Semester I Examinations 2012/2013

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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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, \( R = 8.3143 \, \text{J K}^{-1} \text{mol}^{-1} \)
\[ = 8.3143 \, \text{kPa L K}^{-1} \text{mol}^{-1} \]
Planck constant, \( h = 6.624 \times 10^{-34} \, \text{J s} \)
Electronic charge, \( e = 1.602 \times 10^{-19} \, \text{C} \)
Electronic mass, \( m = 9.109 \times 10^{-31} \, \text{kg} \)
Faraday constant, \( F = 96,485 \, \text{C mol}^{-1} \)

Avogadro constant, \( N_A = 6.022 \times 10^{23} \, \text{mol}^{-1} \)
Velocity of light, \( c = 2.998 \times 10^8 \, \text{m s}^{-1} \)
Boltzmann constant, \( k = 1.381 \times 10^{-23} \, \text{J K}^{-1} \)
Bohr magneton, \( \mu_B = 9.274 \times 10^{-24} \, \text{J T}^{-1} \)
1 atm = 101,325 N m\(^{-2}\) = 101,325 Pa
Section A: Attempt one question from this Section (gases and thermodynamic laws)

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

(a) At 500°C and 93.2 kPa, the density of sulphur vapour is 3.71 g L\(^{-1}\). What is the molecular formula for sulphur under these conditions, given that the atomic mass of sulphur is 32.06 g mol\(^{-1}\)?

[5 marks]

(b) Describe the formulation of the van der Waals equation, below, from the perfect gas equation, identifying the terms in the equation.

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

[10 marks]

(c) How reliable is the perfect gas law in comparison with the van der Waals equation? Calculate the pressure exerted by 1.0 mol of CO\(_2\) gas at 298 K in 1 L vessel behaving as (i) a perfect gas and (ii) a van der Waals gas, where \(a = 365.78\) L\(^2\)mol\(^{-2}\)kPa and \(b = 0.0429\) Lmol\(^{-1}\) and comment on your answer.

[10 marks]

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

(a) Given that the work, \(w\), required to move an object a distance, \(l\), against an opposing force, \(F\), is \(-F.dl\), derive the expression below for the work of isothermal reversible expansion of an ideal gas, explaining the meaning of each term in the equation.

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

[8 marks]

(b) Calculate \(q\), \(w\), \(\Delta U\), and \(\Delta S\) for the isothermal reversible expansion of 1.0 mol of an ideal gas at 273 K from 1 L to 5 L volume.

[8 marks]

(c) Explain the significance of each of the variables \(q\), \(w\), \(\Delta U\), and \(\Delta S\) calculated in (b) above.

[9 marks]
Section B: Attempt one question from this Section (phases and kinetics)

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

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

\[ \Delta G_m = V_m \Delta p - S_m \Delta T \]

(a) If two phases are in equilibrium at a given \( p \) and \( T \), derive the relationship between \( \Delta p \) that we exert and \( \Delta T \) we must make in order to ensure that the two phases remain in equilibrium:

\[ \ln p_2 = \ln p_1 - \frac{\Delta_{vap} H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

[10 marks]

(b) The partial molar enthalpy of vaporization for CS\(_2\) is 27.85 kJ mol\(^{-1}\), and its normal boiling point is 46.5 °C. What is the vapour pressure of CS\(_2\) at 30 °C assuming that \( \Delta C_P = 0 \).

[10 marks]

(c) For methanol in the range \(-10^\circ\text{C} - 80^\circ\text{C}\), \( B = 2002 \text{ K} \) and \( A = 7.927 \). Calculate the standard boiling point of methanol, given the following equation:

\[ \log p \text{ / kPa} = A - \frac{B}{T} \]

[5 marks]

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

(a) Briefly describe the two key methods available for determining the rate law of a reaction.

[7 marks]

(b) Initial rates \( r_0 \) for the reaction: 2A + C \( \rightarrow \) products at 300 K at various sets of initial concentrations are:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Conc. / mol dm(^{-3})</th>
<th>( r_0 ) / mol dm(^{-3}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.9</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Find the rate law for this reaction given \( r_0 = k[A]^a[B]^b \)

[10 marks]

(c) Determine the rate constant for the reaction.

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

5. Answer (a) and (b).

(a) How does the hydration of ions in aqueous solution affect their conductivity? Illustrate your answer with examples and diagrams. [8 marks]

(b) The molar conductivity at infinite dilution ($\Lambda^0$) in S m$^2$ mol$^{-1}$ of aqueous sodium chloride, sodium formate and hydrochloric acid are $1.264 \times 10^{-2}$, $1.046 \times 10^{-2}$ and $4.261 \times 10^{-2}$ respectively at 25°C. The conductivity of 0.01 mol dm$^{-3}$ aqueous formic acid (HCOOH) at this temperature is $5.07 \times 10^{-2}$ S m$^{-1}$. Calculate:
(i) The limiting molar conductivity and the dissociation constant of formic acid in aqueous solution at 25°C.
(ii) The conductivity of 0.001 mol dm$^{-3}$ formic acid solution. [17 marks]

6. Answer (a) and (b).

(a) Quantitatively, how does the EMF of an electrochemical cell vary with concentration? Describe the terms in the equation that links these parameters. [10 marks]

(b) A solution which is 0.01 mol dm$^{-3}$ in AgNO$_3$ and 0.01 mol dm$^{-3}$ in Cu(NO$_3$)$_2$ is electrolysed using platinum electrodes:
(i) Which metal will be deposited at the cathode first?
(ii) Calculate the residual concentration of the cations of the metal which is deposited first at the stage when the other metal starts to deposit.
(iii) What is the potential corresponding to analytical separation (1.0 $\times$ 10$^{-6}$ mol dm$^{-3}$)?

$E^0$ Cu$^{2+}$/Cu = +0.34 V, $E^0$ Ag$^+$/Ag = +0.80 V. [15 marks]
Section D: Attempt one question from this Section (Equilibrium & Spectroscopy)

7. Answer (a) and (b).

In an experiment to study the formation of nitrogen oxides in natural gas fuelled turbines, \( \text{N}_2 \) (0.7 bar) is mixed with \( \text{O}_2 \) (0.2 bar) and the two gases are allowed to come to equilibrium with the product \( \text{NO} \) in a reactor of constant volume. Using spectroscopy the equilibrium partial pressure of \( \text{NO} \) was measured to be 0.0074842 bar.

(a) Calculate the value of the equilibrium constant at 2000 K.

(b) If \( K = 3.4 \times 10^{-21} \) at 800 K, what does this tell you about the enthalpy of the reaction? Explain your reasoning and provide an equation that models the effect of temperature on \( K \).

[18 marks]

[7 marks]

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

The hydrogen fluoride molecule, \(^1\text{H}^{19}\text{F} \), in the gas phase has a single absorption band in the mid-infrared region of the electromagnetic spectrum at a wavenumber of 4,141.3 cm\(^{-1}\):

(a) Calculate the force constant, \( k \), for hydrogen fluoride.

(b) For the \(^1\text{H}^{81}\text{Br} \) molecule, do you expect the absorption band and force constant to be higher or lower. Explain your reasoning.

(c) What would happen to the \(^1\text{H}^{19}\text{F} \) absorption band if you replaced the \(^1\text{H} \) atom with a \(^2\text{D} \) atom? Explain your reasoning.

[15 marks]

[7 marks]

[3 marks]