

## 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

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

1) (a) What do you mean by extensive and intensive properties and give three examples for each.
(b) (i) Write the mathematical expression for the first and second laws of thermodynamics.
(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 $37.0^{\circ} \mathrm{C}$. During the process it absorps 208 J of heat. Calcilate $\mathrm{q}, \mathrm{W}, \Delta \mathrm{U}$ 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

$$
\Delta \mathrm{S}=\mathrm{C}_{\mathrm{V}} \ln \left(\frac{\mathrm{~T}_{2}}{\mathrm{~T}_{1}}\right)
$$

(Assume $C_{v}$ is independent of temperature)
(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 $T_{1}$ to $T_{2}$ is

$$
\Delta S=\alpha \ln \frac{T_{2}}{T_{1}}+\beta\left(T_{2}-T_{1}\right)+\frac{\gamma}{2}\left(T_{2}^{2}-T_{1}^{2}\right)
$$

[20 marks]
(iii) Determine entropy change ( $\Delta S$ ) -when the oxygen is heated from 300 K to 500 K . Where $\alpha=25.503 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}, \beta=13.612 \times 10^{-3} \mathrm{~J} \mathrm{~K}^{-2}$ $\mathrm{mol}^{-1}$ and $\gamma=-42.553 \times 10^{-7} \mathrm{~J} \mathrm{~K}^{-3} \mathrm{~mol}^{-1}$.
2) (a) (i) Show that the Maxwell relation as $\left(\frac{\partial S}{\partial V}\right)_{T}=\left(\frac{\partial P}{\partial T}\right)_{V}$
[15 marks]
(ii) For a gas follows a van der Waals equation of state show that

$$
\left(\frac{\partial S}{\partial V}\right)_{T}=\frac{n R}{V-n b}
$$

$$
\because
$$

[15 marks]
(b) Assume the following reaction occurs in an electrochemical cell

$$
\mathrm{Ca}(\mathrm{~s})+\mathrm{Cu}^{2+} \longrightarrow \mathrm{Cd}^{2+}+\mathrm{Cu}(\mathrm{~s}) \quad, \quad,
$$

(i) What is the cell representation for the cell
(ii) What is standard electrode potential ( $E_{\text {ceil }}^{\theta}$ ) of the cell at $25^{\circ} \mathrm{C}$
(iii) Determine standard change in Gibb's free energy $\left(\Delta G^{\theta}\right)$ and equilibrium constant K of the cell at $25^{\circ} \mathrm{C}$
[40 marks]
(c) Calculate the electrode potential ( $E_{\text {cell }}$ ) of the following cell by using the Nernst equation

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

[30 marks]

$$
\left[E_{C u^{2+}, C u}^{\theta}=0.3394 \mathrm{~V}, E_{C d^{2+}, C d}^{\theta}=-0.40224 \mathrm{~V}, E_{Z n^{2+}, Z n}^{\theta}=-0.7618 \mathrm{~V}\right]
$$

