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Eastern University, Sri Lanka

First Year First Semester Examination in Science

2011/2012 (February/ March 2015)

CH 102 Thermodynamics and Introduction to Electrochemistry

Proper and Repeat

Answer all question

Time Allowed: One hour

R= 8.314 J mol^{-1} K^{-1}, F = 96485 C mol^{-1}

1. a) Define P-V work done for expansion of a gas.

(05 marks)

b) A sample of 4.5 g of methane occupies 12.7 L at 310 K. Calculate $w, q, \Delta U,$ and ΔH when

i) the gas expands isothermally against a constant external pressure 0.25 atm until its volume has increased by 3.3 L.

(25 marks)

ii) the same expansion in (i) occurred reversibly.

(25 marks)

c) Starting with the first law of thermodynamics and the definitions of c_p and c_v, Show that

$$c_p - c_v = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p$$

(20 marks)

d) Use the above result and the expression $p + \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$ to find $c_p - c_v$ for a gas obeying the equation of state $p(V - nb) = nRT$, where b is a constant.

(25 marks)

2. a) Derive the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(10 marks)

b) A gas which follows an equation of state $\left(P + \frac{a}{TV^2}\right)V = nRT$ expands from volume V_1 to V_2, where 'a' is a constant. Determine $\left(\frac{\partial P}{\partial T}\right)_V$ and hence, show that

$$\Delta S = R\, ln\left(\frac{V_2}{V_1}\right) + \frac{a}{T^2}\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

(25 marks)

b) i) Write the Nernst equation and explain the terms involved in it.

ii) For the cell reaction

$$2Al\,(s) + 3Pb^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Pb(s)$$

I) Write the half-cell reactions and indicate which one occurs in the anode and which one in the cathode

II) Calculate the standard electrode potential (E^{θ}_{cell}), standard Gibb's free energy(ΔG^{θ}) and equilibrium constant K

III) Calculate the initial concentration of Pb^{2+}(aq) if the electrode potential (E_{cell}) is 1.572 V and initial concentration of Al^{3+}(aq) is 0.1 M.

(65 marks)

$$\left[E^{\theta}_{Al^{3+},Al} = -1.662\ V;\ E^{\theta}_{Pb^{2+},Pb} = -0.126\ V;\ 2.303\frac{RT}{F} = 0.05091V\right]$$

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