

**Quiz 8**  
**CHEM 323**  
**Fall 2008**

Name: \_\_\_\_\_

1. (10 Points) The equilibrium constant for the reaction shown below was fit to the expression

$\ln K = -1.04 - \frac{1088.}{T} + \frac{1.51 \times 10^5}{T^2}$  between 300. K and 600. K under standard pressure. Note that the units on the right hand side of the equation have been omitted (you will need to add them).



Calculate  $\Delta H^0$  and  $\Delta S^0$  for the reaction at 400.0 K.

**Taking the derivative of  $\ln K$  with respect to  $T$  will allow us to find  $\Delta H^0$  since**

$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2}$ . Note that we could have used  $\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^0}{R}$  and would have gotten the

same equation for  $\Delta H^0$ .

$$\frac{\Delta H^0}{RT^2} = \frac{d \ln K}{dT} = \frac{d}{dT} \left( -1.04 - \frac{1088. \text{ K}}{T} + \frac{1.51 \times 10^5 \text{ K}^2}{T^2} \right) = \frac{1088. \text{ K}}{T^2} - \frac{3.02 \times 10^5 \text{ K}^2}{T^3}$$

$$\Delta H^0 = \left( 1088. \text{ K} - \frac{3.02 \times 10^5 \text{ K}^2}{T} \right) R = \left( (1088.) - \left( \frac{3.02 \times 10^5}{400.0} \right) \right) (8.31447 \text{ J} \cdot \text{mole}^{-1})$$

$$\Delta H^0 = (1088. - 755.0) (8.31447 \text{ J} \cdot \text{mole}^{-1}) = (333.0) (8.31447 \text{ J} \cdot \text{mole}^{-1}) = +2.76_8 \text{ kJ} \cdot \text{mol}^{-1}$$

**Find  $\Delta G^0$  using  $\Delta G = -RT \ln K$  (so we can then use  $\Delta H^0$  to find  $\Delta S^0$  with  $\Delta G = \Delta H - T\Delta S$ ).**

$$\Delta G^0 = -RT \left( -1.04 - \frac{1088. \text{ K}}{T} + \frac{1.51 \times 10^5 \text{ K}^2}{T^2} \right) = -R \left( -1.04T - 1088. \text{ K} + \frac{1.51 \times 10^5 \text{ K}^2}{T} \right)$$

$$\Delta G^0 = -(8.31447 \text{ J} \cdot \text{mole}^{-1}) \left( -1.04(400.0) - 1088. + \frac{1.51 \times 10^5}{400.0} \right)$$

$$\Delta G^0 = -(8.31447 \text{ J} \cdot \text{mole}^{-1}) (-416.0 - 1088. + 377.5) = -(8.31447 \text{ J} \cdot \text{mole}^{-1}) (-1126.5)$$

$$\Delta G^0 = +9.366_2 \text{ kJ} \cdot \text{mole}^{-1}$$

**Now determine  $\Delta S^0$  with  $\Delta G = \Delta H - T\Delta S$ .**

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{(2.76_8 \times 10^3 \text{ J} \cdot \text{mol}^{-1}) - (9.366_2 \times 10^3 \text{ J} \cdot \text{mol}^{-1})}{400.0 \text{ K}}$$

$$\Delta S = \frac{-6.59_7 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{400.0 \text{ K}} = -16.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$$

**For this reaction  $\Delta H^0 = +2.77 \text{ kJ/mole}$  and  $\Delta S^0 = -16.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$  at **400.0 K**.**

2. (8 Points) The vapor pressure above solid  $\text{NH}_4\text{Cl}$  at  $427.0 \text{ }^\circ\text{C}$  is  $608. \text{ kPa}$  due to the decomposition of the  $\text{NH}_4\text{Cl}$  according to the reaction  $\text{NH}_4\text{Cl} (\text{s}) \rightleftharpoons \text{NH}_3 (\text{g}) + \text{HCl} (\text{g})$ . Taking the reference pressure as standard pressure ( $100.00 \text{ kPa}$ ) and assuming the gases are ideal, what is the value of the equilibrium constant for this reaction?

**Since the moles of  $\text{NH}_3$  formed equal the moles of  $\text{HCl}$  formed (and  $\text{NH}_4\text{Cl}$  does not contribute to the pressure), the mole fraction of each gaseous substance is  $1/2$ . This means that the partial pressure of each is  $1/2$  the total pressure. We'll start with the expression for  $K$  and use the definition of the activity of gases ( $a_j = \frac{P_j}{P^0}$ ) to put  $K$  in terms of the partial pressures.**

$$K = a_{\text{NH}_3} a_{\text{HCl}}$$

$$K = \left( \frac{P_{\text{NH}_3}}{P^0} \right) \left( \frac{P_{\text{HCl}}}{P^0} \right) = \frac{P_{\text{NH}_3} P_{\text{HCl}}}{(P^0)^2}$$

**Because  $P_{\text{NH}_3} = P_{\text{HCl}} = \frac{1}{2} P_{\text{total}}$ , we can rewrite this expression in terms of the total pressure as follows, taking our reference as standard pressure ( $100.00 \text{ kPa}$ ) (note that we chose to do that so that pressure units will cancel).**

$$K = \frac{1}{4} \frac{P_{\text{total}}^2}{(P^0)^2} = \frac{1}{4} \frac{(608. \text{ kPa})^2}{(100.000 \text{ kPa})^2} = 9.24$$

**Under these conditions  $K$  for this reaction is  $9.24$ .**

3. (4 Points) Write the cell reaction and the electrode half reactions for the following galvanic cell.

