

FIRST PUBLIC EXAMINATION

Long Vacation 2004

Preliminary Examination in Chemistry

SUBJECT 3. PHYSICAL CHEMISTRY

Tuesday September 21st 2004, 2.30 pm – 5.00 pm

Time allowed: 2 ½ hours

Candidates should answer **all** questions in Section A and any **two** questions in Section B.

Use **SEPARATE** booklets for your answers to Section A and Section B

The numbers in square brackets indicate the weight that the Examiners expect to assign to each part of the question.

Molar gas constant, R	$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Planck constant, h	$= 6.626 \times 10^{-34} \text{ J s}$
Boltzmann constant, k_B	$= 1.381 \times 10^{-23} \text{ J K}^{-1}$
Speed of light, c	$= 2.998 \times 10^8 \text{ m s}^{-1}$
Avogadro number, N_A	$= 6.022 \times 10^{23} \text{ mol}^{-1}$
p^\ominus	$= 1 \text{ bar} = 1 \times 10^5 \text{ Pa} = 760 \text{ mmHg}$
Electron mass, m_e	$= 9.110 \times 10^{-31} \text{ kg}$
Elementary charge, e	$= 1.602 \times 10^{-19} \text{ C}$
Faraday constant, F	$= 9.648 \times 10^4 \text{ C mol}^{-1}$
Atomic mass unit, u	$= 1.661 \times 10^{-27} \text{ kg}$
Molar volume, V_m^\ominus	$= 24.79 \text{ dm}^3 \text{ mol}^{-1}$ at 298K
1 electronvolt	$= 1.602 \times 10^{-19} \text{ J}$

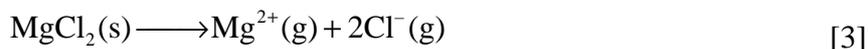
Do not turn over until instructed to do so by an invigilator.

SECTION A

Answer all questions in this section

1. The Paschen series for hydrogen atoms involves electronic transitions from various higher energy levels to the $n = 3$ level. The ionization energy from the atomic ground state is 13.6 eV.
- (a) Give a general expression describing the energy of these transitions. [2]
- (b) Determine the Rydberg constant for this species and calculate the energy of the three lowest energy transitions in the series. [3]
- (c) How would the equation in part (a) be modified if, instead of hydrogen, the emission spectra were obtained for the hydrogenic atom Li^{2+} ? [3]

2. (a) Using the following data at 298 K, calculate the lattice energy of MgCl_2 , which is defined as



the enthalpy of formation of MgCl_2 is $-639.5 \text{ kJ mol}^{-1}$.

- (b) The enthalpy of solution of anhydrous solid MgCl_2 is -150 kJ mol^{-1} . Using the results from (a), calculate the combined enthalpy of hydration of the gaseous ions. [3]
- (c) If one assumes a value of $-383.7 \text{ kJ mol}^{-1}$ for the enthalpy of hydration of a gaseous Cl^{-} ion, what is the enthalpy of hydration for gaseous Mg^{2+} ? The corresponding value for gaseous Ca^{2+} is $-1560 \text{ kJ mol}^{-1}$. Comment. [2]

3. A particle of mass m undergoing circular motion on a ring with radius r can be described by a wavefunction $\psi_{m_l}(\phi) = Ne^{im_l\phi}$, which is a solution to the Schrödinger equation

$$-\frac{h^2}{8\pi^2mr^2} \frac{d^2\psi}{d\phi^2} = E\psi$$

- (a) If the particle is subject to the boundary condition that $\psi_{m_l}(\phi + 2\pi) = \psi_{m_l}(\phi)$, what values can the quantum number m_l take? [2]
- (b) Calculate the normalisation factor, N , for $\psi_{m_l}(\phi)$. [3]
- (c) Demonstrate that the probability density obtainable from this wavefunction is independent of the angle ϕ . [4]

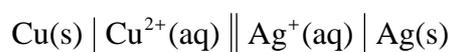
CCHE 4273

4. (a) What is meant by (i) the order and (ii) the molecularity of a chemical reaction? [2]
- (b) An organic acid decarboxylates spontaneously at 298 K and pH = 6. The evolution of CO₂ from 0.01 dm⁻³ of a 10 mmol dm⁻³ solution was measured at various times as follows:

<i>t/s</i>	1500	3000	4500	6000	7500	9000	<i>t</i> _∞
Total CO ₂ evolved/cm ³	0.64	1.10	1.45	1.70	1.90	2.05	2.45

Determine the order and rate constant for this reaction assuming that no CO₂ remains in solution. [6]

5. For the following cell



at 298 K:

- (a) State the cell reaction. [2]
- (b) Give the Nernst equation for the cell. [2]
- (c) Calculate the cell EMF when the aqueous ions are present at activities of (i) 1.0 and (ii) 0.1. [5]

[The standard electrode potentials are $E_{\text{Cu}/\text{Cu}^{2+}}^{\ominus} = +0.34 \text{ V}$ and $E_{\text{Ag}/\text{Ag}^{+}}^{\ominus} = +0.80 \text{ V}$.]

6. (a) Define the terms linear momentum and kinetic energy. How are these two properties related? [3]
- (b) A hydrogen atom and a helium atom travel in the same horizontal direction with velocities $v_{\text{H}} = 400 \text{ ms}^{-1}$ and $v_{\text{He}} = 200 \text{ ms}^{-1}$.
- (i) Calculate v_{CM} , v_{rel} and hence the kinetic energies K_{CM} and K_{rel} , where CM and rel refer to the centre of mass and relative frames of reference respectively. [2]
- (ii) Assuming that the atoms undergo an elastic collision, calculate the velocities after the collision. [3]

[Relative atomic masses: H 1.0 u, He 4.0 u]

SECTION B

Answer any two questions from this section
All questions in this section carry equal marks

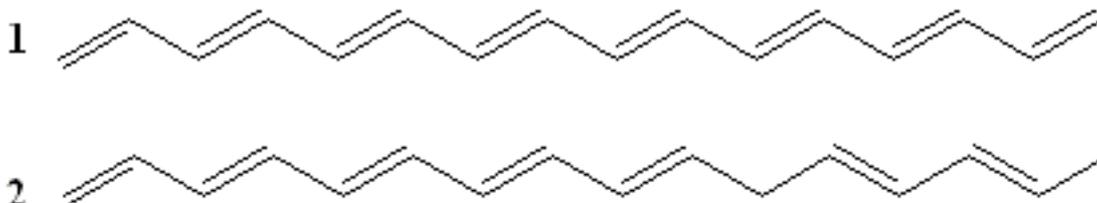
7. For a linear polyene containing five conjugated double bonds, the molecular orbitals of the π -system can be approximated to the solutions of the 'particle in a box', where the length of the box (L) represents the length of the conjugated system.



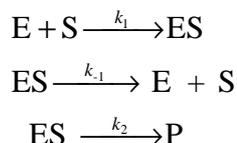
- (a) Describe the boundary conditions for electrons represented by such a model. Is this a good model for these molecules? [3]
- (b) Solutions to this problem are of the form:

$$\psi_n = A \sin\left(\frac{n\pi x}{L}\right)$$

- Calculate the normalization factor A . [5]
- (c) Assuming that the p-electrons fill these energy levels according to the Aufbau principal, sketch the wavefunctions for the occupied levels of the system, and their associated probability densities. [5]
- (d) Assuming a single bond length of 154 pm and a double bond length of 135 pm, give a general expression for the energy difference between two levels. Between which energy levels is the lowest energy electronic transition? What is the energy of this transition? [5]
- (e) We can extend the chain length of the polyene in two ways. In the first, six carbons are added such that the conjugated system is increased in length by three units (structure **1**). In the second the six carbons contain only two double bonds, which are not in conjugation with the rest of the system (structure **2**). Calculate the energy difference between structures **1** and **2**. [7]



8. In enzyme kinetics the enzymic reaction often goes through a pre-equilibrium between the free enzyme and substrate and the bound state. The Michaelis-Menten equation describes rate processes that proceed according to the following pathway:



- (a) Assuming that the bound complex, ES, is a steady state intermediate, show that the rate of reaction, v is given by the Michaelis-Menten equation. (note $[\text{E}]_0 = [\text{E}] + [\text{ES}]$) [10]

$$v = \frac{k_2[\text{E}]_0[\text{S}]}{K_m + [\text{S}]}, \text{ where } K_m = \frac{k_{-1} + k_2}{k_1}$$

- (b) Sketch how the rate of reaction varies with substrate concentration and comment on the limiting behaviour at high substrate concentration. [5]
- (c) Hydrolysis of the ester, methyl 3-phenylpropanoate, is catalysed by the enzyme chymotrypsin. At 298 K and pH = 6, and at constant concentration of the enzyme $[\text{E}]_0$, the following data were obtained for the initial rates of hydrolysis:

$[\text{Ester}]/10^{-3}$ mol dm^{-3}	30.8	14.6	8.57	4.60	2.24	1.28
Initial rate/ 10^{-8} mol $\text{dm}^{-3} \text{s}^{-1}$	20.0	17.5	15.0	11.5	7.5	5.0

Evaluate the maximum rate of reaction (at high substrate concentration) under these conditions and the Michaelis constant K_m . [10]

9. (a) Free energy $\Delta_r G^\ominus$ is related to the equilibrium constant (K) via the equation: $\Delta_r G^\ominus = -RT \ln K$. Derive an expression describing the temperature dependence of the equilibrium constant. Show that in its integrated form the relationship between the equilibrium constants at two temperatures is given by

$$\ln \frac{K_2}{K_1} = -\frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad [6]$$

- (b) For a given reaction the value of the equilibrium constant doubles on changing the temperature from 298 K to 308 K. Calculate $\Delta_r H^\ominus$ for the reaction. [3]

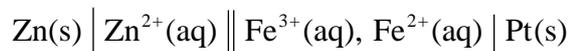
- (c) For the gas phase dissociation reaction



show that the degree of dissociation α can be expressed in terms of K_p as follows, where p is the total pressure. [8]

$$\alpha = \left(\frac{K_p}{K_p + \frac{4p}{p^\ominus}} \right)^{\frac{1}{2}}$$

- (d) For the dissociation of gaseous ethane into methyl radicals calculate K_p and α at pressures $p = 1$ and 10 bar, for temperature $T = 298$ K. $\Delta_f G^\ominus(298\text{K})$ for ethane = -32.82 kJmol⁻¹ and $\Delta_f G^\ominus(298\text{K})$ for the methyl radical = $+147.92$ kJmol⁻¹. [8]
10. (a) Describe how standard electrode potentials can be used to obtain free energies of reaction. [3]
- (b) Explain how the emf of a cell and its variation with temperature can be used to derive $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ for the cell reaction. [5]
- (c) Consider the following electrochemical cell at 298 K



- (i) Write down the two half-cell reactions and hence derive the overall cell reaction. [5]
- (ii) At 298 K, $E^\ominus = 1.53$ V, while at 323 K, $E^\ominus = 1.55$ V. Calculate $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ for the reaction at 310 K. [10]
- (iii) Comment on the value of the entropy change calculated in (ii). [2]