

CHM 3400 – Problem Set 7

Due date: Monday, March 16<sup>th</sup>. NOTE: The second exam is Wednesday, March 18<sup>th</sup>, in class. It will cover material from Chapter 4 and 5 of Atkins. Please bring all the chapter handouts, plus one page of notes.

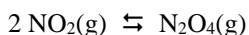
Do all of the following problems. Show your work.

“van’t Hoff was the first chemist to make the connection between free energy and voltage, but Nernst was the one who ended up with his name on the equation.”

- Patrick Coffey

1) Nitrogen oxides play an important role in the chemistry of urban atmospheres. The equilibrium that exists between different nitrogen oxides is potentially important both in the atmosphere and in laboratory experiments.

Consider the dimerization reaction that converts nitrogen dioxide (NO<sub>2</sub>) into dinitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>)



a) Write the expression for K, the equilibrium constant for the above reaction, in terms of the activities of the reactants and products.

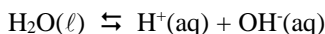
b) Give the expression for K, the equilibrium constant for the above reaction, assuming ideal behavior.

c) Find the value for K for the above reaction at T = 25.0 °C.

Thermochemical data that can be used for the above problem (given at T = 25.0 °C) are given below.

Substance	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/mol·K)	$\Delta G_f^\circ$ (kJ/mol)	$C_{p,m}$ (J/mol·K)
NO <sub>2</sub> (g)	33.18	240.06	51.31	37.20
N <sub>2</sub> O <sub>4</sub> (g)	9.16	304.29	97.89	77.28

2) The self-ionization reaction for water is the process



The value for the equilibrium constant for this reaction is important as it determines the value for pH for a neutral solution.

a) Write the expression for K, the equilibrium constant for the above reaction, in terms of the activities of the reactants and products.

b) Give the expression for K, the equilibrium constant for the above reaction, assuming ideal behavior.

c) Find the value for K for the above reaction at T = 25.0 °C.

d) Find the value for K for the above reaction at T = 37.0 °C (physiological temperature).

e) Using your results for c and d, find the value for pH for a neutral solution at T = 25.0 °C and T = 37.0 °C.

Give your final answer to the nearest ± 0.01 pH units.

Thermochemical data that can be used for the above problem (given at T = 25.0 °C) are given below.

Substance	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/mol·K)	$\Delta G_f^\circ$ (kJ/mol)	$C_{p,m}$ (J/mol·K)
H <sup>+</sup> (aq)	0.0	0.0	0.0	0.0
OH <sup>-</sup> (aq)	- 229.99	- 10.75	- 157.24	- 148.5
H <sub>2</sub> O(ℓ)	- 285.83	69.91	- 237.13	75.29

3) The equilibrium constant for the decomposition reaction



is  $K = 3.98 \times 10^{-4}$  at  $T = 350.0 \text{ K}$ , and  $K = 1.41 \times 10^{-2}$  at  $T = 400.0 \text{ K}$ .

a) Write the expression for  $K$ , the equilibrium constant for the above reaction, in terms of the activities of the reactants and products.

b) Give the expression for  $K$ , the equilibrium constant for the above reaction, assuming ideal behavior.

c) Using the values for  $K$  given above, find the value for  $\Delta H^\circ_{\text{rxn}}$  for the above reaction.

4) Consider the galvanic cell whose cell diagram is given below.



a) Give the half-cell oxidation reaction, the half-cell reduction reaction, and the net cell reaction for the above galvanic cell.

b) Find  $E^\circ_{\text{cell}}$  and  $E_{\text{cell}}$  for the above galvanic cell.

c) Find  $\Delta G^\circ_{\text{rxn}}$  and  $\Delta G_{\text{rxn}}$  for the above galvanic cell.

Half-cell reduction data are given in the Chapter 5 handout, and also in the Appendix of Atkins.

5) Copper I ions can be converted into copper II ions and copper metal by the process



a) Write the expression for  $K$ , the equilibrium constant for the above reaction, in terms of the activities of the reactants and products.

b) Give the expression for  $K$ , the equilibrium constant for the above reaction, assuming ideal behavior.

c) Using the table of half-cell reduction reaction in the Chapter 5 handout, find the value for  $K$  for the above reaction at  $T = 25.0 \text{ }^\circ\text{C}$ .

### Solutions.

1) a) In terms of activities,  $K = \frac{(a_{\text{N}_2\text{O}_4})}{(a_{\text{NO}_2})^2}$

b) If we assume ideal behavior, and substitute for the activities, we get  $K = \frac{(p_{\text{N}_2\text{O}_4})}{(p_{\text{NO}_2})^2}$

c) To do this problem we need to find the change in free energy for the reaction at  $T = 25.0\text{ }^\circ\text{C}$ .

$$\Delta G^\circ_{\text{rxn}} = [ \Delta G^\circ_f(\text{N}_2\text{O}_4(\text{g})) ] - [ 2 \Delta G^\circ_f(\text{NO}_2(\text{g})) ] = (97.89) - 2 (51.31) = - 4.73 \text{ kJ/mol}$$

And so  $\ln(K) = - \frac{(- 4730. \text{ J/mol})}{(8.3145 \text{ J/mol}\cdot\text{K}) (298.15 \text{ K})} = 1.91 \quad K = e^{1.91} = 6.7$

2) a) In terms of activities,  $K = \frac{(a_{\text{H}^+})(a_{\text{OH}^-})}{(a_{\text{H}_2\text{O}})}$

b) If we assume ideal behavior, and substitute for the activities, we get  $K = [\text{H}^+] [\text{OH}^-]$

c) We proceed as in problem 1c

$$\begin{aligned} \Delta G^\circ_{\text{rxn}} &= [ \Delta G^\circ_f(\text{H}^+(\text{aq})) + \Delta G^\circ_f(\text{OH}^-(\text{aq})) ] - [ \Delta G^\circ_f(\text{H}_2\text{O}(\ell)) ] \\ &= [ (0.00) + (- 157.24) ] - (- 237.13) = 79.89 \text{ kJ/mol} \end{aligned}$$

And so  $\ln(K) = - \frac{(79890. \text{ J/mol})}{(8.3145 \text{ J/mol}\cdot\text{K}) (298.15 \text{ K})} = - 32.23 \quad K = e^{-32.23} = 1.01 \times 10^{-14}$

d) Since  $37.0\text{ }^\circ\text{C}$  is close to  $25.0\text{ }^\circ\text{C}$ , we can use the approximate method to find  $K$ . We first need to find the value for the change in enthalpy for the reaction.

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= [ \Delta H^\circ_f(\text{H}^+(\text{aq})) + \Delta H^\circ_f(\text{OH}^-(\text{aq})) ] - [ \Delta H^\circ_f(\text{H}_2\text{O}(\ell)) ] \\ &= [ (0.00) + (- 229.99) ] - (- 285.83) = 55.84 \text{ kJ/mol} \end{aligned}$$

Now, if we let  $T_1 = 25.0\text{ }^\circ\text{C}$  and  $T_2 = 37.0\text{ }^\circ\text{C}$ , then

$$\begin{aligned} \ln(K_2/K_1) &= - (\Delta H^\circ_{\text{rxn}}/R) \{ (1/T_2) - (1/T_1) \} \\ &= - [ (55840. \text{ J/mol})/(8.3145 \text{ J/mol}\cdot\text{K}) ] [ (1/310.15 \text{ K}) - (1/298.15 \text{ K}) ] \\ &= 0.871 \end{aligned}$$

Taking the inverse logarithm of both sides of this equation gives

$$K_2/K_1 = e^{0.871} = 2.39 \quad K_2 = (2.39) K_1 = (2.39) (1.01 \times 10^{-14}) = 2.41 \times 10^{-14}$$

e) Since for a neutral solution  $[H^+] = [OH^-]$ , then based on the answer to part b, we may say

$$[H^+] = K^{1/2} \quad \text{pH} = -\log_{10}[H^+]$$

So  $T = 25.0\text{ }^\circ\text{C} \quad [H^+] = (1.01 \times 10^{-14})^{1/2} = 1.00 \times 10^{-7}\text{ M} \quad \text{pH} = -\log_{10}(1.00 \times 10^{-7}) = 7.00$

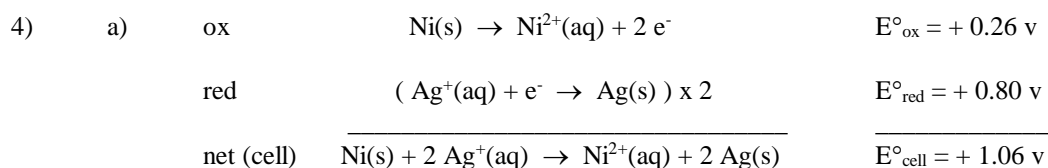
$T = 37.0\text{ }^\circ\text{C} \quad [H^+] = (2.41 \times 10^{-14})^{1/2} = 1.55 \times 10^{-7}\text{ M} \quad \text{pH} = -\log_{10}(1.55 \times 10^{-7}) = 6.81$

3) a) In terms of activities,  $K = \frac{(a_{\text{Ag}_2\text{O}})(a_{\text{CO}_2})}{(a_{\text{Ag}_2\text{CO}_3})}$

b) If we assume ideal behavior, and substitute for the activities, we get  $K = (p_{\text{CO}_2})$

c)  $\ln(K_2/K_1) = -(\Delta H^\circ_{\text{rxn}}/R) \{ (1/T_2) - (1/T_1) \}$

And so  $\Delta H^\circ_{\text{rxn}} = -\frac{R \ln(K_2/K_1)}{\{ (1/T_2) - (1/T_1) \}} = -\frac{(8.3145\text{ J/mol}\cdot\text{K}) \ln(1.41 \times 10^{-2}/3.98 \times 10^{-4})}{\{ (1/400.0\text{ K}) - (1/350.0\text{ K}) \}} = 83.05\text{ kJ/mol}$



b)  $E^\circ_{\text{cell}} = +1.06\text{ v}$  (as shown in part a)

For  $E_{\text{cell}}$ , we use the Nernst equation  $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{vF} \ln(Q)$

$v = 2 \quad Q = \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2} = \frac{(0.500)}{(0.0020)^2} = 1.25 \times 10^5$

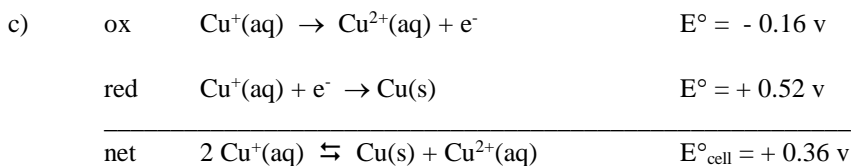
So  $E_{\text{cell}} = 1.06\text{ v} - \frac{(8.3145\text{ J/mol}\cdot\text{K})(298.15\text{ K})}{(2)(96485\text{ C/mol})} \ln(1.25 \times 10^5) = 1.06\text{ v} - 0.15\text{ v} = 0.91\text{ v}$

c)  $\Delta G^\circ_{\text{rxn}} = -vFE^\circ_{\text{cell}} = -(2)(96485\text{ C/mol})(1.06\text{ v}) = -204\text{ kJ/mol}$

$\Delta G_{\text{rxn}} = -vFE_{\text{cell}} = -(2)(96485\text{ C/mol})(0.91\text{ v}) = -176\text{ kJ/mol}$

5) a) In terms of activities,  $K = \frac{(a_{\text{Cu}})(a_{\text{Cu}^{2+}})}{(a_{\text{Cu}^+})^2}$

b) If we assume ideal behavior, and substitute for the activities, we get  $K = \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]^2}$



$\ln K = \frac{vFE^\circ_{\text{cell}}}{RT} = \frac{(1)(96485\text{ C/mol})(+0.36\text{ V})}{(8.3145\text{ J/mol}\cdot\text{K})(29815\text{ K})} = +14.02$  so  $K = e^{14.02} = 1.2 \times 10^6$