



EASERN UNIVERSITY, SRI LANKA

FIRST EXAMINATION IN SCIENCE – PROPER

EXTERNAL DEGREE

FIRST SEMESTER 2003-2004 (OCTOBER 2006)

EXTCH 102 THERMODYNAMICS & INTRODUCTION TO ELECTRO CHEMISTRY

Time allowed: **ONE Hour**

Candidate must NOT start writing their answers until told to do so

You may find the following data useful

Avagadro constant (N_A): $6.023 \times 10^{23} \text{ mol}^{-1}$

Electron charge (e): $1.602 \times 10^{-19} \text{ C}$

Faraday constant (F): $9.648 \times 10^4 \text{ Cmol}^{-1}$

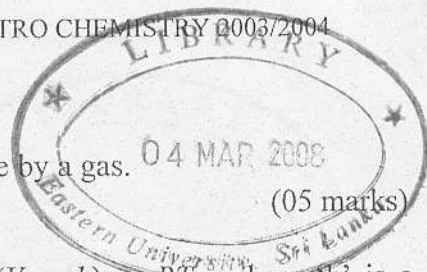
Gas constant (R): $8.314 \text{ JK}^{-1}\text{mol}^{-1}$

Planck's constant (h): $6.626 \times 10^{-34} \text{ Js}$

Rest mass of electron (m_e): $9.1 \times 10^{-31} \text{ kg}$

Velocity of light (c): $3 \times 10^8 \text{ ms}^{-1}$

The use of a non-programmable calculator is permitted



1. a) (i) Write the mathematical form of total work done by a gas. (05 marks)
- (ii) Given that the equation of state of gas is $P(V - nb) = nRT$, where 'b' is a constant. Show that the work done (W) by the gas in a reversible isothermal expansion when the volume is changed from V_1 to V_2 is,

$$W = nRT \ln \left(\frac{V_1 - nb}{V_2 - nb} \right)$$

(25 marks)

- (iii) If the above gas behaves ideally then deduce that $W = nRT \ln \left(\frac{V_1}{V_2} \right)$
- (10 marks)

- (iv) 2 moles of ideal gas at 300 K and 6 atm pressure undergo expansion isothermally to half the initial pressure. Calculate the work done by the gas on the surroundings. ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
- (30 marks)

- b) (i) Define the term 'molar heat capacity'.
- (05 marks)

- (ii) The molar isobaric heat capacity C_p for $\text{NH}_3(\text{g})$ is given by $C_p = a + bT + \frac{c}{T}$, where T is the temperature and 'a', 'b' and 'c' are constants. Show that the change in enthalpy (ΔH) when the temperature of **one mol** of $\text{NH}_3(\text{g})$ is increased from T_1 to T_2 is

$$C_p = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + c \ln \left(\frac{T_2}{T_1} \right)$$

(25 marks)

[Hint: $C_p = \left(\frac{\partial H}{\partial T} \right)_p$]

2. a) Derive the following auxiliary relations for a reversible process

$$(i) dH = TdS + VdP \quad (ii) dG = VdP - SdT$$

$$[\text{Hint: } dU = TdS - PdV]$$

(20 marks)

b) (i) Assuming $G = G(T, P)$, derive the Maxwell relation

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

(20 marks)

(ii) 3 moles of $O_2(g)$ at 300 K is compressed isothermally from 10 to 20 atm. Calculate the change in entropy, assuming that $O_2(g)$ obeys the ideal gas equation

(25 marks)

c) (i) Write the Nernst equation and identify all the terms involved in it.

(10 marks)

(ii) If the electrode potential E for the Fe^{3+}/Fe^{2+} system is 0.889 V

$$\text{calculate } \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad (E_{Fe^{3+}/Fe^{2+}}^\theta = 0.771 \text{ V}; 2.303 RT/F = 0.059)$$

(25 marks)