NUI Galway
OÉ Gaillimh

Autumn Examinations 2011

Exam Code(s)	CH203
Exam(s)	Physical Chemistry
Module Code(s)	
Module(s)	
Paper No.	1
Repeat Paper	
External Examiner(s)	Professor Paul Seakins
Internal Examiner(s)	Professor Paul V. Murphy, Dr William Carroll Dr Henry Curran, Dr Dónal Leech Dr Alan Ryder
Instructions:	All questions carry equal marks, distributed as shown Answer four (4) questions **One (1) from each Section**
Duration	2 hrs
No. of Pages	5
Department(s)	Chemistry
Course Co-ordinator(s)	Dónal Leech

Requirements:

MCQ	Release to Library: Yes ☐ No ☐
Handout	
Statistical/ Log Tables	Yes
Cambridge Tables	
Graph Paper	Yes
Log Graph Paper	
Other Materials	Calculator

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

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

1.

Answer all parts.

(a) Describe the formulation of the van der Waals equation, below, from the perfect gas equation, identifying each term, and associated units, in the equation.

$$P = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

[10 marks]

(b) The vapour of an organic substance, at 100.0 kPa pressure, was found to have a mass of 1.3447 g, when heated to 100.0 °C in a vessel of 535 mL volume. Determine the molecular weight of the organic substance.

[5 marks]

(c) 0.600 mol H_2 and 1.50 mol He are mixed in a 5.0 L container at 20 °C. Calculate the partial pressures of the two gases and the total pressure.

[10 marks]

2.

Answer all parts.

(a) Show that if expansion from initial volume V_i to final volume V_f of an ideal gas takes place reversibly and isothermally the work done is

[15 marks]

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

(b) Estimate the work, heat and entropy change of the gas for the isothermal reversible compression of 1.0 mol of a perfect gas at 273 K from 5 L to 1 L volume, explaining the significance of each. Evaluate, and comment on, the entropy change in the **surroundings** for this reversible compression.

[10 marks]

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

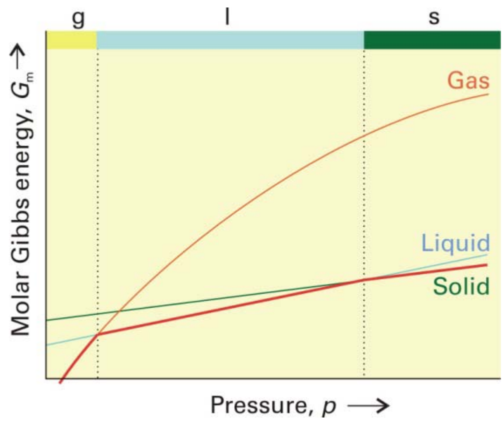
3.

Answer all parts.

The Master Equation for the change in Molar Gibbs energy can be written as:

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

At right is a phase diagram for the variation of the molar Gibbs energy with pressure at constant temperature:

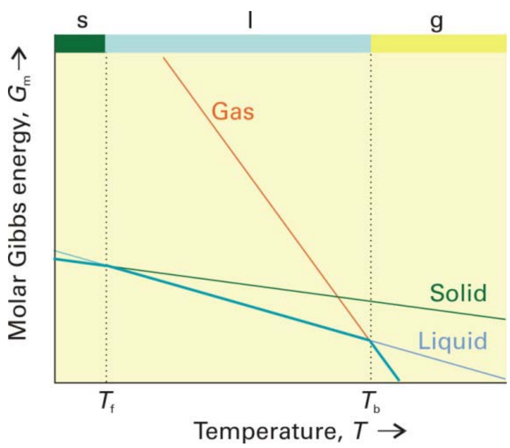


(a) What happens to equation (1) at constant temperature?

[5 marks]

(b) Why is the Molar Gibbs energy weakly dependent on pressure in the liquid and solid phases but strongly dependent on pressure in the gas phase? **[5 marks]**

At right is a phase diagram for the variation of the molar Gibbs free energy with temperature at constant pressure:



(c) What happens to equation (1) at constant pressure?

[5 marks]

(d) Why is the Molar Gibbs energy weakly dependent on temperature in the liquid and solid phases but strongly dependent on temperature in the gas phase?

[5 marks]

(e) For benzene in the range 42–100^{o}C, B = 1687 K and A = 6.7795. Estimate the normal boiling point of benzene, given the following equation:

$$\text{Log } p \text{ / kPa} = A - B/T$$

[5 marks]

4.

Answer all parts.

The following data were obtained for the hydrolysis of sugar in aqueous solution at 23^{o}C.

Time (min)	0	60	130	180
Sugar conc. (mol dm^{-3})	1.00	0.807	0.630	0.531

(a) Show that this reaction is first order and calculate the rate constant for the hydrolysis of sugar.

[15 marks]

(b) The relationship between the rate constant, *k*, and the half-life, τ, for a first-order reaction, X → P +Q, is given by:

$$k = \frac{\ln 2}{\tau}$$

If the rate constant for the disappearance of species X is 2.88×10^{-6} s^{-1}, how long will it take for ¼ of X to react?

[5 marks]

(c) The reaction between carbon monoxide and oxygen to form carbon dioxide has an equilibrium constant, *K*, greater than 1×10^{45} dm^{3} mol^{-1} at room temperature:

$$2CO + O_2 \rightleftharpoons 2CO_2$$

Yet it is known that CO does not *spontaneously* convert into CO_2 in the air around us. Can you reconcile these two facts?

[5 marks]

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

5.

Answer all parts.

(a) Describe some of the more important uses of conductivity measurements.

[10 marks]

(b) The conductivity of a 1.0×10^{-4} mol dm^{-3} solution of a monobasic organic acid in water is 5.0×10^{-4} S m^{-1}. If the molar conductance at infinite dilution of sodium nitrate, nitric acid and the sodium salt of the acid are 12.1. 42.1 and 9.10 mS m^{-2} mol^{-1}, respectively, determine the acid dissociation constant and the pK_a for the acid.

[15 marks]

6.

Answer all parts.

(a) According to thermodynamic calculations the potential required to start the electrolysis of water is −1.23V. However with platinum electrodes it is only at a potential of 1.83 V that appreciable amounts of hydrogen and oxygen are produced. Why is this so?

[10 marks]

(b) Write the cell reaction and calculate the EMF for the following cell:

Pt | TiO^{2+} (3.0×10^{-4} M), Ti^{3+} (7.2×10^{-2} M), H^+ (4.0×10^{-3} M) || Cu^{2+} (2.5×10^{-2} M) | Cu

E^0 Cu^{2+}/ Cu = +0.34 V

E^0 $TiO^{2+} + 2H^+ + e^- \rightarrow Ti^{3+} + H_2O$ = +0.1 V.

[15 marks]

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

7.

Answer all parts.

For the dissociation of ethane into methyl radicals, the equilibrium constant *K*, at 1000 K is equal to 1.102 x 10^{-11}. The reaction equation is:

$$C_2H_6\,(g) \rightleftharpoons 2CH_3\,(g)$$

(a) Write down the equilibrium constant relationship for this reaction.

[3 marks]

(b) If we introduce ethane into a reactor at 1 bar pressure what are the equilibrium partial pressures of ethane and methyl radicals at 1000 K?

[22 marks]

8.

Answer all parts.

(a) How many vibrational modes do the following molecules have: HCl, HBr, CO_2, methane, and benzene?

[6 marks]

(b) What is the wavelength in nanometers (nm) of a molecular vibration that is observed at 1500 cm^{-1}? What region of the electromagnetic spectrum does this wavelength correspond to?

[4 marks]

(c) The force constant of the fundamental vibration transition of Br_2 is 245.6 Nm^{-1}. Calculate the wavenumber at which this transition is observed.

[15 marks]