RDCH 702 Name:_____

Quiz 2

Assigned 8 Oct 2018

1st due date: 14 October 2018

2nd due date: 18 October 2018

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. (30 Points) Using CHESS, answer the questions below for the following conditions.

1.1. 1E-6 M/L Pu^{4+} from pH 0 to pH 12

1.1.1. Primary Pu specie at 1 M acid _____

1.1.2. Primary Pu specie at neutral pH _____

1.1.3. pH where the $PuOH^{3+}$ is equal to that of plutonium dioxide _ _

1.2. 5E-3 M/L UO_2^{2+} from pH 2 to pH 12

1.2.1. Solution condition for studying the chemistry of UO_2^{2+} _____

1.2.2. Solution condition with the highest concentration of dimer or trimer uranyl species ____

1.2.3. Primary uranyl chemical form at pH 11.5

❒ UO_2^{2+} ❒ $(UO_2)_2(OH)_2^{2+}$ ❒ Schoepite ❒ UO_2OH^+ ❒ $UO_2(OH)_2$ ❒ $UO_2(OH)_3^-$

1.3. 1E-6 M/L Am^{3+} at pH 2 with total SO_4^{2+} from 0.01 mmol/L to 10 mmol/L.

1.3.1. Primary Am specie at 4E-3 M free SO_4^{2-} _____

1.3.2. Free SO_4^{2-} concentration where free trivalent Am concentration is equal to $AmSO_4^+$

_____

1.3.3. Identify the americium species that have concentrations greater than 5E-8 M at 5 mM free SO_4^{2-}.

❒ Am^{3+} ❒ $AmOH^{2+}$ ❒ $Am(OH)_2^+$ ❒ $Am(OH)_{3aq}$ ❒ $AmSO_4^+$ ❒ $Am(SO_4)_2^-$

2. (50 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	[PuL] M	$[L]_t$ M	$[Pu]_t$ M	$[L]_f$ M	$[Pu]_f$ M
298	1.99E-05	5.00E-05	2.00E-05	3.01E-05	5.44E-08
298	2.98E-05	4.00E-05	3.00E-05	1.02E-05	2.38E-07
298	2.19E-05	2.50E-05	2.25E-05	3.08E-06	5.82E-07
310	8.92E-06	1.00E-05	1.00E-05	1.08E-06	1.08E-06
325	8.61E-06	1.00E-05	1.00E-05	1.39E-06	1.39E-06
340	8.26E-06	1.00E-05	1.00E-05	1.74E-06	1.74E-06
355	7.88E-06	1.00E-05	1.00E-05	2.12E-06	2.12E-06
370	7.46E-06	1.00E-05	1.00E-05	2.54E-06	2.54E-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 340 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 100 mM ligand and 50 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.

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

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

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

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

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4. (10 Points) Provide the solubility constants, as log K_{sp}, for the following using the table below

   4.1. Pentavalent Np hydroxide: _____

   4.2. Crystalline plutonium dioxide: _____

   4.3. Amorphous trivalent americium hydroxide: _____

   4.4. Hexavalent uranyl hydroxide: _____

   4.5. Hexavalent plutonyl hydroxide: _____

   4.6. If you have an excess of amorphous $Pu(OH)_3$ in solution, what is the concentration of free Pu^{3+} at the following pHs

      4.6.1. pH 2.5 _____ mol/L

      4.6.2. pH 7.0 _____ mol/L

      4.6.3. pH 10.0 _____ mol/L

Table 1 Solubility products log K°_{sp} of actinide oxides/hydroxides at 25 °C (from the NEA-TDB reviews [1–4] and values for $An(OH)_4$(am) from ref. [9], except otherwise stated).

	Th	U	Np	Pu	Am
AnO_2OH(am)			–8.7 ± 0.2	–9.0 ± 0.5	–8.7 ± 0.5
$AnO_2(OH)_2$(s)		–22.8 ± 0.4[a]	–22.5 ± 0.4	–22.5 ± 1.0	
$AnO_3 \cdot 2H_2O$(cr)		–23.2 ± 0.4*			
$An(OH)_3$(am)				–26.2 ± 1.5	–25.1 ± 0.8
$An(OH)_3$(cr)					–26.4 ± 0.6
$An(OH)_4$(am)	–47.0 ± 0.8	–54.5 ± 1.0	–56.7 ± 0.5	–58.5 ± 0.7	
AnO_2(cr)	–53.2 ± 0.4[b]				
	–54.2 ± 1.3*[c]	–60.9 ± 0.4*	–63.7 ± 1.8*[c]	–64.0 ± 0.5*	–65.4 ± 1.7*

*Calculated from thermochemical data.
[a]Mean value from solubility studies [26–31] discussed in ref. [4].
[b]From solubility data for microcrystalline thorium dioxide [50].
[c]From Rai et al. [18]. A noticeable deviation is observed for the NEA-TDB value of log $K^{\circ}_{sp}[NpO_2(cr)] = -65.8 \pm 1.1$ calculated with $S^{\circ}_m[Np^{4+}(aq)] = -(426 \pm 12)$ $JK^{-1}mol^{-1}$ [3], which differs from $S^{\circ}_m[Np^{4+}(aq)] = -(389 \pm 21)$ $JK^{-1}mol^{-1}$ [19] used by Rai et al. [18].

http://wipp.energy.gov/library/cra/2009_cra/references/Others/Fanghanel_Neck_2002_Aquatic_Chemistry_and_Solubility_Phenomena_of_An_Oxides_Hydroxides.pdf