Autumn Examinations 2011/2012

Exam Code(s) CHEMISTRY CH203
Exam(s) Second Year Physical Chemistry

Module Code(s) CH203
Module(s) PHYSICAL CHEMISTRY

Paper No. 1
Repeat Paper

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

Duration Two (2) Hours
No. of Pages 6
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 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 all parts.
   (a) Given that the density of dry air at 98.2 kPa and 10°C is 1.204 kg m⁻³, calculate the mole fractions and partial pressures of nitrogen and oxygen assuming that air consists only of these gases.  

[10 marks]

   (b) Describe the formulation of the van der Waals equation, below, defining all terms in the equation.

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

[10 marks]

   (c) Calculate the pressure exerted by 1.0 mol of Ar gas confined at 298 K in 0.1 L, behaving as (i) a perfect gas and (ii) a van der Waals gas. \( a = 135.5 \text{ L}^2 \text{ mol}^{-2} \text{ kPa} \) and \( b = 0.032 \text{ L mol}^{-1} \). Comment on the difference, if any.  

[5 marks]

2. Answer all parts.
   (a) Given that the work, \( w \), required to move an object a distance, \( l \), against an opposing force, \( F \), is \( -Fd\), derive the expression below for the work of isothermal reversible expansion of a perfect gas.  

[10 marks]

   \[ w = -nRT \ln \frac{V_f}{V_i} \]

   (b) 1 mole of an ideal gas at 273 K is compressed reversibly and isothermally from 48 L to 24 L volume. Calculate \( w \) and \( \Delta S \) for the process, defining each term and explaining the significance of each value calculated.  

[10 marks]

   (c) A strip of Mg metal mass 10 g is dropped into a beaker of dilute HCl. Calculate the work done by the system as a result of the reaction that occurs, at 100 kPa and 25°C.  

[5 marks]
3. Answer all parts.
The Master Equation for the change in Molar Gibbs energy can be written as:

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

The following are phase diagrams for the variation of the molar Gibbs energy with (i) pressure at constant temperature and (ii) temperature at constant pressure:

(i)

(ii)

(a) What happens to the Master Equation at constant temperature? 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? Derive an expression for the variation of $\Delta G_m$ with pressure at constant temperature.

[10 marks]

(b) What happens to the Master Equation at constant pressure? 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?

[10 marks]

(c) For benzene in the range 42–100°C, $B = 1687$ K and $A = 6.7795$. Estimate the normal boiling point of benzene, given the following equation:

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

[5 marks]
4. **Answer all parts.**

Initial rates, \( r_0 \), for the reaction \( A + B \rightarrow \text{products} \) at 300 K at various sets of initial concentrations are as follows:

<table>
<thead>
<tr>
<th>[A] (mol dm(^{-3}))</th>
<th>[B] (mol dm(^{-3}))</th>
<th>( r_0 ) (mol dm(^{-3}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td>0.3</td>
<td>0.1</td>
<td>90</td>
</tr>
<tr>
<td>0.3</td>
<td>0.3</td>
<td>270</td>
</tr>
</tbody>
</table>

(a) Write a general form of the rate law showing the dependence of the rate on both reactants.  

[5 marks]

(b) Determine the partial orders of the reaction with respect to A and B.  

[10 marks]

(c) Evaluate the rate constant for the reaction.  

[10 marks]
Section C: Attempt one question from this Section (Ionics and Electrochemistry)

5. Answer all parts.

(a) Show how conductivity measurements can be used to determine the dissociation constant of a weak acid or base.

[10 marks]

(b) The conductivity of ethanoic acid (1.58 x 10⁻² mol dm⁻³) is 2.15 x 10⁻² Ω⁻¹ m⁻¹. The limiting ionic conductances (Λₒ) of the hydrogen and ethanote ions are 34.98 x 10⁻³ and 4.09 x 10⁻³ Ω⁻¹ m² 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 all parts.

(a) From thermodynamic calculations the applied potential required to begin the decomposition of water into hydrogen and oxygen is 1.23 V. However under experimental conditions decomposition does not begin until the potential is at least 1.83 V. Account for this extra voltage requirement.

[10 marks]

(b) Lead is to be deposited at a cathode from a solution that is 0.125 M in Pb²⁺ and 0.250 M in HClO₄. Oxygen is evolved at a pressure of 0.80 atm at a 30 cm² platinum anode. The cell has a resistance of 0.95 Ω.

(i) Calculate the thermodynamic (zero current) potential of the cell.

[10 marks]

(ii) Estimate the total applied potential required to cause electrodeposition if a current of 0.30 A is used.

[5 marks]

E⁰ Pb²⁺/ Pb = –0.126 V and E⁰ for ½O₂ + 2H⁺ + 2e⁻ → H₂O = 1.23 V.
Section D: Attempt one question from this Section (Equilibrium & Spectroscopy)

7. Answer all parts.
(a) Write down the correct expression for the reaction quotient for a general type of reaction: \(2A + 3B \rightleftharpoons C\) \([5 \text{ marks}]\)
(b) The magnitude of the equilibrium constant \(K\) is a qualitative indicator of the feasibility of a reaction. Describe what happens in a reaction mixture when:
(i) \(K\) is much greater than one \(K > 10^3\), and
(ii) \(K\) is much greater than one (e.g. \(K < 10^{-3}\)). \([4 \text{ marks}]\)
(c) What is the value of standard reaction Gibbs Energy \((\Delta_r G^\circ)\) for the reaction:
\[N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)\]
given that the equilibrium constant is \(1.6 \times 10^{-7}\) at \(400^\circ\text{C}\). Is this a spontaneous reaction? \([8 \text{ marks}]\)
(d) Using the standard Gibbs energy of formation below, calculate the standard Gibbs energy change \((\Delta_r G^\circ)\) at 298.15 K for the reaction:
\[PCl_5 (g) \rightarrow PCl_3 (g) + Cl_2 (g)\]
\[\Delta G^\circ_{f}(PCl_5) = 269.610 \text{ kJmol}^{-1}\]
\[\Delta G^\circ_{f}(PCl_3) = 290.271 \text{ kJmol}^{-1}\]
Is the reaction spontaneous at this temperature? Explain your reasoning during the calculation. \([8 \text{ marks}]\)

8. Answer all parts.
A 0.45 mol.dm\(^{-3}\) solution of a metal complex was analysed using UV-visible spectroscopy. The cuvette had a pathlength of 2.0 cm, and at a wavelength of 260 nm the measured transmittance was 62%.
(a) Calculate the molar absorption coefficient. \([11 \text{ marks}]\)
(b) What thickness of a 0.75 mol dm\(^{-3}\) solution would be required to transmit 2% of the incident radiation? \([8 \text{ marks}]\)
(c) Arrange the following types of spectroscopic transition in order of increasing energy: vibrational, electronic, rotational. \([3 \text{ marks}]\)
(d) In which regions of the electromagnetic spectrum do each of the transitions above occur? \([3 \text{ marks}]\)