



## EASTERN UNIVERSITY, SRI LANKA

## FIRST YEAR FIRST SEMESTER EXAMINATION IN SCIENCE-2010/2011 (NOVEMBER 2012)

## CH 102 INTRODUCTION TO ELECTROCHEMISTRY AND THERMODYNAMICS

Answer all questions

Time: 01 hour

## $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ , 2.303 RT/F = 0.5091 V

 (a) What do you mean by extensive and intensive properties and give three examples for each.

[10 marks]

(b) (i) Write the mathematical expression for the first and second laws of thermodynamics.

[10 marks]

(ii) A piston filled with 0.04 mole of an ideal gas expand reversibly from 50.0 ml to 375.0 ml at a constant temperature of 37.0  $^{\circ}$ C. During the process it absorbs 208 J of heat. Calculate q, W,  $\Delta$ U and  $\Delta$ H.

[30 marks]

(c) (i) Using the combination of first and second laws of thermodynamics show that the entropy change ( $\Delta S$ ) on heating of the 'n' moles of substance reversibly from temperature  $T_1$  to  $T_2$  at constant volume is

$$\Delta S = C_v ln \left(\frac{T_2}{T_1}\right)$$

(Assume  $C_v$  is independent of temperature)

[15 marks]

Contd...

(ii)The heat capacity of oxygen at constant volume is given by the empirical equation

$$C_v = \alpha + \beta T + \gamma T^2$$

Where  $\alpha$ ,  $\beta$  and  $\gamma$  are constants. Show that the entropy change ( $\Delta S$ ) of oxygen is heated from T1 to T2 is

$$\Delta S = \alpha ln \frac{T_2}{T_1} + \beta (T_2 - T_1) + \frac{\gamma}{2} (T_2^2 - T_1^2)$$

[20 marks]

(iii) Determine entropy change ( $\Delta S$ ) -when the oxygen is heated from 300 K to 500 K. Where  $\alpha$  = 25.503 J K<sup>-1</sup> mol<sup>-1</sup>,  $\beta$  =13.612x10<sup>-3</sup> J K<sup>-2</sup>  $\text{mol}^{-1}$  and  $\gamma = -42.553 \times 10^{-7} \, \text{J K}^{-3} \, \text{mol}^{-1}$ .

[15 marks]

2) (a) (i) Show that the Maxwell relation as  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ 

23 AUG 2013

[15 marks]

(ii) For a gas follows a van der Waals equation of state show that  $\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V - nb}$ 

[15 marks]

(b) Assume the following reaction occurs in an electrochemical cell  $Cd(s) + Cu^{2+} \longrightarrow Cd^{2+} + Cu(s)$ 

- What is the cell representation for the cell (i)
- What is standard electrode potential ( $E_{cell}^{\theta}$ ) of the cell at 25 °C (ii)
- (iii) Determine standard change in Gibb's free energy( $\Delta G^{\theta}$ ) and equilibrium constant K of the cell at 25 °C

[40 marks]

(c) Calculate the electrode potential (Ecell) of the following cell by using the Nernst equation

$$Zn(s) / Zn^{2+}$$
(0.004 M) //  $Cu^{2+}$ (0.033 M)/  $Cu$  (s)

[30 marks]

$$[E_{Cu^{2+},Cu}^{\theta} = 0.3394 \, V, E_{Cd^{2+},Cd}^{\theta} = -0.40224 \, V, \ E_{Zn^{2+},Zn}^{\theta} = -0.7618 \, V]$$