CHEM 273 TEST

Tuesday, September 11, 2007

Time allowed: ONE hour

ANSWER ALL QUESTIONS:

1. The Gibbs Helmholtz equation can be written as

$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_p = -\frac{\Delta H}{T^2}$$

(a) Given that $\Delta G^0 = RT \ln K$, show how the Gibbs-Helmholtz equation can be used to obtain the temperature dependence of the equilibrium constant, K.

$$\ln(K_{T2}/K_{T1}) = -\frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (1)$$

Comment on any approximations made in the derivation of equation (1).

(b) Calculate the equilibrium constant at 25˚C for the dimerization reaction of NO_2 from the data given below.

$$NO_2(g) + NO_2(g) \rightleftharpoons N_2O_4(g)$$

	ΔH^0_f/kJ mol^{-1}	S^0/J K^{-1} mol^{-1}
$NO_2(g)$	33.2	240.1
$N_2O_4(g)$	9.2	304.3

(c) Derive an equation showing how to calculate the equilibrium pressure of $N_2O_4(g)$ when 55 Torr of pure $NO_2(g)$ is placed in an evacuated flask at 25˚C. (DO NOT EVALUATE your equation)

(d) What additional information is needed to give a better evaluation of K at 500 ˚C than that represented by equation (1)?

($R = 8.314$ J mol^{-1} K^{-1})

2. A concentration electrochemical cell at 25 ˚C may be represented in a cell diagram as

$$Ag(s) \;|\; Ag^{+}\,(m \text{ mol } L^{-1}) \;\|\; Ag^{+}\,(0.01 \text{ mol } L^{-1}) \;|\; Ag(s)$$

(a) Explain the significance of the vertical lines in the cell diagram.

(b) Write down the cell equation that applies to this cell.

(c) Write down the Nernst equation that applies to this cell.

(d) Calculate the ionic strength I in the right hand half cell given that the cell electrolyte is $AgNO_3$.

(e) Calculate the activity coefficient $\gamma_{\pm}$ for the Ag^{+} ion in the right hand half cell.

(f) If potassium chloride was titrated into the left hand half cell, explain briefly how the solubility product Ksp of AgCl could be obtained.

(g) What thermodynamic state functions can be obtained from cell EMF measurements? What additional measurements need to be made to obtain the additional state functions?

($I = \frac{1}{2}\sum_i C_i Z_i^2$; $\log_{10}\gamma_{\pm} = -0.509\,|Z^{+}Z^{-}|(I/\text{mol } L^{-1})^{1/2}$; $F = 96{,}485 \text{ C mol}^{-1}$; $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.)