RDCH 702 Last Name:_____
Quiz 2
Assigned 23-Sep-15
Due 30-Sep-15 First Name:_____

Quiz Topics: Speciation, Kinetics, Thermodynamics
Use the lecture notes, chart of the nuclides, table of the isotopes, and web links to answer the following questions.

1. **(20 Points) Using CHESS, provide speciation data for the following conditions. Provide dominant species for the specified condition. You should show the graphs of % species against the condition on a separate page.**

   1.1. 1E-9 M/L Pu^{4+} from pH 5 to pH 10, dominate specie at pH 6.5

   _____

   1.2. 1E-3 M/L UO_2^{2+} from pH 2 to pH 10, dominate specie at pH 6

   _____

   1.3. 1E-6 M/L UO_2^{2+} from pH 2 to pH 12 at 200 mV Eh, dominate specie at pH 8

   _____

   1.4. 1 mmol/L Pu^{4}+ from 100 mV to 1250 mV Eh at pH 4, dominate specie at 500 mV

   _____

   1.5. 50E-6 M/L Am(III) with 0.1 fugacity carbon dioxide from pH 2 to pH 12

   _____

2. (40 Points) Consider the complexation of Pu^{4+} with a monoprotic ligand (LH). The reaction is:

$Pu^{4+}+L^{-} \leftrightarrows PuL^{3+}$

The only Pu species in solution are Pu^{4+} and PuL^{3+}. The total Pu concentration in the solution is 1E-5 M. You determine the free ligand and free Pu concentration as a function of temperature. The ligand species are free ligand and the Pu-L complex. The total ligand concentration is $[L]_t$. The data are below.

Concentration of species as a function of temperature (K)

T K	$[L]_t$ M	$[L]_f$ M	$[Pu]_f$ M
298	2.50E-05	1.50E-05	1.19E-08
298	2.00E-05	1.00E-05	1.78E-08
298	1.00E-05	4.14E-07	4.14E-07
283	1.00E-05	2.66E-07	2.66E-07
325	1.00E-05	8.18E-07	8.18E-07
335	1.00E-05	1.02E-06	1.02E-06
345	1.00E-05	1.25E-06	1.25E-06
355	1.00E-05	1.52E-06	1.52E-06
365	1.00E-05	1.81E-06	1.81E-06

Please provide the following. Ignore activities for this question. Energy should be in J. Provide units for ΔG, ΔH, and ΔS. The subscript on ΔG is the temperature in K.

2.1. ΔG_{298} _____

2.2. The equilibrium constant at 298 K _____

2.3. The equilibrium constant at 355 K _____

2.4. ΔG_{325} _____

2.5. ΔH **over the experimental range** _____

2.6. ΔS **over the experimental range** _____

2.7. Using the complexation constant calculate the speciation of Pu at 330 K for 10 mM ligand and 5 mM Pu.

Free Pu _____ **mM**

PuL^{3+} _____**mM**

3. (10 Points) Select the equation below to describe the speciation of uranyl, uranyl monohydroxide, uranyl dihydroxide, uranyl trihydroxide and diuranyl monohydroxide to find the total uranium concentration. This equation should show the total uranyl concentration as a function of free uranyl, hydroxide, and the complexation constants. The complexation constant nomenclature is β_{xy}, where x is the number of UO_2^{2+} and y is the number of hydroxides, i.e., β_{12} is the complexation constant for uranyl dihydroxide.

3.1. $[U]_{tot} = [UO_2^{2+}](1 + \beta_{11}[OH^-] + \beta_{12}[OH^-]^2 + \beta_{13}[OH^-]^3 + 2\beta_{21}[UO_2^{2+}][OH^-]^2)$

3.2. $[U]_{tot} = [UO_2^{2+}](1 + \beta_{11}[OH^-] + \beta_{12}[OH^-]^2 + \beta_{13}[OH^-]^3 + 2\beta_{21}[UO_2^{2+}][OH^-])$

3.3. $[U]_{tot} = (1 + \beta_{11}[OH^-] + \beta_{12}[OH^-]^2 + \beta_{13}[OH^-]^3 + 2\beta_{21}[UO_2^{2+}][OH^-])$

3.4. $[U]_{tot} = [UO_2^{2+}](\beta_{11}[OH^-] + \beta_{12}[OH^-]^2 + \beta_{13}[OH^-]^3 + 2\beta_{21}[UO_2^{2+}][OH^-])$

3.5. $[U]_{tot} = [UO_2^{2+}](1 + \beta_{11}[OH^-] + \beta_{12}[OH^-]^2 + \beta_{13}[OH^-]^3 + 2\beta_{21}[UO_2^{2+}]^2[OH^-])$

3.6. $[U]_{tot} = [UO_2^{2+}](1 + \beta_{11}[OH^-] + \beta_{12}[OH^-]^2 + \beta_{13}[OH^-]^3 + \beta_{21}[UO_2^{2+}]^2[OH^-])$

Correct equation: _____

4. (10 Points) Provide the speciation of acetic acid at pH 3.5, 4.5, and 5.5. The speciation should give the percentage protonated and the percentage free. The pKa is 4.75.

4.1. pH 3.5: % free acetic acid _____; % protonated acetic acid _____

4.2. pH 4.5: % free acetic acid _____; % protonated acetic acid _____

4.3. pH 5.5: % free acetic acid _____; % protonated acetic acid _____

5. (10 Points) The log K_{sp} of $Am(OH)_3$ is -25.1 (ref. Pure Appl. Chem., 74(10), 1895, 2002). If you have an excess of $Am(OH)_3$ in solution, what is the concentration of free Am^{3+} at the following pHs

5.1. pH 2.5 _____ mol/L

5.2. pH 4.5 _____ mol/L

5.3. pH 7.0 _____ mol/L

5.4. pH 8.5 _____ mol/L

5.5. pH 10.0 _____ mol/L

6. (10 Points) Provide the solubility constants, as log K_{sp}, for the following:

6.1. Pentavalent Np hydroxide: _____

6.2. Crystalline uranium dioxide: _____

6.3. Amorphous trivalent plutonium hydroxide: _____

6.4. Hexavalent uranyl hydroxide: _____

6.5. Hexavalent plutonyl hydroxide: _____