

CHEM 273 TEST

Tuesday, September 11, 2007

Time allowed: ONE hour

ANSWER ALL QUESTIONS:

1. The Gibbs Helmholtz equation can be written as

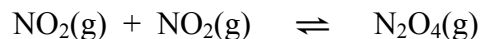
$$\left(\frac{\partial(\Delta G/T)}{\partial T} \right)_p = -\frac{\Delta H}{T^2}$$

- (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 .

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

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

- (b) Calculate the equilibrium constant at 25°C for the dimerization reaction of NO₂ from the data given below.

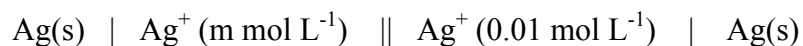


	$\Delta H_f^0/\text{kJ mol}^{-1}$	$S^0/\text{J K}^{-1} \text{mol}^{-1}$
NO ₂ (g)	33.2	240.1
N ₂ O ₄ (g)	9.2	304.3

- (c) Derive an equation showing how to calculate the equilibrium pressure of N₂O₄(g) when 55 Torr of pure NO₂(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)?

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

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



- (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 γ_{\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 K_{sp} 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?

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