

FIRST PUBLIC EXAMINATION

Long Vacation 2003

Preliminary Examination in Chemistry

SUBJECT 3. PHYSICAL CHEMISTRY

Tuesday September 23rd 2003, 9.30 am – 12.00 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 | $= 24.79 \text{ dm}^3 \text{ mol}^{-1} \text{ at } 298\text{K}$ |
| 1 electron volt | $= 1.6022 \times 10^{-19} \text{ J}$ |

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

SECTION A

Answer all questions in this section

- Describe the photoelectric effect and discuss its consequences for the properties of light. [3]
 - The threshold wavelength for photoemission of electrons from potassium is 564 nm. Calculate the maximum velocity of photoelectrons if the metal is irradiated with light of wavelength 300 nm. [3]
 - Derive the term symbols for the ground state and first electronically excited state of potassium. [2]

- The Clausius-Clapeyron equation is

$$\left(\frac{d \ln p}{dT} \right) = \frac{\Delta_{\text{vap}} H}{RT^2}$$

- Derive the integrated form of this expression. [2]
- The vapour pressures of liquid butane at a series of temperatures are given in the table. Using a graphical procedure calculate the enthalpy of vaporization ($\Delta_{\text{vap}} H$) of butane. What is the boiling point of butane? [6]

| | | | | | |
|-----------------|--------|--------|--------|--------|--------|
| T/K | 195.12 | 212.68 | 226.29 | 262.28 | 272.82 |
| p/mmHg | 9.90 | 36.26 | 85.59 | 503.34 | 764.50 |

(1 bar = 760 mmHg)

- Describe what is meant by normalization of a wavefunction. [2]
 - The ground state of the hydrogen atom is described by the wavefunction $\psi = Ne^{-r/a_0}$, where r is the distance from the electron to the nucleus and a_0 is the Bohr radius. Calculate the normalization factor N . [3]
 - Determine the average distance of the electron from the nucleus. [4]

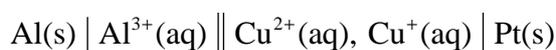
$$\left[\text{note } \int_0^{\infty} x^n e^{-bx} dx = \frac{n!}{b^{n+1}} \right]$$

4. (a) What is meant by the order and molecularity of a chemical reaction. [2]
- (b) Describe how the isolation method can be used to determine the order of a chemical reaction. [2]
- (c) The following set of data was obtained for a reaction $A \rightarrow X$.

| | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|
| t/s | 0 | 180 | 360 | 540 | 720 | 900 |
| $[A]/\text{mol dm}^{-3}$ | 1.000 | 0.952 | 0.909 | 0.870 | 0.833 | 0.800 |

Using the integrated rate law for a 1st order reaction show that the reaction is 1st order with respect to $[A]$ and calculate the rate constant. [4]

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 $E_{\text{Al}/\text{Al}^{3+}}^{\ominus} = -1.61 \text{ V}$ and $E_{\text{Cu}^{+}/\text{Cu}^{2+}}^{\ominus} = +0.15 \text{ V}$.)

6. (a) Define the term electric dipole moment. [3]
- (b) The CsCl molecule has an equilibrium internuclear distance of 360 pm. Assuming there is complete charge transfer, calculate:
- (i) its electric dipole moment in debye (D); [2]
- (ii) the coulombic contribution to the bond energy. [3]

$$(1.0 \text{ D} = 3.34 \times 10^{-30} \text{ Cm})$$

SECTION B

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

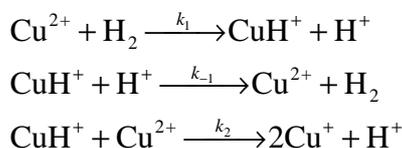
7. The one dimensional Schrödinger equation for a simple harmonic oscillator is

$$\frac{-\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2\psi = E\psi$$

- (a) Give the general expression for the energies of solutions to this equation. [2]
- (b) Sketch the three lowest energy wavefunctions and their associated probability densities. [6]
- (c) Show that the wavefunction $\psi_0 = N_0 e^{-ax^2}$ is a solution to this equation if $a = \frac{1}{2\hbar} \sqrt{k\mu}$. What is the energy of the state represented by ψ_0 ? [12]
- (d) The vibrational transition from $v = 0$ to $v = 1$ for carbon monoxide occurs at 2143.3 cm^{-1} . Calculate the value of the force constant for this bond. [5]
[relative atomic masses: C 12.01, O 16.00]
8. (a) Outline the assumptions made in the *steady state approximation* when applied to chemical rate laws. Your answer should make reference to the rates of the individual elementary reactions and the time dependence of reactant and product concentrations. [7]
- (b) The reaction of H_2 with Cu^{2+} in aqueous acidic solution is as follows



and can be accounted for by the following mechanism



Assuming that steady state conditions apply, show that the reaction obeys the following rate law [15]

$$r = \frac{k_1 k_2 [\text{H}_2] [\text{Cu}^{2+}]^2}{k_2 [\text{Cu}^{2+}] + k_{-1} [\text{H}^+]}$$

- (c) How might the order of reaction with respect to Cu^{2+} vary as the pH of the solution is increased. [3]

CCHE 4273

9. (a) What is meant by a standard electrode potential? Discuss the use of such quantities. [5]

(b) For an electrochemical equilibrium with a net transfer of one electron between species the Gibbs energy is given by $\Delta G^\ominus = -FE^\ominus$. Derive expressions relating the standard entropy and enthalpy changes to the temperature dependence of the standard EMF. [10]

(b) E^\ominus for the cell $\text{Pt(s)} \mid \text{H}_2(\text{g}) \mid \text{HCl(aq)} \mid \text{Hg}_2\text{Cl}_2(\text{s}) \mid \text{Hg(l)}$ is +0.2699 V at 293 K and +0.2669 V at 303 K.

(i) Write down the cell equation [2]

(ii) Calculate $\Delta_r S^\ominus$, $\Delta_r H^\ominus$ and the equilibrium constant K at 298 K. [8]

10. (a) For the gas phase dissociation reaction



show that the degree of dissociation α in terms of the equilibrium constant can be expressed in terms of K_p as follows [12]

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

(b) For the dissociation of gaseous N_2O_4 to 2NO_2 calculate K_p and α at pressures $p = 1$ and 10 bar, for temperatures $T = 198, 298$ and 398 K. $\Delta_r H^\ominus(298\text{K}) = +57.2 \text{ kJmol}^{-1}$ and $\Delta_r S^\ominus(298\text{K}) = +176 \text{ J K}^{-1} \text{ mol}^{-1}$. [13]