GX352

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

SUMMER EXAMINATIONS 2002

FINAL EXAMINATION FOR THE DEGREE OF B Sc

HONOURS CHEMISTRY (CH 401)
CHEMISTRY AND APPLIED CHEMISTRY, DENOMINATED (CH 401)

First Paper: Physical Chemistry

All questions carry 100 marks, distributed as shown where appropriate

Answer *five* (5) questions.

Professor K Waugh
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 Clausius-Clapeyron equation which allows the calculation of the vapour pressure of a liquid as a function of temperature; list any necessary assumptions.

[50 marks]

The vapour pressure of liquid water at 25°C is 23.76mm Hg.
Calculate the change in this pressure when the liquid is subjected to an external pressure of 1000 atm.

[50 marks]

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2. Show how thermodynamic data of the type listed in the table below can be measured and calculated for gases and solids.

[40 marks]

The table gives data for the equilibrium $Br_2(g) = 2Br(g)$
Calculate K_p for the equilibrium at both temperatures, 1173 and 1273 K and the average value of ΔH in this temperature range.

[3×15 marks]

Also calculate ΔH° at 298 K.

[15 marks]

	$-\left(\frac{G^\circ - H_0^\circ}{T}\right)$ / J K^{-1}mol^{-1}			
	1000 K	**1500 K**	$\left(H_{298}^\circ - H_0^\circ\right)$ / kJ mol^{-1}	ΔH_0° / kJ mol^{-1}
Br_2	254.5	269.2	9.73	35.0
Br	179.4	187.9	6.20	117.94

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3. One mole of an ideal monatomic gas of relative molecular mass (molecular weight) 40 and initially at STP undergoes a single-step process in which its volume and absolute temperature are each doubled.
Calculate ΔG for the change.

[100 marks]

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4. Answer <u>four</u> of the following — each part carries 25 marks.

(i) Write an account of the synthesis of ammonia using heterogeneous catalysis.

(ii) Write an account of the Langmuir-Hinshelwood method of interpretation of the kinetics of heterogeneous catalytic reactions.

(iii) The standard free energies of formation at 600 K of three isomers of pentane A, B and C are 141.24, 136.52 and 146.63 kJ mol^{-1} respectively. Calculate the composition of the mixture obtained at equilibrium over a suitable catalyst at 600 K.

(iv) Write an account of the Kelvin Equation and its use to obtain the diameters of micropores.

(v) Write an account of the several types of isotherms encountered in the study of adsorption of gases on solids.

(vi) Write an account of the methods used to obtain the surface area of microporous solids.

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5. Answer (a) and (b).

(a) Show how the 'Linear Polarisation Technique' can be used to obtain accurate corrosion rate measurements from potentiodynamic polarisation plots.

[50 marks]

(b) The corrosion potential of iron immersed in deaerated acidic solution o pH = 3 is – 0.40V. A Tafel plot of cathodic current density versus overpotential yields a slope of $18.0V^{-1}$ and the hydrogen ion exchange current density (i_0) = 0.10 μA cm^{-2}. Calculate the corrosion current for this system.

[50 marks]

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6. The molecular ion H_3^+ is the simplest polyatomic species known and has been found in the atmospheres of some planets in our solar system.
The cyclic structure is more stable than a linear one; how would you use the assumptions of Hückel theory to verify this observation?

[100 marks]

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7. Answer (a) and (b).

(a) The centre of the ESR spectrum of nitrogen dioxide, NO_2, is found at 333.64 mT with an applied frequency of 9.302 GHz. Calculate the g-value.

[40 marks]

(b) Analysis of the ESR spectra of NO_2 reveal an isotropic coupling constant, a_N, of 5.7 mT and an anisotropic coupling of 1.3 mT.
Calculations show that a 2s electron on a nitrogen atom experiences a hyperfine interaction of 55 mT whilst a 2p electron on nitrogen should experience a field of 3.4 mT.

What proportion of its time does the unpaired electron on NO_2 spend in:
(i) An s orbital on nitrogen
(ii) A p orbital on nitrogen
(iii) What is the probability of finding the unpaired electron on the O atoms?
(iv) What are the implications for the structure of NO_2?

[60 marks]

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

(a) The Beer-Lambert law can be written in the form:

$$I_T = I_0 10^{-\varepsilon C}$$

Show that the intensity of light absorbed, I_A, is given by:

$$I_A = I_0\left[1 - 10^{-\varepsilon C}\right]$$

[20 marks]

(b) Solar radiation at 305 nm is absorbed by a 1 km thick layer of the stratosphere which has an average temperature of 220 K and which contains ozone at a concentration of 8×10^{-9} mol dm^{-3}. The molar absorptivity of ozone under these conditions is 260 dm^3 mol^{-1} s^{-1}. Calculate the fraction of light absorbed.

[40 marks]

(c) This UV light photolyses ozone with a quantum efficiency of 0.94:

$$O_3 + h\nu \rightarrow O_2 + O$$

What is the rate law for this photochemical reaction? Is it:

$$-\frac{d[O_3]}{dt} = \frac{\phi I_A}{V} \quad \text{or} \quad -\frac{d[O_3]}{dt} = \frac{\phi V}{I_A} \quad \text{or} \quad -\frac{d[O_3]}{dt} = \frac{V I_A}{\phi}$$

If the flux of solar radiation at 305 nm is 1×10^{14} photons s^{-1} incident on a 1 cm^2 area, at what rate is ozone being destroyed?

[40 marks]
