NUI Galway
OÉ Gaillimh

Semester I Examinations 2010/ 2011

Exam Code(s)	**CHEMISTRY CH203**
Exam(s)	**Second Year Physical Chemistry**
Module Code(s)	**CH203**
Module(s)	**PHYSICAL CHEMISTRY**
Paper No.	**1**
Repeat Paper	
External Examiner(s)	**Prof. Paul Seakins**
Internal Examiner(s)	**Prof. P. Murphy, Dr. W. M. Carroll, Dr. H. Curran, Dr. D. Leech, Dr. A. Ryder**

Instructions: **ANSWER FOUR (4) QUESTIONS, ONE FROM EACH SECTION**

Duration	**Two (2) Hours**
No. of Pages	**5**
Department(s)	**Chemistry**
Course Co-ordinator(s)	**Dr. D. LEECH**

Requirements:

MCQ — Release to Library: Yes X No ☐

Statistical/ Log Tables — x

Graph Paper — x

Gas constant, $R = 8.3143\ \text{J K}^{-1}\ \text{mol}^{-1}$	Avogadro constant, $N_A = 6.022 \times 10^{23}\ \text{mol}^{-1}$
Planck constant, $h = 6.624 \times 10^{-34}\ \text{J s}$	Velocity of light, $c = 2.998 \times 10^{8}\ \text{m s}^{-1}$
Electronic charge, $e = 1.602 \times 10^{-19}\ \text{C}$	Boltzmann constant, $k = 1.381 \times 10^{-23}\ \text{J K}^{-1}$
Electronic mass, $m = 9.109 \times 10^{-31}\ \text{kg}$	Bohr magneton, $\mu_B = 9.274 \times 10^{-24}\ \text{J T}^{-1}$
Faraday constant, $F = 96{,}485\ \text{C mol}^{-1}$	$1\ \text{atm} = 101{,}325\ \text{N m}^{-2} = 101{,}325\ \text{Pa}$

Section A: Attempt one question from this Section (gases and thermodynamic laws)

1.

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

(a) The mass percentage composition of dry air at sea level is approximately 75.52 N_2 (molar mass 28.01 g mol^{-1}), 23.15 O_2 (molar mass 32.0 g mol^{-1}), 1.28 Ar (atomic mass 39.95 g mol^{-}) and 0.046 CO_2 (molar mass 44.01 g mol^{-1}). What are the partial pressures when the total pressure is 100 kPa? **[8 marks]**

(b) Define the compression factor and explain how it varies as a function of pressure and temperature. Describe how the compression factor reveals information about intermolecular interactions in real gases. **[12 marks]**

(c) Define all of the terms in Graham's law of effusion, below, and use the law to estimate the relative rate of effusion of hydrogen (molar mass 2.016 g mol^{-1}) and carbon dioxide (molar mass 44.01 g mol^{-1}) under the same conditions of temperature and pressure. **[5 marks]**

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

2.

Answer (a) and (b).

(a) In an experiment to measure the heat released by combustion of a sample of nutrient, the compound was burned in a calorimeter and the temperature rose by 2.98°C. When a current of 1.18 A from a 12 V source flows through a heater in the same calorimeter for 120 s, the temperature rose by 4.37°C. What is the heat released by the combustion reaction? **[8 marks]**

(b) Given that the work, w, required to move an object a distance, l, against an opposing force, F, is $-F.\mathrm{d}l$, derive the expression below for the work of isothermal reversible expansion of an ideal gas. Estimate the work, heat and entropy change for the isothermal reversible expansion of 1.0 mol of an ideal gas at 273 K from 1 L to 2 L volume, commenting on the values obtained.

$$w = -nRT \ln \frac{V_f}{V_i}$$

[17 marks]

Section B: Attempt one question from this Section (phases and kinetics)

3.

Answer (a) and (b).

(a) For the reaction A → products, derive the following equation for a first-order reaction: **[10 marks]**

$$\ln[A]_t = [A]_0 - kt$$

(b) For the reaction in A → products, data for a run with $[A]_0 = 0.60$ mol dm^{-3} are:

t / s	0	300	1000
$[A] / [A]_0$	1.0	0.50	0.248

Show that the reaction obeys first order kinetics. **[10 marks]**
Determine the rate constant for the reaction. **[5 marks]**

4.

Answer (a) and (b).

(a) The Master equation for the change in Molar Gibbs energy can be written as:

$$\Delta G_m = V_m \Delta p - S_m \Delta T$$

If two phases are in equilibrium at a given p and T, derive the approximate relationship below, between Δp that we exert and ΔT we must make to ensure that the two phases remain in equilibrium:

$$\ln p_2 = \ln p_1 - \frac{\Delta_{vap} H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \text{constant}$$

[8 marks]

(b) The normal boiling temperature of water is 373.15 K. Evaluate $\Delta_{vap}H$ at 298.15 K for the process $H_2O(l) \rightarrow H_2O(g)$ using the standard partial molar enthalpies $H_l^0 = -285.83$ kJ mol^{-1}, and $H_{gas}^0 = -241.82$ kJ mol^{-1}, and compute the equilibrium vapour pressure of water at 50°C assuming that $\Delta C_P = 0$. **[10 marks]**

(c) A sample of ethanol vapour at 100°C is compressed isothermally from 800 cm^3 to 200 cm^3. What is the change in its molar Gibbs energy? **[7 marks]**

Section C: Attempt one question from this Section (Ionics and Electrochemistry)

5.

Answer (a) and (b).

(a) Show how conductivity measurements can be used to determine the dissocation constant of a weak acid or base. **[10 marks]**

(b) The conductivity of ethanoic acid at a concentration of 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. Calculate the degree of dissociation and the dissociation constant for ethanoic acid.
What would be the pH of 0.1 mol dm^{-3} ethanoic acid? **[15 marks]**

6.

Answer (a) and (b).

(a) Show that you understand what is meant by the term "overvoltage" **[10 marks]**

(b) Nickel is to be deposited from a solution that is 0.20 M 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 298 K.
Calculate:

(i) The thermodynamic potential needed to initiate the deposition of nickel.

(ii) The IR (Ohmic) drop for a current of 2.10 A.

(iii) The initial applied potential, given that the oxygen overvoltage is 0.85 V.

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

[15 marks]

Section D: Attempt one question from this Section (Equilibrium & Spectroscopy)

7.

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

(a) What are the thermodynamic criteria for spontaneity for endothermic and exothermic reactions? You should describe the four significant cases. **[10 marks]**

(b) For the reaction: $A + 2B \leftrightarrows C + 4D$, where $\Delta_r G^\theta = 0$.
What is the reaction quotient and the numerical value of the constant for the reaction? **[5 marks]**

(c) Calculate the equilibrium constant of the reaction:

$$PbO\ (s) + CO\ (g) \leftrightarrows Pb\ (s) + CO_2\ (g)$$

at 25ºC, given that $\Delta_r G^\theta = -68.26\ kJ\ mol^{-1}$. **[10 marks]**

8.

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

(a) Describe, illustrating with appropriate examples, the gross selection rules for vibrational transitions in Raman and IR absorption spectroscopy. **[6 marks]**

(b) How many vibrational modes do a non-linear and a linear molecule have? Calculate the number of vibrational modes for H-C≡C-H, anthracene ($C_{14}H_{10}$), and methane. **[6 marks]**

(c) The wavenumber of the fundamental vibration transition of Br_2 is at 323.2 cm^{-1}, calculate the force constant. Br relative atomic mass is 79.9 **[13 marks]**
