A1756

LPDR

Wm-10 (2)
Wm-11 (2)
Wm-16 (2)

DEC 16 1986

WK/86/12/05 ?5 ✓

Dr. Malcolm D. Siegel
Division 6431
Sandia National Laboratories
Albuquerque, NM 87185

Dear ~~Dr. Siegel~~ Malcolm:

SUBJECT: CONTRACT NO. 50-19-03-01/FIN A-1756, "GEOCHEMICAL SENSITIVITY ANALYSIS"

I have reviewed the October, 1986 monthly progress report for the above contract, dated November 15, 1986. Based on my review of this report, progress to date is satisfactory.

I am enclosing information on my preliminary review of the Pu data in the Aqueous Solutions Database. I have calculated ΔGr° and log K values to check for accuracy and internal consistency. I have acquired some literature on Pu and will be using it for further review of the data in the ASD. I have not been able to contact the NBS yet.

The action taken by this letter is considered to be within the scope of the current contract FIN A-1756. No changes to costs or delivery of contract products is authorized. Please notify me immediately if you believe this letter would result in changes to costs or delivery of contracted products.

Sincerely,

/S/

Walton R. Kelly
Geochemistry Section
Geotechnical Branch
Division of Waste Management
Office of Nuclear Material Safety
and Safeguards

Enclosure:
As stated

WM-RES
WM Record File
A1756
SNL

WM Project 10,11,16
Docket No.
PDR ✓
LPDR ✓ (B,N,S)

Distribution:

(Return to WM, 623-SS)

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ΔG°_r values were calculated for the reactions listed in table 1 in three ways. The first two ways used the equation $\Delta G^\circ_r = \Delta H^\circ_r - (0.001)T\Delta S$: (1) using ΔH°_r and ΔS° data presented in FORM2 tables for reactions, and (2) calculating ΔH°_r and ΔS° from ΔH°_f and S data presented in FORM1 tables for aqueous species, gases, and solids. I expected that these two methods should produce the same results, although that was not always the case. The third method was to calculate ΔG°_r directly from ΔG°_f data presented in FORM1 tables. Log K values were calculated for each of the ΔG°_r values by $\ln K = -\Delta G^\circ_r/RT$, or $\log K = -\Delta G^\circ_r/5.709$. ΔG°_r and log K values calculated by all three methods are presented in table 2. Log K (log Q) values listed in FORM2 tables for 25°C and I = 0 are also presented in table 2.

For most of the reactions considered, good agreement was reached by the different methods. There are problems or discrepancies for a few reactions, which are discussed below.

PU17: There is a significant error here. Log K values were calculated to be between 10.61 and 11.26, but a value of 40.74 is presented in the FORM2 table.

PU22: There apparently is an error in ΔH°_f data in the FORM1 table, probably for $PuF_4(s)$.

PU30 & PU38: $PuO_2(OH)(s)$ is used in these reactions (FORM2); it (apparently) appears as $PuO_2(OH)(am)$ in the FORM1 table. ΔH°_f data for $PuO_2(OH)(am)$ are missing.

PU31 & PU39: The difference in log K values calcuated by the first two methods seems excessive for these reactions. The problem may lie with the ΔH°_f data for $PuO_2(OH)_2(s)$, although there is also a significant discrepancy in ΔS° for equation PU39.

PU35 & PU37: No log K (log Q) data for T < 150°C are presented in the FORM2 tables for these reactions. I suspect that because these values are the only ones < -100.00, the formatted field length in the program is too short and the computer did not print them out.

Table 1. Pu reactions considered in the ASD.

DTR> PLUTONIUM

RC	REACTION
PU1	PuO2++ + H2O = PuO2OH+ + H+
PU10	PuO2++ + F- = PuO2F+
PU11	PuO2++ + 2F- = PuO2F2(aq)
PU12	PuO2++ + 3F- = PuO2F3-
PU13	PuO2++ + 4F- = PuO2F4--
PU14	PuO2++ + Cl- = PuO2Cl+
PU15	Pu++++ + Cl- = PuCl+++
PU16	PuO2++ + 2CO3-- = PuO2(CO3)2--
PU17	Pu++++ + CO3-- = PuCO3++
PU18	PuO2++ + SO4-- = PuO2SO4(aq)
PU19	Pu++++ + SO4-- = PuSO4++
PU2	2PuO2++ + 2H2O = (PuO2)2(OH)2++ + 2H+
PU20	Pu+++ + SO4-- = PuSO4+
PU21	PuF3(s) = Pu+++ +3F-
PU22	PuF4(s) = Pu++++ + 4F-
PU23	4PuO2(s) + 12H+ = 4Pu+++ + 6H2O+ O2(g)
PU24	4PuO2(s) + 4H+ + O2(g) = 4PuO2+ + 2H2O
PU25	2PuO2(s) + 4H+ + O2(g) = 2PuO2++ + 2H2O
PU26	Pu(OH)3(s) + 3H+ = Pu+++ + 3H2O
PU27	Pu(OH)4(s) + 4H+ = Pu++++ + 4H2O
PU28	Pu2O3(s) + 6H+ = 2Pu+++ + 3H2O
PU29	PuO2(s) + 4H+ = Pu++++ + 2H2O
PU3	3PuO2++ + 5H2O = (PuO2)3(OH)5+ + 5H+
PU30	PuO2(OH)(s) + H+ = PuO2+ + H2O
PU31	PuO2(OH)2(s) + 2H+ = PuO2++ + 2H2O
PU32	4PuO2++ + 4H+ = 4Pu+++ + 2H2O + 3O2(g)
PU33	2PuO2++ + 4H+ = 2Pu++++ + 2H2O + O2(g)
PU34	4PuO2++ + 2H2O = 4PuO2+ + 4H+ + O2(g)
PU35	4PuO2(s) + 6H2O = 4Pu(OH)3(s) + O2(g)
PU36	PuO2(s) + 2H2O = Pu(OH)4(s)
PU37	4PuO2(s) = 2Pu2O3(s) + O2(g)
PU38	4PuO2(s) + O2(g) + 2H2O = 4PuO2(OH)(s)
PU39	2PuO2(s) + O2(g) + 2H2O = 2PuO2(OH)2(s)
PU4	Pu++++ + H2O = PuOH+++ + H+
PU5	Pu++++ + 2H2O = Pu(OH)2++ + 2H+
PU6	Pu++++ + 3H2O = Pu(OH)3+ + 3H+
PU7	Pu++++ + 4H2O = Pu(OH)4(aq) + 4H+
PU8	Pu++++ + 5H2O = Pu(OH)5- + 5H+
PU9	Pu+++ + H2O = PuOH++ + H+

Table 2. Calculated ΔG^{o}_{r} and log K values for reactions involving Pu for the ASD.

Reaction Number	(method 1)* ΔG^{o}_{r}	(method 1)* log K	(method 2)* ΔG^{o}_{r}	(method 2)* log K	(method 3)* ΔG^{o}_{r}	(method 3)* log K	FORM2 reported log K**
PU1	32.29	-5.66	32.30	-5.66	32.13	-5.63	-5.66
PU10	-32.42	5.68	-32.42	5.67	-32.35	5.67	5.68
PU11	-62.67	10.98	-62.67	10.98	-62.60	10.97	10.98
PU12	-91.00	15.94	-91.00	15.94	-90.85	15.91	15.95
PU13	-107.26	18.79	-107.26	18.79	-107.10	18.76	18.79
PU14	0.67	-0.12	0.67	-0.12	1.13	-0.20	-0.12
PU15	-5.25	0.92	-5.25	0.92	-5.17	0.91	0.92
PU16	-85.31	14.94	-85.15	14.92	-85.48	14.97	14.95
PU17	-64.26	11.26	-61.95	10.85	-60.59	10.61	40.74
PU18	-18.59	3.26	-18.59	3.26	-18.57	3.25	3.25
PU19	-32.85	5.75	-32.85	5.75	-32.87	5.76	5.75
PU2	47.38	-8.30	47.40	-8.30	47.06	-8.24	-8.30
PU20	-19.92	3.49	-20.22	3.54	-19.87	3.48	3.48
PU21	58.10	-10.18	62.32	-10.92	58.15	-10.19	-10.19
PU22	75.31	-13.19	39.13	-6.85	75.40	-13.21	-13.21
PU23	254.77	-44.63	254.96	-44.66	254.83	-44.64	-44.64
PU24	118.48	-20.75	117.98	-20.67	118.54	-20.76	-20.77
PU25	7.89	-1.38	7.60	-1.33	7.94	-1.39	-1.39
PU26	-128.00	22.42	-127.73	22.37	-127.99	22.42	22.42
PU27	-4.15	0.73	-4.20	0.74	-4.12	0.72	0.72
PU28	-274.63	48.10	-274.08	48.01	-274.59	48.10	48.10
PU29	42.09	-7.37	42.07	-7.37	42.14	-7.38	-7.38
PU3	123.22	-21.58	123.28	-21.59	123.35	-21.61	-21.59
PU30	-30.94	5.42	---	---	-30.93	5.42	5.42
PU31	-20.17	3.53	-15.12	2.65	-20.16	3.53	3.53
PU32	238.60	-41.79	239.77	-42.00	238.94	-41.85	-41.79
PU33	76.57	-13.41	76.54	-13.41	76.34	-13.37	-13.42
PU34	102.76	-18.00	102.78	-18.00	102.66	-17.98	-17.99
PU35	766.76	-134.31	765.90	-134.16	766.77	-134.31	---
PU36	46.24	-8.10	46.27	-8.10	46.25	-8.10	-8.10
PU37	804.03	-140.84	803.12	-140.68	804.00	-140.83	---
PU38	242.22	-42.43	---	---	242.26	-42.43	-42.44
PU39	48.21	-8.44	37.84	-6.63	48.26	-8.45	-8.46
PU4	2.91	-0.51	2.92	-0.51	2.83	-0.50	-0.51
PU5	13.22	-2.32	13.24	-2.32	13.16	-2.31	-2.31
PU6	30.06	-5.26	30.09	-5.27	29.99	-5.25	-5.26
PU7	54.18	-9.49	54.23	-9.50	54.12	-9.48	-9.50
PU8	85.29	-14.94	85.35	-14.95	85.25	-14.93	-14.94
PU9	45.46	-7.96	45.17	-7.91	45.43	-7.96	-7.96

Table 2. Calculated ΔG^{o}_{r} and log K values for reactions involving Pu from the ASD (cont.).

* method 1: ΔG^{o}_{r} calculated from ΔH^{o}_{r} and ΔS data presented in FORM2 tables.

method 2: ΔG^{o}_{r} calculated from ΔH^{o}_{r} and ΔS values calculated from ΔH^{o}_{f} and S values in FORM1 tables.

method 3: ΔG^{o}_{r} calculated from ΔG^{o}_{f} values in FORM1 tables.

** T = 25°C; I = 0.

OFFICIAL CONCURRENCE AND DISTRIBUTION RECORD

LETTER TO: Dr. Malcolm D. Siegel

FROM: Walton Kelly

SUBJECT: CONTRACT NO. 50-19-03-01/FIN A-1756, "GEOCHEMICAL SENSITIVITY ANALYSIS"

DATE: 86/12/05

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NO ACTION NECESSARY		COMMENT		BY XXXXXXX 12/16/8

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Monthly Report on FIN A-1756 for October

REFERRED TO	DATE	RECEIVED BY	DATE
Phil Justus, WMGT	12/2	PJustus	12/2
		WRK	12/3

ENCLOSURES

Action closed per letter to Dr. Malcolm D. Siegel, SNL from Walt Kelly, WMGT/WM dated 12/16/86.

REMARKS

logged in by LJ 12/2

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