CCHE 4273

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

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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, $R$ | $= 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$ |
| Planck constant, $h$ | $= 6.626 \times 10^{-34}\ \mathrm{J\ s}$ |
| Boltzmann constant, $k_B$ | $= 1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}$ |
| Speed of light, $c$ | $= 2.998 \times 10^{8}\ \mathrm{m\ s^{-1}}$ |
| Avogadro number, $N_A$ | $= 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$ |
| $p^{\ominus}$ | $= 1\ \mathrm{bar} = 1 \times 10^{5}\ \mathrm{Pa} = 760\ \mathrm{mmHg}$ |
| Electron mass, $m_e$ | $= 9.110 \times 10^{-31}\ \mathrm{kg}$ |
| Elementary charge, $e$ | $= 1.602 \times 10^{-19}\ \mathrm{C}$ |
| Faraday constant, $F$ | $= 9.648 \times 10^{4}\ \mathrm{C\ mol^{-1}}$ |
| Atomic mass unit, u | $= 1.661 \times 10^{-27}\ \mathrm{kg}$ |
| Molar volume, $V_m$ | $= 24.79\ \mathrm{dm^3\ mol^{-1}}$ at 298K |
| 1 electron volt | $= 1.6022 \times 10^{-19}\ \mathrm{J}$ |

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

## SECTION A

**Answer all questions in this section**

1. (a) Describe the photoelectric effect and discuss its consequences for the properties of light. [3]

   (b) 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]

   (c) Derive the term symbols for the ground state and first electronically excited state of potassium. [2]

2. The Clausius-Clapeyron equation is

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

   (a) Derive the integrated form of this expression. [2]

   (b) 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 ($\Delta_{vap}H$) 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)

3. (a) Describe what is meant by normalization of a wavefunction. [2]

   (b) 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]

   (c) 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]/mol dm$^{-3}$ | 1.000 | 0.952 | 0.909 | 0.870 | 0.833 | 0.800 |

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

5. For the following cell

$$Al(s) \mid Al^{3+}(aq) \parallel Cu^{2+}(aq),\ Cu^{+}(aq) \mid Pt(s)$$

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 $E^{\ominus}_{Al/Al^{3+}}$ = -1.61 V and $E^{\ominus}_{Cu^{+}/Cu^{2+}}$ = +0.15 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 D = 3.34 x 10$^{-30}$ 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 $\psi_0$? [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

$$2Cu^{2+} + H_2 \rightleftharpoons 2Cu^{+} + 2H^{+}$$

and can be accounted for by the following mechanism

$$Cu^{2+} + H_2 \xrightarrow{k_1} CuH^{+} + H^{+}$$
$$CuH^{+} + H^{+} \xrightarrow{k_{-1}} Cu^{2+} + H_2$$
$$CuH^{+} + Cu^{2+} \xrightarrow{k_2} 2Cu^{+} + H^{+}$$

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

$$r = \frac{k_1 k_2 [H_2][Cu^{2+}]^2}{k_2[Cu^{2+}] + k_{-1}[H^{+}]}$$

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

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 $Pt(s) \mid H_2(g) \mid HCl(aq) \mid Hg_2Cl_2(s) \mid Hg(l)$ 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

$$A_2(g) \rightleftharpoons 2A(g)$$

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

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

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

**CCHE 4273** **End of examination**