CHM 3400 – Problem Set 7

Due date: Monday, March 16th. NOTE: The second exam is Wednesday, March 18th, 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_2) into dinitrogen tetroxide (N_2O_4)

$$2\ NO_2(g) \leftrightarrows N_2O_4(g)$$

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	$\Delta H°_f$ (kJ/mol)	S° (J/mol•K)	$\Delta G°_f$ (kJ/mol)	$C_{p,m}$ (J/mol•K)
$NO_2(g)$	33.18	240.06	51.31	37.20
$N_2O_4(g)$	9.16	304.29	97.89	77.28

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

$$H_2O(\ell) \leftrightarrows H^+(aq) + OH^-(aq)$$

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	$\Delta H°_f$ (kJ/mol)	S° (J/mol•K)	$\Delta G°_f$ (kJ/mol)	$C_{p,m}$ (J/mol•K)
$H^+(aq)$	0.0	0.0	0.0	0.0
$OH^-(aq)$	- 229.99	- 10.75	- 157.24	- 148.5
$H_2O(\ell)$	- 285.83	69.91	- 237.13	75.29

3) The equilibrium constant for the decomposition reaction

$Ag_2CO_3(s) \leftrightarrows Ag_2O(s) + CO_2(g)$

is $K = 3.98 \times 10^{-4}$ at T = 350.0 K, and $K = 1.41 \times 10^{-2}$ at T = 400.0 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 $\Delta H°_{rxn}$ for the above reaction.

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

$Ni(s) | Ni^{2+}$(aq, M = 0.500 M) || Ag^{+}(aq, M = 0.0020 M) | Ag(s)

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

b) Find $E°_{cell}$ and E_{cell} for the above galvanic cell.

c) Find $\Delta G°_{rxn}$ and ΔG_{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

$2\ Cu^{+}(aq) \leftrightarrows Cu(s) + Cu^{2+}(aq)$

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) Usin 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 °C.