

Ollscoil na hÉireann, Gaillimh
National University of Ireland, Galway

AUTUMN EXAMINATIONS 2002

SECOND YEAR CHEMISTRY

Physical Chemistry (CH 203)

All questions carry equal marks

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

1. Outline the derivation of the following equation and explain the meaning of the various terms

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_p dT$$

[10marks]

Calculate ΔH when one mole of a perfect gas with

$$C_p / \text{J K}^{-1} \text{mol}^{-1} = 20.17 + 0.3665 T$$

is heated from 25 °C to 200 °C at constant pressure.

[15 marks]

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2. What is the difference between isothermal and adiabatic processes?

[5 marks]

Work out a relationship between T and V for the adiabatic reversible expansion of an ideal monatomic gas and show how the final temperature may be calculated.

[20 marks]

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3. Derive a relationship for the dependence of the entropy of an ideal gas on its volume and temperature and hence calculate ΔS when 2 moles of neon are heated from 300 to 500 K and the volume is doubled.

[25 marks]

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4. At 330 K the vapour pressure of n-hexane is $0.68 \times 10^5 \text{ N m}^{-2}$ and that of n-heptane $0.24 \times 10^5 \text{ N m}^{-2}$. Solutions of these two liquids are made; what is the mol fraction of n-hexane in the vapour at equilibrium over an 0.25 n-heptane mol fraction at this temperature? Sketch and label the P-x and T-x phase diagrams.

[25 marks]

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5. The conductivity of ethanoic acid ($1.58 \times 10^{-2} \text{ mol dm}^{-3}$) is $2.15 \times 10^{-2} \Omega^{-1} \text{ m}^{-1}$. The limiting ionic conductances (Λ_0) of the hydrogen and ethanoate ions are 34.98×10^{-3} and $4.09 \times 10^{-3} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$, respectively.

- (a) Calculate the degree of dissociation and the dissociation constant for ethanoic acid.

[15 marks]

- (b) What would be the pH of 0.1 mol dm^{-3} ethanoic acid?

[10 marks]

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6. Answer (a) and (b).

- (a) Show that you understand what is meant by the term “overvoltage”.

[12 marks]

(b) Nickel is to be deposited from a solution that is 0.20M in Ni^{2+} and buffered to a pH of 2.0. Oxygen is evolved at a pressure of 1.0 atm at a platinum anode. The cell has a resistance of 3.15Ω and the temperature is 298K.

Calculate

- (i) the thermodynamic potential needed to initiate the deposition of nickel.
- (ii) The IR drop for a current of 1.10 A.
- (iii) The initial applied potential, given that the oxygen overvoltage is 0.85V.

[13 marks]

$$E^0 \text{Ni}^{2+}/\text{Ni} = -0.24\text{V}, E^0 \text{for } \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} = 1.23\text{V}.$$

7. Write down the Beer–Lambert law and briefly describe each of the terms in the equation.

[16 marks]

What effect, for a particular setup, does:

(a) Doubling the concentration of an absorbing species have

[3 marks]

(b) Doubling the pathlength of the light

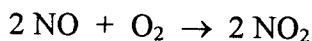
[3 marks]

(c) Doubling the wavelength of the light used

[3 marks]

on the absorbance of the sample?

8. The oxidation of nitrogen oxide is a very important reaction in the polluted atmospheres of cities:



because NO is emitted by vehicle exhausts and NO_2 goes on to form acid rain.

The experimental rate law for the oxidation reaction is:

$$\text{Rate}, \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k[\text{NO}]^2[\text{O}_2]$$

(a) The rate of reaction has been defined in terms of changes in the concentration of the product; write down two other possible definitions for the rate of this reaction.

[5 marks]

(b) What are the units for the rate of reaction?

[4 marks]

(c) What is the *order* of this oxidation reaction?

[4 marks]

(d) If this reaction took place at the molecular level as written, what would you expect the rate law to look like for the elementary reaction?

[4 marks]

(e) What conclusion can you draw from the fact that an experimental rate law and a theoretical rate law agree with each other?

[4 marks]

(f) What is the molecularity of the elementary reaction?

[4 marks]