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**Thermodynamic Constants for Actinide Oxides and Oxyhydroxides Relevant
to Actinide Volatility Calculations for Thermal Oxidation Processes**

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The purpose of this report is to provide input of thermodynamic data on actinide volatilities to EERC for use in their computer code for modeling of metal volatilities in incinerators. It is also anticipated that the data may be documented later in an EPA sponsored "Metals Bible." It should be noted that only upper limits for the volatility of $\text{PuO}_2(\text{s})$ due to $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ and the volatility of AmO_2 in $\text{PuO}_2(\text{s})$ due to $\text{AmO}_3(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ could be set. The data on the americium vapor species are intended for calculations where AmO_2 is present as a solid solution in $\text{PuO}_2(\text{s})$.

The thermodynamic constants, S°_{298}/R and $\Delta H^\circ_{f,298}/R$, and thermodynamic functions, Cp/R , of the actinide vapor species are given in Tables 1 through 6. Cp/R is given in the form

$$\text{Cp}/R = a_1 + a_2 \times T + a_3 \times T^2 + a_4 \times T^3 + a_5 \times T^4. \quad (1)$$

The entered and fitted Cp values are given in each table indicating the accuracy of the fit.

The Cp/R function and the S°_{298}/R values for the gaseous species, $\text{PuO}_3(\text{g})$, $\text{AmO}_3(\text{g})$, $\text{UO}_2(\text{OH})_2(\text{g})$, $\text{PuO}_2(\text{OH})_2(\text{g})$, and $\text{AmO}_2(\text{OH})_2(\text{g})$, are calculated from the molecular constant method using estimated molecular constants. The translational contributions are calculated from the molecular weights of the molecules. The electronic contribution to $\text{UO}_2(\text{OH})_2(\text{g})$ is assumed to be zero. The electronic contributions to $\text{PuO}_3(\text{g})$ and $\text{PuO}_2(\text{OH})_2(\text{g})$ are calculated from the degeneracy of the ground state which is assumed to be 9. The electronic contributions to $\text{AmO}_3(\text{g})$ and $\text{AmO}_2(\text{OH})_2(\text{g})$ are also calculated from the degeneracy of the ground state which is assumed to be 10. The rotational contributions for $\text{PuO}_3(\text{g})$ and $\text{AmO}_3(\text{g})$ are calculated by using the same parameters Green [1] used for $\text{UO}_3(\text{g})$. The rotational contributions for $\text{UO}_2(\text{OH})_2(\text{g})$, $\text{PuO}_2(\text{OH})_2(\text{g})$, and $\text{AmO}_2(\text{OH})_2(\text{g})$ are calculated by assuming a C_{2v} symmetry of the molecules, a U-O, Pu-O, and Am-O bond length of 0.180 nm, a U-OH, Pu-OH, and Am-OH bond length of 0.212 nm, a U-O-H, Pu-O-H, and Am-O-H bond angle of 105° , and an O-H bond length of 0.097 nm. The internal rotations of the OH groups were treated by assuming a potential barrier to rotation of 3.14 kJ/mol. The vibrational contributions for $\text{PuO}_3(\text{g})$ and $\text{AmO}_3(\text{g})$ are calculated by using the same vibrational wave numbers Green [1] used for $\text{UO}_3(\text{g})$. The vibrational contributions to $\text{UO}_2(\text{OH})_2(\text{g})$, $\text{PuO}_2(\text{OH})_2(\text{g})$, and $\text{AmO}_2(\text{OH})_2(\text{g})$ are calculated from the wave numbers, 776 cm^{-1} , 765 cm^{-1} , 470 cm^{-1} , 440 cm^{-1} , $100(2) \text{ cm}^{-1}$, $225(2) \text{ cm}^{-1}$, 180 cm^{-1} , $296(2) \text{ cm}^{-1}$, $3000(2) \text{ cm}^{-1}$. The Cp/R function and the S°_{298}/R values for $\text{UO}_3(\text{g})$ are taken from Green [2].

The $\Delta H^\circ_{f,298}$ values for all of the gaseous species are calculated from our data [3] using the 3rd law method. The $\Delta H^\circ_{f,298}$ values for $\text{PuO}_3(\text{g})$, $\text{PuO}_2(\text{OH})_2(\text{g})$, $\text{AmO}_3(\text{g})$, and $\text{AmO}_2(\text{OH})_2(\text{g})$ are minimum values and thus yield maximum values for the vapor pressures of these species. The $\Delta H^\circ_{f,298}$ values for $\text{UO}_3(\text{g})$ and $\text{UO}_2(\text{OH})_2(\text{g})$ are taken from our volatility measurements in the temperature range of 1173 to 1573 K and are thus most accurate for calculations in this range.

In our 3rd law treatments of the actinide oxide volatility data, we used the thermodynamic tables for the actinide oxides, $\text{U}_3\text{O}_8(\text{s})$, $\text{PuO}_2(\text{s})$, and $\text{AmO}_2(\text{s})$, given by Cordfunke, et al. [4]. The S°_{298}/R values, $\Delta H^\circ_{f,298}/R$ values, and fitted C_p/R functions for $\text{U}_3\text{O}_8(\text{s})$, $\text{PuO}_2(\text{s})$, and $\text{AmO}_2(\text{s})$ are given in Tables 7, 8, and 9, respectively.

References

1. D. W. Green, "Standard Enthalpies of Formation of Gaseous Thorium, Uranium, and Plutonium Oxides," *Int. J. Thermophys.*, **1**, 61-71 (1980).
2. D. W. Green, "Calculation of the Thermodynamic Properties of Fuel Vapor Species from Spectroscopic Data," Argonne National Laboratory Report, ANL-CEN-RSD-80-2, Sept. 1980, 87 pp.
3. O. H. Krikorian, B. B. Ebbinghaus, M. G. Adamson, A. S. Fontes, Jr., D. L. Fleming, "Experimental Studies and Thermodynamic Modeling of Volatilities of Uranium, Plutonium, and Americium from Their Oxides and from Their Oxides Interacted with Ash," LLNL Report, UCRL-ID-114774, Sept. 1993, 81 pp.
4. E. H. P. Cordfunke, R. J. M. Konings, P. E. Potter, G. Prins, and M. H. Rand, Thermochemical Data for Reactor Materials and Fission Products, editors E. H. P. Cordfunke and R. J. M. Konings, North Holland, Amsterdam, 1990.

Table 1. Thermodynamic parameters of $\text{UO}_2(\text{OH})_2(\text{g})$ in the temperature range of 298.15 to 2300 K.

Cp/R Coefficients

$$\begin{aligned} a_1 &= 11.5066 \\ a_2 \times 10^3 &= 10.3764 \\ a_3 \times 10^6 &= -8.68413 \\ a_4 \times 10^9 &= 3.65483 \\ a_5 \times 10^{12} &= -0.589306 \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{f,298}/R &= -138.506 \pm 0.902 \text{ (kK)} \\ S^\circ_{298}/R &= 47.913 \end{aligned}$$

Check of Cp/R Fit

T (K)	Cp/R Entered	Cp/R Fitted	Difference
298.15	13.8172	13.9206	0.10340
300	13.8349	13.9319	0.09702
400	14.5704	14.4865	-0.08390
500	15.0260	14.9438	-0.08222
600	15.3473	15.3192	-0.02804
700	15.6065	15.6270	0.02053
800	15.8335	15.8798	0.04625
900	16.0393	16.0889	0.04964
1000	16.2267	16.2644	0.03770
1100	16.3966	16.4146	0.01798
1200	16.5496	16.5467	-0.00293
1300	16.6865	16.6663	-0.02021
1400	16.8084	16.7776	-0.03081
1500	16.9168	16.8836	-0.03322
1600	17.0130	16.9856	-0.02746
1700	17.0984	17.0836	-0.01485
1800	17.1744	17.1762	0.00177
1900	17.2420	17.2606	0.01860
2000	17.3023	17.3326	0.03033
2100	17.3562	17.3865	0.03035
2200	17.4044	17.4153	0.01087
2300	17.4478	17.4104	-0.03743

Table 2. Thermodynamic parameters of $\text{PuO}_2(\text{OH})_2(\text{g})$ in the temperature range from 298.15 to 2300 K.

Cp/R Coefficients

$$\begin{aligned} a_1 &= 11.5066 \\ a_2 \times 10^3 &= 10.3764 \\ a_3 \times 10^6 &= -8.68413 \\ a_4 \times 10^9 &= 3.65483 \\ a_5 \times 10^{12} &= -0.589306 \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{f,298}/R &= -109.225 \text{ minimum (kK)} \\ S^\circ_{298}/R &= 50.115 \end{aligned}$$

Check of Cp/R Fit

T (K)	Cp/R Entered	Cp/R Fitted	Difference
298.15	13.8172	13.9206	0.10340
300	13.8349	13.9319	0.09702
400	14.5704	14.4865	-0.08390
500	15.0260	14.9438	-0.08222
600	15.3473	15.3192	-0.02804
700	15.6065	15.6270	0.02053
800	15.8335	15.8798	0.04625
900	16.0393	16.0889	0.04964
1000	16.2267	16.2644	0.03770
1100	16.3966	16.4146	0.01798
1200	16.5496	16.5467	-0.00293
1300	16.6865	16.6663	-0.02021
1400	16.8084	16.7776	-0.03081
1500	16.9168	16.8836	-0.03322
1600	17.0130	16.9856	-0.02746
1700	17.0984	17.0836	-0.01485
1800	17.1744	17.1762	0.00177
1900	17.2420	17.2606	0.01860
2000	17.3023	17.3326	0.03033
2100	17.3562	17.3865	0.03035
2200	17.4044	17.4153	0.01087
2300	17.4478	17.4104	-0.03743

Table 3. Thermodynamic parameters of $\text{AmO}_2(\text{OH})_2(\text{g})$ in the temperature range of 298.15 to 2300 K.

Cp/R Coefficients

$$\begin{aligned} a_1 &= 11.5066 \\ a_2 \times 10^3 &= 10.3764 \\ a_3 \times 10^6 &= -8.68413 \\ a_4 \times 10^9 &= 3.65483 \\ a_5 \times 10^{12} &= -0.589306 \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{f,298}/R &= -93.797 \text{ minimum (kK)} \\ S^\circ_{298}/R &= 50.230 \end{aligned}$$

Check of Cp/R Fit

T (K)	Cp/R Entered	Cp/R Fitted	Difference
298.15	13.8172	13.9206	0.10340
300	13.8349	13.9319	0.09702
400	14.5704	14.4865	-0.08390
500	15.0260	14.9438	-0.08222
600	15.3473	15.3192	-0.02804
700	15.6065	15.6270	0.02053
800	15.8335	15.8798	0.04625
900	16.0393	16.0889	0.04964
1000	16.2267	16.2644	0.03770
1100	16.3966	16.4146	0.01798
1200	16.5496	16.5467	-0.00293
1300	16.6865	16.6663	-0.02021
1400	16.8084	16.7776	-0.03081
1500	16.9168	16.8836	-0.03322
1600	17.0130	16.9856	-0.02746
1700	17.0984	17.0836	-0.01485
1800	17.1744	17.1762	0.00177
1900	17.2420	17.2606	0.01860
2000	17.3023	17.3326	0.03033
2100	17.3562	17.3865	0.03035
2200	17.4044	17.4153	0.01087
2300	17.4478	17.4104	-0.03743

Table 4. Thermodynamic Parameters of $\text{UO}_3(\text{g})$ in the temperature range of 298.15 to 2300 K.

Cp/R Coefficients

$$\begin{aligned} a_1 &= 5.2282 \\ a_2 \times 10^3 &= 11.2054 \\ a_3 \times 10^6 &= -9.56125 \\ a_4 \times 10^9 &= 3.83713 \\ a_5 \times 10^{12} &= -0.583315 \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{f,298}/R &= -94.799 \pm 0.842 \text{ (kK)} \\ S^\circ_{298}/R &= 50.230 \end{aligned}$$

Check of Cp/R Fit

T (K)	Cp/R Entered	Cp/R Fitted	Difference
298.15	7.7646	7.8162	0.05163
300	7.7797	7.8282	0.04848
400	8.4490	8.4112	-0.03778
500	8.9270	8.8838	-0.04327
600	9.2793	9.2626	-0.01668
700	9.5561	9.5631	0.00699
800	9.7775	9.7990	0.02153
900	9.9586	9.9830	0.02437
1000	10.1046	10.1262	0.02160
1100	10.2253	10.2382	0.01289
1200	10.3260	10.3275	0.00151
1300	10.4065	10.4009	-0.00561
1400	10.4769	10.4639	-0.01300
1500	10.5424	10.5208	-0.02158
1600	10.5927	10.5741	-0.01856
1700	10.6380	10.6253	-0.01267
1800	10.6782	10.6742	-0.00400
1900	10.7084	10.7194	0.01100
2000	10.7386	10.7580	0.01941
2100	10.7638	10.7858	0.02198
2200	10.7889	10.7969	0.00799
2300	10.8091	10.7845	-0.02460

Table 5. Thermodynamic Parameters of $\text{PuO}_3(\text{g})$ in the temperature range of 298.15 to 2300 K.

Cp/R Coefficients

$$\begin{aligned} a_1 &= 5.1937 \\ a_2 \times 10^3 &= 11.8567 \\ a_3 \times 10^6 &= -11.54557 \\ a_4 \times 10^9 &= 4.98031 \\ a_5 \times 10^{12} &= -0.789264 \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{f,298}/R &= -65.060 \text{ minimum (kK)} \\ S^\circ_{298}/R &= 39.442 \end{aligned}$$

Check of Cp/R Fit

T (K)	Cp/R Entered	Cp/R Fitted	Difference
298.15	7.7626	7.8282	0.06563
300	7.7770	7.8397	0.06270
400	8.4301	8.3876	-0.04243
500	8.8665	8.8089	-0.05766
600	9.1557	9.1248	-0.03089
700	9.3517	9.3548	0.00310
800	9.4888	9.5165	0.02771
900	9.5877	9.6256	0.03794
1000	9.6611	9.6959	0.03482
1100	9.7167	9.7392	0.02242
1200	9.7599	9.7655	0.00556
1300	9.7941	9.7829	-0.01116
1400	9.8215	9.7977	-0.02381
1500	9.8439	9.8141	-0.02977
1600	9.8623	9.8346	-0.02770
1700	9.8777	9.8596	-0.01804
1800	9.8907	9.8879	-0.00278
1900	9.9016	9.9161	0.01447
2000	9.9111	9.9390	0.02794
2100	9.9192	9.9497	0.03057
2200	9.9263	9.9392	0.01293
2300	9.9325	9.8966	-0.03593

Table 6. Thermodynamic Parameters of $\text{AmO}_3(\text{g})$ in the temperature range of 298.15 to 2300 K.

Cp/R Coefficients

$$\begin{aligned} a_1 &= 5.1937 \\ a_2 \times 10^3 &= 11.8567 \\ a_3 \times 10^6 &= -11.54557 \\ a_4 \times 10^9 &= 4.98031 \\ a_5 \times 10^{12} &= -0.789264 \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{f,298}/R &= -49.642 \text{ minimum (kK)} \\ S^\circ_{298}/R &= 39.558 \end{aligned}$$

Check of Cp/R Fit

T (K)	Cp/R Entered	Cp/R Fitted	Difference
298.15	7.7626	7.8282	0.06563
300	7.7770	7.8397	0.06270
400	8.4301	8.3876	-0.04243
500	8.8665	8.8089	-0.05766
600	9.1557	9.1248	-0.03089
700	9.3517	9.3548	0.00310
800	9.4888	9.5165	0.02771
900	9.5877	9.6256	0.03794
1000	9.6611	9.6959	0.03482
1100	9.7167	9.7392	0.02242
1200	9.7599	9.7655	0.00556
1300	9.7941	9.7829	-0.01116
1400	9.8215	9.7977	-0.02381
1500	9.8439	9.8141	-0.02977
1600	9.8623	9.8346	-0.02770
1700	9.8777	9.8596	-0.01804
1800	9.8907	9.8879	-0.00278
1900	9.9016	9.9161	0.01447
2000	9.9111	9.9390	0.02794
2100	9.9192	9.9497	0.03057
2200	9.9263	9.9392	0.01293
2300	9.9325	9.8966	-0.03593

Table 7. Thermodynamic Parameters of $\text{U}_3\text{O}_8(\text{s})$ in the temperature range of 298.15 to 2000 K.

Cp/R Coefficients

$$\begin{aligned} a_1 &= 17.8879 \\ a_2 \times 10^3 &= 52.3300 \\ a_3 \times 10^6 &= -57.93523 \\ a_4 \times 10^9 &= 29.67526 \\ a_5 \times 10^{12} &= -5.517670 \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{f,298}/R &= -429.947 \pm 0.301 \text{ (kK)} \\ S^\circ_{298}/R &= 33.983 \pm 0.060 \end{aligned}$$

Check of Cp/R Fit

T (K)	Cp/R Entered	Cp/R Fitted	Difference
298.15	28.7397	29.0829	0.34305
300	28.8177	29.1294	0.31170
400	31.6689	31.3083	-0.36063
500	33.1662	32.9337	-0.23259
600	34.1304	34.1241	-0.00648
700	34.8432	34.9845	0.14127
800	35.4216	35.6070	0.18534
900	35.9223	36.0705	0.14820
1000	36.3744	36.4401	0.06588
1100	36.7950	36.7686	-0.02634
1200	37.1940	37.0944	-0.09933
1300	37.5777	37.4439	-0.13383
1400	37.9503	37.8291	-0.12135
1500	38.3151	38.2494	-0.06567
1600	38.6736	38.6910	0.01746
1700	39.0270	39.1266	0.09939
1800	39.3768	39.5154	0.13857
1900	39.7239	39.8043	0.08052
2000	40.0683	39.9264	-0.14211

Table 8. Thermodynamic Parameters of $\text{PuO}_2(\text{s})$ in the temperature range of 298.15 to 2000 K.

Cp/R Coefficients

$$\begin{aligned} a_1 &= 3.2417 \\ a_2 \times 10^3 &= 22.8903 \\ a_3 \times 10^6 &= -25.61218 \\ a_4 \times 10^9 &= 13.08138 \\ a_5 \times 10^{12} &= -2.432309 \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{f,298}/R &= -126.983 \pm 0.120 \text{ (kK)} \\ S^\circ_{298}/R &= 7.954 \pm 0.036 \end{aligned}$$

Check of Cp/R Fit

T (K)	Cp/R Entered	Cp/R Fitted	Difference
298.15	7.9658	8.1172	0.15134
300	7.9997	8.1371	0.13739
400	9.2337	9.0748	-0.15897
500	9.8694	9.7669	-0.10247
600	10.2687	10.2658	-0.00288
700	10.5555	10.6178	0.06228
800	10.7818	10.8635	0.08173
900	10.9723	11.0375	0.06527
1000	11.1398	11.1688	0.02902
1100	11.2919	11.2804	-0.01155
1200	11.4333	11.3894	-0.04383
1300	11.5663	11.5073	-0.05898
1400	11.6931	11.6395	-0.05354
1500	11.8146	11.7858	-0.02889
1600	11.9322	11.9399	0.00771
1700	12.0460	12.0898	0.04380
1800	12.1568	12.2179	0.06106
1900	12.2648	12.3003	0.03546
2000	12.3702	12.3076	-0.06262

Table 9. Thermodynamic Parameters of AmO₂(s) in the temperature range of 298.15 to 2000 K.

Cp/R Coefficients

$$\begin{aligned} a_1 &= 3.1716 \\ a_2 \times 10^3 &= 22.0495 \\ a_3 \times 10^6 &= -25.80612 \\ a_4 \times 10^9 &= 13.26836 \\ a_5 \times 10^{12} &= -2.467024 \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{f,298}/R &= -112.117 \pm 0.361 \text{ (kK)} \\ S^\circ_{298}/R &= 8.058 \pm 1.203 \end{aligned}$$

Check of Cp/R Fit

T (K)	Cp/R Entered	Cp/R Fitted	Difference
298.15	7.6303	7.7838	0.15355
300	7.6627	7.8021	0.13939
400	8.8097	8.6484	-0.16125
500	9.3532	9.2492	-0.10402
600	9.6602	9.6573	-0.00291
700	9.8567	9.9199	0.06320
800	9.9953	10.0782	0.08287
900	10.1009	10.1672	0.06630
1000	10.1869	10.2163	0.02941
1100	10.2606	10.2488	-0.01177
1200	10.3266	10.2823	-0.04437
1300	10.3880	10.3281	-0.05988
1400	10.4462	10.3919	-0.05425
1500	10.5028	10.4735	-0.02938
1600	10.5586	10.5664	0.00778
1700	10.6142	10.6587	0.04445
1800	10.6701	10.7321	0.06195
1900	10.7267	10.7627	0.03604
2000	10.7842	10.7206	-0.06357

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