NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF APPLIED CHEMISTRY
END OF SEMESTER EXAMINATIONS - MAY 2001
PHYSICAL CHEMISTRY II - SCH 2204
TIME: 3 HOURS

INSTRUCTIONS TO CANDIDATES

Answer **ALL** questions from Section A and **ANY THREE** from Section B.

Gas Constant R = 8.314 J K^{-1} mol^{-1} 0^{o} C = 273.15 K
Faraday's Constant F = 9.6485 x 10^{4} C mol^{-1} Avogadro's Number N_A = 6.022 x 10^{23} mol^{-1}

SECTION A

1. Given the standard reduction potentials at 298K for the reactions:

Cl_2 (g) + 2 e^- → 2 Cl^- (aq) +1.36 V and

Br_2 (l) + 2 e^- → 2 Br^- (aq) +1.09 V

what are the values of ΔG^o and the equilibrium constant K for the following reactions:

Cl_2 (g) + 2 Br^- (aq) → 2 Cl^- (aq) + Br_2 (l) and

$\frac{1}{2}$ Cl_2 (g) + Br^- (aq) → Cl^- (aq) + $\frac{1}{2}$ Br_2 (l)?

(8 marks)

2. The Weston standard cell is

Cd, Hg | $CdSO_4.8/3H_2O$ (saturated soln.) | $HgSO_4$ (s), Hg.

(a) What is the principle use of the Weston cell? (2 marks)

(b) Sketch the cell, and state the reactions occurring at each electrode, and the overall cell reaction. (8 marks)

(c) At 298 K its emf is 1.01832 V and $\partial E^o/\partial T$ = -5.00 x 10^{-5} V K^{-1}. Calculate ΔG^o, ΔH^o and ΔS^o. (6 marks)

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3. (a) Given the relation

$$D = \lambda kT/z^2eF$$

between the ionic conductance and the diffusion constant, and

$$j_L = (zFD/\delta)\, c$$

derive an expression for the thickness of the diffusion layer in terms of the electrolyte concentration, limiting current density and the ionic conductance. (4 marks)

(b) The ionic conductance of Fe^{2+} is 40 S cm^2 mol^{-1}. The limiting current at a Pt electrode of area 40 cm^2 in a 0.250 M solution of iron(II) chloride at 298 K was 215 mA. Calculate the thickness of the diffusion layer. (6 marks)

4. The gas phase reaction 2 A → B is second order in A, and takes place in a reaction vessel of constant volume and temperature with a half-life of 1 h. If the initial pressure of A is 1 atmosphere, what is the total pressure in the vessel after 2 h? (6 marks)

5. Show that the the interconversion of ortho- and para-hydrogen will be $\frac{3}{2}$ order, as obtained experimentally in the range 600 - 750°C, if the rate-determining step is that between atoms and molecules of hydrogen

$$H + \text{para-}H_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} H + \text{ortho-}H_2$$

(6 marks)

6. The data for the adsorption isotherm for ammonia on barium fluoride at 18.6 C are reported below. Confirm that they fit a BET isotherm and find values of the constants. ($p^* = 3222$ Torr)

p/Torr	62.7	108	219	466	555	601	765
V/cm^3	9.8	10.3	11.3	12.9	13.1	13.4	14.1

(9 marks)

SECTION B

7. (a) What is the ionic strength and mean activity coefficient of a 0.01 M solution of $LaCl_3$? (Debye-Hückel A = 0.509) (10 marks)

(b) If the standard reduction potential for Ag | AgCl | Cl^- at 298 K is 0.2221 V, what would be its electrode potential if immersed in the solution described in (a)? (5 marks)