6x357

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.

Professor K Waugh
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. 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

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

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

[15 marks]

---

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]

---

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]

---

4. At 330 K the vapour pressure of n-hexane is 0.68×10^5 N m^{-2} and that of n-heptane 0.24×10^5 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]

---

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

---

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 3.15 Ω 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 Ni^{2+}/Ni = -0.24V, E^0 for $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$ = 1.23V.

---

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:

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

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:

$$\text{Rate, } \frac{1}{2}\frac{d[NO_2]}{dt} = k[NO]^2[O_2]$$

(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]
