Autumn Examinations 2012

Exam Code: Chemistry CH301
Exam: 3rd Year Chemistry

Module Code(s): CH313
Module: Physical Chemistry

Paper No.: 1
Repeat Paper: yes

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

All questions carry equal marks, distributed as shown

Instructions:
Answer four (4) questions
One (1) from each Section

Duration: 2 hrs
No. of Pages: 5
Department(s): Chemistry
Course Co-ordinator(s): Dr. Henry Curran

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, \( R = 8.3143 \ \text{J K}^{-1} \ \text{mol}^{-1} \)
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, \( m = 9.109 \times 10^{-31} \ \text{kg} \)
Faraday constant, \( F = 96,485 \ \text{C mol}^{-1} \)
1 atmosphere = 101,325 N m\(^{-2}\)
Vacuum permittivity, \( \varepsilon_0 = 8.854 \times 10^{-12} \ \text{J}^{-1} \ \text{C}^2 \ \text{m}^{-1} \)
Section A

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

(a) Define the term lattice enthalpy. [5 marks]

(b) Calculate the lattice enthalpy at 298 K of CaCl₂, defined as:
CaCl₂ (s) = Ca²⁺ (g) + 2Cl⁻ (g)
using the following data.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Enthalpy of reaction, ΔHӨ / kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca (s) = Ca (g)</td>
<td>178.2</td>
</tr>
<tr>
<td>Ca (g) = Ca²⁺ (g)</td>
<td>1740.0</td>
</tr>
<tr>
<td>Cl₂ (g) = 2Cl (g)</td>
<td>241.6</td>
</tr>
<tr>
<td>Cl (g) = Cl⁻ (g)</td>
<td>−364.9</td>
</tr>
</tbody>
</table>

and the enthalpy of formation of CaCl₂ (s) of −795.8 kJ mol⁻¹. [5 marks]

(c) Given the equation for the potential energy of interaction between two dipoles is:

\[ V = \frac{\mu_1 \mu_2 (1 - 3 \cos^2 \theta)}{4 \pi \varepsilon_0 r^3} \]

Define all the terms in the equation above and calculate the molar potential energy of the dipolar interaction between two peptide links separated by 2.5 nm in different regions of a polypeptide chain with \( \theta = 165° \), \( \mu_1 = \mu_2 = 2.4 \) D.

[15 marks]

(1 D = 3.34 ×10⁻³⁰ C m)

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

(a) Explain what is meant by the terms: (i) A-factor and (ii) activation energy in the context of the Arrhenius equation. [6 marks]

(b) Rate constants for the gas-phase reaction \( \text{H}_2 + \text{I}_2 \rightarrow 2\text{HI} \) at various temperatures are:

<table>
<thead>
<tr>
<th>(c) ( 10^7 k / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} )</th>
<th>0.54</th>
<th>2.5</th>
<th>14</th>
<th>25</th>
<th>64</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T / \text{K} )</td>
<td>599</td>
<td>629</td>
<td>666</td>
<td>683</td>
<td>700</td>
</tr>
</tbody>
</table>

Calculate the pre-exponential A-factor and activation energy (\( Ea \)) for this reaction. [13 marks]

(c) The reaction \( 2\text{DI} \rightarrow \text{D}_2 + \text{I}_2 \) has a rate constant \( k = 2.8 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) at 660 K and an activation energy \( Ea = 190 \text{ kJ mol}^{-1} \). Calculate \( k \) at 720 K for this reaction. [6 marks]


Section B

3.  Answer (a) and (b)

(a) Explain how colligative properties can be used to determine molar mass.

[15 marks]

(b) Hexane and perfluorohexane show partial miscibility below 22.7°C, with the mole fraction, of perfluorohexane being \(x(C_6F_{14}) = 0.355\) at this upper critical temperature. At 22.0°C the two solutions in equilibrium have \(x(C_6F_{14})\) of 0.24 and 0.48, respectively, whilst at 21.5°C the mole fractions are 0.22 and 0.51. Sketch the temperature-composition phase diagram for the system indicating regions of single-, and two-phase, liquid mixture composition.

[10 marks]

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

(a) Fractions of a polymer, when dissolved in an organic solvent gave the following intrinsic viscosities \([\eta]\) at 25°C:

<table>
<thead>
<tr>
<th>(M, \text{ g mole}^{-1})</th>
<th>34,000</th>
<th>61,000</th>
<th>130,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\eta])</td>
<td>1.02</td>
<td>1.60</td>
<td>2.75</td>
</tr>
</tbody>
</table>

Determine the value of the constants \(\alpha\) and \(K\) in the Mark-Houwink equation.

[13 marks]

(b) What are the major differences between amorphous and crystalline polymers?

[12 marks]
Section C

5. Answer (a) and (b)

(a) Describe the important role diffusion processes can play in electrode reactions. [12 marks]

(b) In the electrolysis of an unstirred 0.02 mol dm\(^{-3}\) dicyanoargentate (I) solution at 15\(^\circ\)C the limiting current was found to be 5.0 \times 10^{-4} \text{ A cm}^{-2}. Given that the molar conductance of this ion is 49.5 \times 10^{-4} \text{ } \Omega^{-1} \text{ m}^2 \text{ mol}^{-1} at 15\(^\circ\)C, calculate the thickness of the diffusion layer. [13 marks]

6. Answer (a) and (b)

(a) The Gibbs Adsorption Isotherm may be written as:

\[
\Gamma_s = -\frac{c}{RT} \frac{d\gamma}{dc}
\]

where \(c\) is the concentration of solute, \(s\), in the solution, \(\Gamma_s\) is the surface excess of the solute in the surface layer and \(\gamma\) is the surface tension.

Explain what is meant by the terms (i) surface tension and, by making reference to the above equation, (ii) surface excess. [13 marks]

(b) Show how the Langmuir equation may be used to obtain a value of \(V_\infty\) the volume corresponding to complete coverage for a given gas solid system. [12 marks]
7. Answer (a), (b), (c) and (d)

(a) \[ E(n_1, n_2) = \left( n_1^2 + n_2^2 \right) \frac{\hbar^2}{8} \]

The equation above describes the energy of a particle confined by an infinite potential in a 2-dimensional square. What are the two missing terms? Give the meaning and units for each term in the equation. [7 marks]

(b) Calculate the energy separation between the two lowest energy levels for an Ar atom in a two-dimensional square box of length 5 nanometres. Give your answers in Jmol\(^{-1}\). [8 marks]

(c) What would happen if you replaced the argon atom with a neon atom? Calculate the energy separation between the two lowest energy levels. [5 marks]

(d) For a square well, how many degenerate energy levels are there in the first three energy states? [5 marks]

8. Answer (a) and (b)

\(^{14}\text{N}\(^{16}\text{O}\) has an equilibrium bond length of 115 pm and assumed to be a linear rotor with little centrifugal distortion.

(a) Calculate the moment of inertia for this molecule. [8 marks]

(b) Calculate the wavelength at which the \( J=8 \leftarrow 7 \) transition in the pure rotational spectrum of \(^{14}\text{N}\(^{16}\text{O}\) is observed. [17 marks]