Autumn Examinations 2013

Exam Code
Chemistry CH301

Exam
3rd Year Chemistry

Module Code(s)
CH313

Module
Physical Chemistry

Paper No.
Repeat Paper
X

External Examiner(s)
Professor Paul Seakins

Internal Examiner(s)
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Instructions:
All questions carry equal marks, distributed as shown
Answer four (4) questions
One (1) from each Section

Duration
2 hrs

No. of Pages

Department(s)
Chemistry

Course Co-ordinator(s)
Prof Henry Curran

Requirements:
MCQ
Handout
Statistical/ Log Tables
Cambridge Tables
Graph Paper
Log Graph Paper
Other Materials
Release to Library: Yes ☐ No ☐
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, \( h = 6.626 \times 10^{-34} \text{ J s} \)
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, \( \varepsilon_0 = 8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1} \)
1 Debye = 3.34 \times 10^{-30} \text{ C m}
1. Answer (a), (b), (c) and (d).

(a) Define the term dipole moment.

(b) The HCl molecule has an equilibrium inter-nuclear distance of 22.5 pm. Assuming there is complete charge transfer, calculate:

(i) its electric dipole moment in Debye (D):

(ii) the Coulombic contribution to the bond energy.

(c) Define the term lattice enthalpy.

(d) Using the following data at 298 K, calculate the lattice enthalpy of CaCl₂, which is defined for the following reaction: CaCl₂ (s) → Ca²⁺ (g) + 2Cl⁻ (g)

\[ \begin{align*}
\text{Ca (s) → Ca (g)} & : & \Delta H^\theta = 178.2 \text{ kJ mol}^{-1} \\
\text{Ca (g) → Ca}^{2+} (g) & : & \Delta H^\theta = 1740.0 \text{ kJ mol}^{-1} \\
\text{Cl}_2 (g) → 2\text{Cl} (g) & : & \Delta H^\theta = 241.6 \text{ kJ mol}^{-1} \\
\text{Cl (g) → Cl}^- (g) & : & \Delta H^\theta = -364.9 \text{ kJ mol}^{-1}
\end{align*} \]

The enthalpy of formation of CaCl₂ is –795.8 kJ mol⁻¹.

2. Answer (a) and (b)

(a) The following is a diagram of a representation of a gas flow through a plug-flow reactor:

where \([A]_i = \text{inlet concentration of } A, [A]_o = \text{outlet concentration of } A, V\) is the volume of the reactor and \(v\) is the flow rate or flow velocity.

Derive the following equation for the dependence of the concentrations on the flow rate for a 1st-order reaction in a plug-flow reactor:

\[
\ln \left( \frac{[A]_o}{[A]_i} \right) = -k \left( \frac{V}{v} \right)
\]

(b) Peracetic acid vapour at 2% by volume in nitrogen carrier gas at a total pressure of 101 kPa and 490 K flows through 1.4 mm radius Teflon tubing and is sampled 1.2 m downstream with the following results:

<table>
<thead>
<tr>
<th>([\frac{[A]_o}{[A]_i}])</th>
<th>0.346</th>
<th>0.578</th>
<th>0.718</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v) (m³ s⁻¹)</td>
<td>(3.71 \times 10^{-5})</td>
<td>(7.20 \times 10^{-5})</td>
<td>(1.19 \times 10^{-4})</td>
</tr>
</tbody>
</table>

Show that reaction follows first order kinetics and calculate the rate constant, \(k\).
Section B

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

(a) Explain how a colligative property can be used to determine molar mass. [8 marks]

(b) Define each of the terms in the equation below, for the mixing of two perfect gases, and use the expression to justify the statement that perfect gases mix spontaneously in all proportions. [7 marks]

\[ \Delta G_{\text{mix}} = nRT \{ x_A \ln x_A + x_B \ln x_B \} \]

(c) A mixture of 50 g of hexane and 50 g of nitrobenzene was prepared at 290 K and 1 bar pressure. From the temperature-composition diagram, at 1 bar pressure, below:

(i) define, and estimate, the upper critical solution temperature for the system. [3 marks]

(ii) estimate the compositions of the phases and in what proportions they occur in the sample mixture. [5 marks]

(iii) To what temperature must the sample mixture be heated to obtain a single phase? [2 marks]

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

(a) A normal polymer sample contains molecules with a variety of lengths and it is only possible to quote an average value of the molar mass. Discuss. How are these average values obtained experimentally? [10 marks]

(b) In relation to polymers what is the polydispersity index (PI)? [5 marks]

(c) What are the major differences between amorphous and crystalline polymers? [10 marks]
Section C

5. Answer (a) and (b)

(a) Describe the interfacial changes which occur when a copper electrode is initially immersed in a Cu\(^{2+}\) solution. How does the Cu\(^{2+}\) concentration influence the change?

[10 marks]

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

[15 marks]

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

(a) List the assumptions involved in the formulation of the Langmuir adsorption isotherm and derive the equation for the isotherm.

[10 marks]

(b) Show how the equation may be modified to take account of dissociative adsorption.

[7 marks]

(c) Show how the equation may be used to obtain a value of \(V_\infty\) the volume corresponding to complete coverage for a given gas solid system. Show how this \(V_\infty\) value be used to obtain the surface area of the adsorbent?

[8 marks]
Section D

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

The particle in a cube model can be used as a starting point to explain the behavior of nano-scopic semi-conductor particles (e.g. quantum dots) which have interesting optical properties. The energy of a particle of mass, \( m \), confined to a three-dimensional cube with a side length \( L \), where the potential energy is equal to zero between \( x=0 \) and \( x=L \) is given by:

\[
E_{n_x,n_y,n_z} = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2),
\]

Where \( n_x \) (the quantum numbers) = 1, 2, 3, ....

For a particle of mass \( m \) confined to a cube of dimensions: \( L_1 = L_2 = L_3 \)

(a) What are the quantum numbers associated with the first 4 energy levels?

(b) How many degenerate energy levels are present in each case?

(c) Calculate the energy required for a \(^6\text{Li} \) atom trapped in a 3-dimensional cube of side 2 nm to go from the 3\(^{\text{rd}}\) to the 4\(^{\text{th}}\) highest energy level.

(d) What wavelength of electromagnetic radiation does this correspond to?

(e) What will happen to the wavelength of the electromagnetic radiation required for this transition if instead you had a hydrogen atom in the box?

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

The following description and equation are incomplete. Fill in the blanks.

The \( \square \) energy levels of \( \square \) molecules are given by the following equation: \( \varepsilon_j = \frac{J^2}{8J^2} J(J+1) \), where \( J=0,1,2 \)

(a) Explain the meaning of each of the missing terms in the equation.

(b) Microwave emission spectroscopy is often used to identify molecular species in outer space. Given that the bond length of CO is 112.82 pm, at what wavelength would you search for the \( J=10 \) to \( J=9 \) transition for \(^{13}\text{C}^{16}\text{O} \)?

(c) Would the wavelength of the \( J=10 \rightarrow 9 \) transition be longer or shorter for \(^{12}\text{C}^{16}\text{O} \)? Explain your reasoning.