



NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY  
DEPARTMENT OF APPLIED CHEMISTRY  
SUPPLEMENTARY EXAMINATIONS – AUGUST 2010  
PHYSICAL CHEMISTRY II – SCH 2204  
TIME: THREE HOURS (3 HRS)

INSTRUCTIONS TO CANDIDATES

MATERIAL

Reduction potential tables

INSTRUCTIONS TO STUDENTS

Answer All questions.

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} = 0.08205 \text{ dm}^3 \text{ atm}^{-1} \text{ K}^{-1} \text{ mol}^{-1}.$$

$$F = eN_A = 96\,485 \text{ C mol}^{-1}$$

$$1 \text{ atm} = 760 \text{ torr} = 760 \text{ mmHg} = 101\,325 \text{ Pa}$$

$$\ln x = 3.303 \log x$$

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**SECTION A** Answer ALL questions. Each question carries 10 marks.

- The cell constant was given to be  $0.400 \text{ cm}^{-1}$ . A  $0.100 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl (aq)}$  solution had a resistance of  $28.49 \Omega$ . Calculate the molar conductivity of  $\text{NH}_4\text{Cl (aq)}$  at this concentration. [4 marks]
    - The limiting molar conductivities of  $\text{KCl}$ ,  $\text{KNO}_3$ , and  $\text{AgNO}_3$  at standard conditions are  $149.9 \text{ Scm}^2 \text{ mol}^{-1}$ ,  $145.0 \text{ Scm}^2 \text{ mol}^{-1}$ , and  $133.4 \text{ Scm}^2 \text{ mol}^{-1}$ , respectively. What is the limiting molar conductivity of  $\text{AgCl}$  at this temperature? [6 marks]
  - Calculate the ionic strength of an aqueous solution of Calcium chloride at 298K having a molality equal to  $0.002 \text{ mol kg}^{-1}$  and, using the Debye-Huckel limiting law, estimate
    - The activity coefficients of the  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  ions in this solution, and
    - The mean activity coefficients of these ions[10 marks]
- $$[ I = \frac{1}{2} \sum m_i z_i^2 ; \log \gamma = -Az^2 \sqrt{I} ; A = 0.51 \text{ kg}^{\frac{1}{2}} \text{ mol}^{\frac{1}{2}} \text{ for aqueous solutions at 298K}]$$
- State the conditions of temperature and pressure in which the Langmuir isotherm is strongly obeyed. [2 marks]
    - Derive the Langmuir's isotherm. Include the steps for its conversion to the linear form. [6 marks]
    - When is the term *physisorption* used? [2 marks]
  - State the size range of colloidal particles. What kind of particles are above and below this range. [2 marks]

- (b) What is Rayleigh scattering? [2 marks]
- (b) Outline the formation of an electric double layer on the surface of a colloidal particle. State the prime role of the electric double layer and how this role is performed. [6 marks]

### **SECTION B**

*Answer ALL questions from this section.*

5. (a) The cell  $\text{Mg} \mid \text{Mg SO}_4(\text{aq}, a = 1) \parallel \text{CuSO}_4(\text{aq}, a = 1) \mid \text{Cu}$  was set up in a laboratory experiment.
- Calculate (i) the e.m.f of the cell at standard conditions  
(ii) the value of  $\Delta G_r^\ominus$  for the cell reaction  
(iii) the equilibrium constant for the cell reaction.
- Which electrode is more positive, and which way do electrons flow? [8 marks]
- (b) Write the cell reactions and half-reactions for the following cells:  
(i)  $\text{Pt} \mid \text{SnCl}_2(\text{aq}), \text{SnCl}_4(\text{aq}) \parallel \text{MnCl}_2(\text{aq}), \text{HCl}(\text{aq}) \mid \text{MnO}_2(\text{s}) \mid \text{Pt}$   
(ii)  $\text{Pt} \mid \text{Fe}^{3+}(\text{aq}), \text{Fe}^{2+}(\text{aq}) \parallel \text{Sn}^{4+}(\text{aq}) \mid \text{Sn}^{2+}(\text{aq}) \mid \text{Pt}$  [6 marks]
- (c) Using electrode potentials, calculate the equilibrium constant for the following reactions at 25°C.  
(i)  $\text{Sn}(\text{s}) + \text{SnCl}_4(\text{aq}) \longrightarrow 2\text{SnCl}_2(\text{aq})$   
(ii)  $\text{Sn}(\text{s}) + 2\text{AgCl}(\text{s}) \longrightarrow \text{SnCl}_2(\text{aq}) + 2\text{Ag}(\text{s})$  [6 marks]
6. (a) State the four common kinds of electrodes used in electrochemical cells [4 marks]
- (b) State the two types of concentration cells and highlight the major difference between them [2 marks]
- (c) Draw a rough graph that describes the variation in the conductance of:  
(i) A strong acid titrated with a strong base  
(ii) A weak acid titrated with a strong base  
(iii) A strong acid titrated with a weak base [6 marks]
- State two titrimetric analyses in which conductometric methods may be more preferable. [2 marks]
- (d) With the aid of a diagram, outline the moving boundary method for determining transport numbers of ions [6 marks]

7. The data below relates to the adsorption of carbon monoxide on charcoal at 273K. Confirm that they fit the Langmuir isotherm, and find:

- (a) The constant  $k$
- (b) The volume corresponding to complete coverage

In each case  $V$  has been corrected to 1 atm

P/Torr	100	200	300	400	500	600	700
V/cm <sup>3</sup>	10.3	19.3	27.3	34.1	40.0	45.5	48.0

The Langmuir's isotherm:  $\theta = \frac{kP}{(1 + kP)}$  [20 marks]

***END OF QUESTION PAPER!!!***