CCHE 4273
CMET 4273

FIRST PUBLIC EXAMINATION

Long Vacation 2001

Preliminary Examination in Chemistry

SUBJECT 3. CHEMISTRY 3: PHYSICAL CHEMISTRY

also

Preliminary Examination in Metallurgy and Science of Materials

Tuesday, 18th September 2001, 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.

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 bar = 760 Torr
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, m_u	$= 1.661 \times 10^{-27}\ \text{kg}$
Molar volume, V_m	$= 24.79\ \text{dm}^3\ \text{mol}^{-1}$ at 298K
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

1. (a) Explain what is meant by *normalisation* of a wavefunction. [2]

(b) Show that for the following wavefunction,

$$\psi(r) = Ne^{-r/a}$$

the normalisation factor is $\frac{1}{(\pi a^3)^{\frac{1}{2}}}$. The volume element $d\tau$ for a spherically symmetric function is $d\tau = 4\pi r^2 dr$, where $0 \leq r < \infty$. [6]

(*Note* $\int_0^\infty x^n e^{-\alpha x} dx = \frac{n!}{\alpha^{n+1}}$).

2. (a) For a weak acid HA in equilibrium with H^+ and A^- show that the relationship between its dissociation constant K_a and pH is given by

$$\text{pH} = \text{p}K_a - \log_{10} \frac{[\text{HA}]}{[\text{A}^-]}$$ [4]

(b) Sketch how the pH varies as a weak acid is titrated against a strong base. [2]

(c) How can the pK_a of the weak acid be determined experimentally? [2]

3. The reactant A is converted into product D via an intermediate C using the following series of elementary reactions

$$\text{A(g)} + 2\text{B(g)} \xrightarrow{k_1} 2\text{C(g)} \qquad (1)$$
$$2\text{C(g)} \xrightarrow{k_{-1}} \text{A(g)} + 2\text{B(g)} \qquad (2)$$
$$\text{C(g)} \xrightarrow{k_3} \text{D(g)} \qquad (3)$$

(a) Write down the rate equations for each reaction. State the order of reaction (1) with respect to A; what is the molecularity of this reaction? [4]

(b) Describe how the relative values of the rate constants k_1 and k_3 will affect the overall rate of production of D. [3]

(c) What effect would addition of an inert gas have on the position of equilibrium of reaction (1)? [2]

4. (a) Describe what is meant by an *ideal solution* of two liquids. [2]

(b) Illustrate how the vapour pressure of a two component ideal liquid would vary with mole fraction. [2]

(c) Calculate the vapour pressure of benzene at 298 K in a solution containing 1 mole of o-xylene (1, 2-dimethyl benzene) in 500g of benzene. The vapour pressure of pure benzene at 298 K is 94.6 Torr. Assume an ideal solution. (The relative atomic masses of carbon and hydrogen are 12.01 and 1.008 respectively.) [4]

5. (a) Explain the origin of the quantum numbers L, S and J when determining spin-orbit coupled term symbols. [6]

(b) Determine the term symbols for the configurations $1s^2$ and $1s^1\ 2s^1$. [3]

6. (a) Starting from the relationship $dU = dq + dw$, combine the first and second laws of thermodynamics to derive an expression, $dU = TdS - pdV$, for the internal energy in terms of entropy (S) and volume (V). [4]

(b) Use the relationship determined in (a) to derive the Maxwell relation [4]

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

SECTION B

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

7. (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. [10]

(b) The mechanism for the decomposition of N_2O_5, in the presence of a third body M, is

$$N_2O_5 + M \xrightarrow{k_1} NO_2 + NO_3 + M$$
$$NO_2 + NO_3 + M \xrightarrow{k_{-1}} N_2O_5 + M$$
$$NO_2 + NO_3 \xrightarrow{k_2} NO + O_2 + NO_2$$
$$NO + NO_3 \xrightarrow{k_3} 2NO_2$$

Using the steady state approximation derive the rate equation for the depletion of N_2O_5 showing that it has a first order dependence on $[N_2O_5]$. [15]

8. (a) For a wavefunction, ψ, a solution to the Schrödinger equation, what is the significance of the quantity $|\psi|^2$. [5]

(b) Show that the wavefunction $\psi(x) = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\frac{\pi x}{L}$, is a solution to the Schrödinger equation for a particle in a one-dimensional box of length L

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x).$$

Calculate the probability of finding a particle between x = $\frac{L}{2}$ and x = $\frac{3L}{4}$. [15]

(note $\int (\sin^2 ax)dx = \frac{1}{2}x - \frac{1}{4a}\sin 2ax$)

(c) If the walls of the box present a barrier of finite potential, is the particle constrained to remain in the box? Explain your answer. [5]

9. (a) For a system doing no non-expansive work, the temperature dependence of the entropy is given by

$$S(T_f) - S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T}$$

Using the definition of C_p (the heat capacity at constant pressure), produce an alternative expression for the temperature dependence of the entropy. [6]

(b) How must the expression derived in (a) be modified if a phase change occurs between T_i and T_f? [9]

(c) Calculate the molar entropy change when aluminium is heated from 873 K to 973 K. The melting point of Al is 933 K; the enthalpy of fusion is 393 J g^{-1}; relative atomic mass of aluminium is 26.98; the heat capacities of the solid and liquid in the temperature range are 31.8 J K^{-1} mol^{-1} and 34.4 J K^{-1} mol^{-1} respectively. [10]

10. (a) For the cell $Ag(s) \mid AgBr(s) \mid Br^-(aq) \parallel Ag^+(aq) \mid Ag(s)$ write down the two half-cell reactions and the overall cell reaction. [7]

(b) Construct the appropriate Nernst equation for this cell. [6]

(c) If $E_R^\circ = 0.8$ V and $E_L^\circ = 0.07$ V, calculate the free energy difference, $\Delta_r G^\circ$, for the cell reaction at 298 K. [6]

(d) Calculate the solubility product for AgBr at 298 K. [6]

CCHE 4273 **End of examination**