NUI Galway
OÉ Gaillimh

Autumn Examinations 2011

Exam Code	Chemistry CH301
Exam	3rd Year Chemistry
Module Code(s)	CH313
Module	Physical Chemistry
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
	All questions carry equal marks, distributed as shown
Instructions:	Answer four (4) questions **One (1) from each Section**
Duration	2 hrs
No. of Pages	
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 $= 101{,}325\ \text{N m}^{-2}$	Vacuum permittivity, $\varepsilon_0 = 8.854 \times 10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1}$

Section A

1.
Answer (a) and (b)

(a) 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 2.8 nm in different regions of a polypeptide chain with $\theta = 120^o$, $\mu_1 = \mu_2 = 2.7$ D corresponding to 9.1×10^{-30} C m.

[15 marks]

(b) What strength of electric field is required to induce an electric dipole moment of 1μD in a molecule of polarizability volume 1.1×10^{-31} m^3?

$$\alpha' = \frac{\alpha}{4\pi\varepsilon_0}$$

[10 marks]

(**N. B.** 1 Debye = 3.34×10^{-30} C m)

2.
Answer (a) and (b)

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

[10 marks]

(b) Food rots 40 times faster at room temperature, 25ºC, than it does in a fridge at 4ºC. Calculate the overall activation energy of this complex series of chemical reactions.

[15 marks]

Section B

3.

Attempt sections (a) and (b).

(a) Derive the expression below for the depression of freezing point upon addition of a non-volatile solute (B) to a solvent, where T^* is the freezing point of the pure solvent. **[10 marks]**

$$\Delta T = \frac{x_B\{RT^{*2}\}}{\Delta_{fus}H}$$

(b) A solution containing a mole fraction of 0.0046 potassium chloride in glacial acetic acid yields a ΔT of 0.470 K. Using the equation in (a) above, where $\Delta_{fus}H$ = 11.4 kJ/mol and T^* = 290 K, estimate an apparent mole fraction for the solution and suggest an interpretation that may account for differences between the known and apparent values**.**

[15 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.

[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.

[10 marks]

(b) In the electrolysis of an unstirred 0.02 mol dm^{-3} dicyanoargentate (1) solution at 15^0C the limiting current was fond to be 5.0×10^{-4} A cm^{-2}. Given that the molar conductance of this ion is 49.5×10^{-4} Ω^{-1} m^2 mol^{-1} at 15^0C, 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_∞ the volume corresponding to complete coverage for a given gas solid system.

[8 marks]

Section D

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

The energy of a particle of mass, m, confined by an infinite potential for x>L and x<0, to a region along the x-axis of zero potential energy between x=0 and x=L is given by:

$$E = \frac{n_x{}^2 h^2}{8mL^2} \qquad \text{with} \qquad n_x = 1,2,3,\ldots$$

(a) What are the corresponding expressions for a particle confined to a three-dimensional cube?

[8 marks]

(b) Calculate the lowest allowed energy of an electron trapped in a 3-dimensional cube of side 5 nm.

[8 marks]

(c) Calculate the next highest energy of an electron trapped in a 3-dimensional cube of side 5 nm. How many degenerate energy levels occur in this state?

[6 marks]

(d) What is the wavelength of light required to excite the electron from the lowest to the first excited state?

[3 marks]

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

Two of the adjacent absorption lines in the pure microwave spectrum of a diatomic molecule occur at 108.457 and 117.489 GHz. You can assume that the molecule behaves as a linear rotor.

(a) What transitions do these frequencies represent?

[6 marks]

(b) Calculate the moment of inertia for this molecule.

[14 marks]

(c) If this molecule was $^{23}Na^{81}Br$, calculate the bond length for the molecule.

[5 marks]