that for an ideal binary solution the addition of component B lowers the melting point of component A.

[8 marks]

(iii) Explain the connection between an equilibrium constant and standard free energy.

[8 marks]

(iv) What are the fundamental principles involved in the calculation of entropy changes in irreversible processes?

[8 marks]

(v) Show how Van't Hoff's equation explains Le Chatelier's Principle.

[8 marks]

(vi) Gaseous I_2 (maintained at a total pressure of 1 atm) is 1% dissociated into atoms at 600 °C and is 25% dissociated at 800 °C. Calculate ΔH for the dissociation.

[9 marks]

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3. Given the following table of data for the electronic levels of Te

Level	Degeneracy	$\bar{\nu}/\text{cm}^{-1}$
ground	5	0
1	1	4707
2	3	4751
3	5	10559

calculate the electronic partition function and the fraction of the Te atoms in the ground state at 5000 K.

[25 marks]

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4. List the assumptions involved in the Langmuir adsorption isotherm.

[5 marks]

Derive the equation for the isotherm

[10 marks]

and show how:

(i) it may be extended to account for dissociative adsorption;

[5 marks]

(ii) it can be used to obtain surface areas of microporous solids;

[5 marks]

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

(a) Describe the important role diffusion processes can play in electrode reactions.

[13 marks]

(b) In an experiment on the Pt/ H_2 / H^+ electrode in dilute H_2SO_4 the following current densities were observed at 298K.

η/mV	50	100	150	200	250
i/mA cm^{-2}	2.66	8.91	29.9	100	335

Evaluate the transfer coefficient (α) and the equilibrium exchange current density (i_0) for the electrode.

[12 marks]

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

(a) The energy levels of an electron of mass, m_e, confined to a region along the x-axis of zero potential energy between $x = 0$ and $x = L$ are given by:

$$E_n = n^2h^2/8m_eL^2 \qquad n = 1,2,3\ldots$$

Draw a diagram to scale on graph paper showing the position of the three lowest energy levels.

Superimpose on each energy level the probability of finding the electron at each point from x=0 to L.

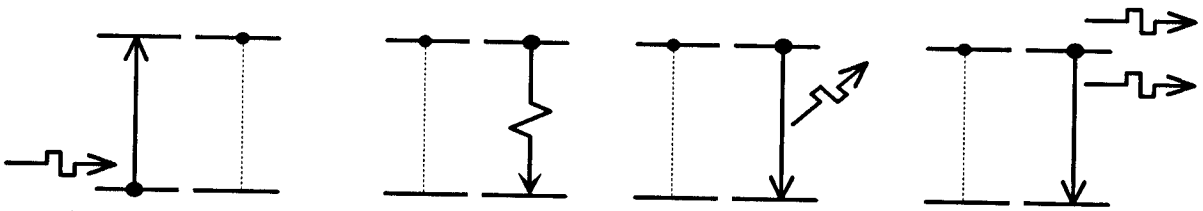
[13 marks]

(b) "An extraordinary revitalization of the study of surfaces took place about a decade ago with the introduction of a technique based on the quantum mechanical ability of electrons to tunnel into and through regions where they were forbidden to go classically."
Briefly discuss the above quotation.

[12 marks]

7.

(a) Provide an explanation for the following spectroscopic diagrams.



[10 marks]

(b) What is the relevance of the Boltzmann Distribution Law:

$$n_j \propto g_j \exp\left(-\frac{\varepsilon_j}{kT}\right)$$

to the study of transitions?

[10 marks]

(c) How can it be used to measure temperature?

[5 marks]

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

(a) Distinguish between a (i) thermal explosion and (ii) a chain-branching explosion.

[5 marks]

(b) Sketch an apparatus that could be used to measure the explosion limits of a gas-phase reaction and indicate the data that would be collected.

[10 marks]

(c) What would the results of such a study look like for a stoichiometric hydrogen–oxygen mixture?

[10 marks]
