426.1

426.1 87/08/11 W.K.



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

Dear Dr. Siegel:

SUBJECT: PLUTONIUM THERMOCHEMISTRY NETWORK

Dr. Garvin at the NBS has completed the calculations for the second set of Pu data I sent him (enclosed). I sent him data for a total of 35 reactions involving Pu. Most of the data were selected using the evaluation of Schwab and Felmy rather than Lemire and Tremaine, which is used in the ASD. I did this because the evaluation of Schwab and Felmy is more thorough and recent, and the experimental data were easier to trace. Nevertheless, the results calculated by the CATCH System generally show fairly good agreement with the ASD data (as of November 3, 1986), with the exception of $PuO_2(OH)(am)$ and the fluoride complexes. The reactions involving Pu-fluoride complexes had very poor fits. Dr. Garvin provided additional data as they were needed, such as for the ligands. Dr. Garvin indicated that data for additional Pu-nitrate and phosphate complexes are available, and we may wish to include them for completeness sake.

Please forward the results to Sid Phillips if you believe they are beneficial.

Sincerely,

ORIGINAL SIGNED BY

Walton R. Kelly
Geochemistry Section
Technical Review Branch
Division of High-Level Waste Management
Office of Nuclear Material Safety
and Safeguards

Enclosure: As stated

AUG 12 1987

426.1 87/08/11 W.K.



OFFICIAL CONCURRENCE AND DISTRIBUTION RECORD

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

FROM: Walton R. Kelly
Gechemistry Section
Technical Review Branch
Division of High-Level Waste Management
Office of Nuclear Material Safety
and Safeguards

SUBJECT: PLUTONIUM THERMOCHEMISTRY NETWORK

DATE:

DISTRIBUTIONS

| | | |
|---|---|---|
| HLWM/SF | NMSS RF | RBrowning, HLWM |
| MBell, HLWM | JBunting, HLSE | JLinehan, HLOB |
| RBallard, HLTR | WKelly, HLTR & RF | DBrooks, HLTR |
| PBembia, HLTR | | |

CONCURRENCES

| ORGANIZATION/CONCUREE | INITIALS | DATE CONCURRED |
|---|---|---|
| WKelly/HLTR/lw | WRK | 87/08/12 |

Original sent out by: LW 8/12/87

CATCH Thermochemical System. Calcula values. 30 JUL 87 T = 298.15 K IO D SOLN - LST. SQUARES
PLUTONIUM EQUILIBRIA, [PLUTO12.CYBR] TWO SETS, KELLY

SEE NOTES AFTER THE LISTING OF AUXILIARY DATA FOR EXPLANATION OF ENTRIES.

| COMPOUND | MOLAR MASS g.mol-1 | DfH0 +- SIGMA kJ.mol-1 | DfG0 +- SIGMA kJ.mol-1 | S0 +- SIGMA J.(mol.K)-1 | REACTIONS |
|---|---|---|---|---|---|
| Pu+3(Ao) | 239.0504 | -592.036+- 2.092 | -578.725+- 3.258 | -184.514+- 8.368 | 14 15 17 56 56 56 13 16 12 |
| 76FUG/OET | | | | | |
| Pu+4(Ao) | 239.0498 | -536.389+- 2.959 | -481.656+- 3.271 | -388.783+-14.800 | 54 54 54 14 15 |
| 76FUG/OET | | | | | |
| Pu(Cs) | 239.0520 | [ .000+- .000][ | .000+- .000][ | 56.149+- .418] | |
| 76FUG/RAN | | | | | |
| Pu(Cr) | 239.0520 | [ .000+- .000] | | | |
| 76FUG/RAN | | | | | |
| PuO2(Cr) | 271.0508 | -1055.800+- .800 | -997.642+- .813 | 66.130+- .260 | 57 57 57 18 19 |
| 78GUR/VEI, vol. 4. Unc. on S from gef. | | | | | |
| PuO2+(Ao) | 271.0503 | -914.752+- 7.073 | -850.121+- 7.504 | -20.920+- 8.400 | 60 60 60 30 32 |
| 76FUG/OET. At 1 atm. | | | | | |
| PuO2+2(Ao) | 271.0497 | -822.282+- 6.616 | -757.169+- 3.319 | -87.876+-24.830 | 55 55 55 17 30 16 |
| 76FUG/OET. At 1 atm. | | | | | |
| PuOH+3(Ao) | 256.0577 | | -716.275+- 3.421 | | 1 |
| PuO2(OH)(Am) | 288.0581 | | -1056.470+- 9.608 | | 51 |
| Pu(OH)2+2(Ao) | 273.0656 | | -949.184+- 3.835 | | 2 |
| Pu(OH)3+(Ao) | 290.0735 | | -1167.533+- 3.836 | | 3 |
| Pu(OH)4(Am) | 307.0814 | | -1425.762+- 6.836 | | 50 |
| Pu(OH)4(Ao) | 307.0814 | | -1368.752+- 5.977 | | 4 |
| (PuO2)2(OH)2+2(Ao) | 576.1152 | | -1941.726+- 6.714 | | 8 |
| (PuO2)4(OH)7+(Ao) | 1203.2540 | | -4522.808+-13.364 | | 9 |
| PuF+3(Ao) | 258.0488 | | -789.706+- 3.336 | | 7 |
| PuF2+2(Ao) | 277.0477 | | -1088.206+- 3.526 | | 45 |
| PuF3(Cr) | 296.0472 | -1585.736+- 2.929 | -1515.949+- 2.934 | 126.106+- .377 | 58 58 58 20 21 |
| PuF4(Cr) | 315.0456 | -1846.399+- 2.092 | -1752.702+- 2.099 | 147.250+- .370 | 59 59 59 27 28 |
| 83FUG/PAR | | | | | |
| PuO2F+(Ao) | 290.0487 | | -1044.869+- 3.435 | | 46 |
| PuCl+2(Ao) | 274.5039 | | -709.976+- 3.474 | | 44 |
| PuCl+3(Ao) | 274.5034 | | -613.767+- 3.279 | | 5 |
| PuCl2+2(Ao) | 309.9569 | | -740.508+- 3.315 | | 6 |
| PuO2Cl+(Ao) | 306.5033 | | -888.420+- 3.358 | | 10 |
| PuO2Cl2(Ao) | 341.9568 | | -1015.271+- 3.472 | | 11 |
| Pu(OH)2.5Cl0.5(Cr) | 299.2969 | | -1151.893+- 6.829 | | 49 |
| PuSO4+(Ao) | 335.1091 | | -1338.778+- 3.410 | | 33 |
| PuSO4+2(Ao) | 335.1085 | | -1253.169+- 3.423 | | 35 |
| PuO2SO4(Ao) | 367.1084 | | -1519.192+- 3.777 | | 37 |
| Pu(SO4)2(Cr) | 431.1672 | | -2012.316+- 4.444 | | 52 |
| Pu(SO4)2(Ao) | 431.1672 | | -2019.102+- 3.867 | | 36 |

| COMPOUND | MOLAR MASS g.mol-1 | DfH0 +- SIGMA kJ.mol-1 | DfG0 +- SIGMA kJ.mol-1 | S0 +- SIGMA J.(mol.K)-1 | REACTIONS |
|---|---|---|---|---|---|
| Pu(SO4)2-(Ao) | 431.1678 | | -2093.411+- 3.825 | | 34 |
| PuNO3+2(Ao) | 301.0558 | | -694.171+- 3.495 | | 38 |
| PuNO3+3(Ao) | 301.0553 | | -595.952+- 3.350 | | 41 |
| PuO2NO3+(Ao) | 333.0552 | | -868.045+- 4.426 | | 43 |
| Pu(NO3)2+(Ao) | 363.0613 | | -807.327+- 3.761 | | 39 |
| Pu(NO3)2+2(Ao) | 363.0607 | | -709.688+- 3.421 | | 42 |
| Pu(NO3)3(Ao) | 425.0667 | | -918.203+- 4.524 | | 40 |
| PuH2PO4+2(Ao) | 336.0381 | | -1724.442+- 3.637 | | 47 |
| Pu(HPO4)2(Am) | 431.0106 | | -2827.946+- 4.869 | | 53 |
| Pu(H2PO4)2+(Ao) | 433.0259 | | -2865.699+- 4.520 | | 48 |

AUXILIARY DATA USED IN SOLUTION

| COMPOUND | MOLAR MASS g.mol-1 | DfH0 +- UNC. kJ.mol-1 | DfG0 +- UNC. kJ.mol-1 | S0 +- UNC. J.(mol.K)-1 |
|---|---|---|---|---|
| O2(G) | 31.9988 | .000+- .000 | | |
| 86WAG | | | | |
| O2(Gs) | 31.9988 | .000+- .000 | .000+- .000 | 205.043+- .005 |
| 86WAG | | | | |
| H+(Ao) | 1.0074 | .000+- .000 | .000+- .000 | |
| CONVENTION | | | | |
| H2(G) | 2.0159 | .000+- .000 | .000+- .000 | |
| 86WAG | | | | |
| OH-(Ao) | 17.0079 | | -157.269+- .040 | |
| 86WAG | | | | |
| H2O(L) | 18.0153 | -285.830+- .040 | -237.189+- .040 | |
| 86WAG | | | | |
| H2O(G) | 18.0153 | -241.826+- .040 | | |
| 86WAG | | | | |
| F-(Ao) | 18.9990 | -335.350+- .650 | -281.560+- .650 | |
| 86WAG | | | | |
| F2(G) | 37.9968 | .000+- .000 | | |
| 86WAG | | | | |
| F2(Gs) | 37.9968 | .000+- .000 | .000+- .000 | 202.682+- .005 |
| HF(G) | 20.0063 | -273.300+- .700 | | |
| 86WAG | | | | |
| Cl-(Ao) | 35.4536 | | -131.251+- .100 | |
| 86WAG | | | | |
| SO4-2(Ao) | 96.0587 | | -744.100+- .400 | |
| 86WAG | | | | |
| HSO4-(Ao) | 97.0661 | | -755.413+- 1.000 | |
| [87COX/WAG], DFG CALC. | | | | |
| SF4(G) | 108.0536 | -788.684+- 4.184 | | |
| FROM [76PAR/WAG] | | | | |
| SF6(G) | 146.0504 | -1220.766+- 1.004 | | |
| FROM [76PAR/WAG] | | | | |
| NO3-(Ao) | 62.0055 | | -110.876+- .400 | |
| CODATA BULL. 10 FOR ION ENTROPY. DHF FROM TN-270-3 | | | | |
| 84COD | | | | |
| HPO4-2(Ao) | 95.9804 | | -1096.100+- 1.500 | |
| H2PO4-(Ao) | 96.9878 | | -1137.267+- 1.500 | |
| 87COX/WAG, DFG CALC (DG) | | | | |

NOTES ON DELTA HF(298), DELTA GF(298) AND S(298)

T[illegible]: ARE PRODUCED IN A SIMULTANEOUS SOLUTION OF THE REACTIONS LISTED SEPARATELY, EITHER BY LEAST SQUARES OR LEAST SUMS. THE REACTIONS IN WHICH A COMPOUND APPEARS AND WHICH ARE USED IN SETTING ITS PROPERTIES ARE LISTED BY NUMBER.

COMPOUNDS ARE LISTED ACCORDING TO THE STANDARD ORDER OF ARRANGEMENT (APPROXIMATELY).

THE PARENTHETICAL EXPRESSION AT THE RIGHT-HAND END OF A CHEMICAL FORMULA SHOWS THE PHYSICAL STATE OF, OR THE MEDIUM CONTAINING THE COMPOUND. COMMON ABBREVIATIONS ARE:
C = CRYSTALLINE, L = LIQUID, G= GASEOUS, OR, FOR ELEMENTS IN THEIR REFERENCE STATES, CS, LS, AND GS.
AM = AMORPHOUS, GL = GLASSY, A = HYPOTHETICAL STANDARD STATE, M = 1, IN AQUEOUS SOLUTION.
AO = AQUEOUS, UNDISSOCIATED, AU = AQUEOUS, UNSPECIFIED CONCENTRATION, USUALLY DILUTE.
250 H2O, ETC. = SOLUTION OF SPECIFIED CONCENTRATION., D:=DIFFERENTIAL (PARTIAL MOLAL) PROPERTY.

FORMULA WEIGHTS ARE ON THE 1981 ATOMIC WEIGHT SCALE.

SIGMA = 1 STANDARD DEVIATION. (NOT DEFINED FOR LEAST SUMS). THE MAGNITUDE OF SIGMA REFLECTS THE OVER-ALL FIT OF THE NETWORK. WHEN SIGMAS ARE USED IN THE USUAL SQUARE-ROOT-OF-SUM-OF-SQUARES FORMULA TO PREDICT THE STD. DEV. OF A SOLRSORRSOLERSORULT IS TOO LARGE BECAUSE PROPERTIES ARE HIGHLY CORRELATED. SEE LIST OF REACTIONS FOR BETTER ESTIMATES.

SEE NOTES AT END OF THE LISTING OF THE REACTIONS FOR EXPLANATION OF ENTRIES.

| NO. | REACTION | PROP. MEAS. | OBSVD. kJ/mol or J/(mol.K) | +- UNC. | RESID. (OB-CAL) | STD. DEV. | AVE. FIT | WT. | STD. RES. | REFERENCE |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Pu+4(Ao) + H2O(L) = PuOH+3(Ao) + H+(Ao) | DG= | 2.57 | 1.00 | .000 | | -1.0 | | | 73MET |
| 2 | Pu+4(Ao) + 2 H2O(L) = Pu(OH)2+2(Ao) + 2 H+(Ao) | DG= | 6.85 | 2.00 | .000 | | -1.0 | | | 73MET |
| 3 | Pu+4(Ao) + 3 H2O(L) = Pu(OH)3+(Ao) + 3 H+(Ao) | DG= | 25.69 | 2.00 | .000 | | -1.0 | | | 73MET |
| 4 | Pu+4(Ao) + 4 H2O(L) = Pu(OH)4(Ao) + 4 H+(Ao) | DG= | 61.66 | 5.00 | .000 | | -1.0 | | | 73MET |
| 5 | Pu+4(Ao) + Cl-(Ao) = PuCl+3(Ao) | DG= | -0.86 | 0.20 | .000 | | -1.0 | | | 76BAG/RAM |
| 6 | Pu+4(Ao) + 2 Cl-(Ao) = PuCl2+2(Ao) | DG= | 3.65 | 0.50 | .000 | | -1.0 | | | 76BAG/RAM |
| 7 | Pu+4(Ao) + F-(Ao) = PuF+3(Ao) | DG= | -26.49 | 0.05 | .000 | | -1.0 | | | 76BAG/RAM |
| | 2 PuO2+2(Ao) + 2 H2O(L) = (PuO2)2(OH)2+2(Ao) + 2 H+(Ao) | DG= | 46.99 | 1.00 | .000 | | -1.0 | | | 75SCH |
| 9 | 4 PuO2+2(Ao) + 7 H2O(L) = (PuO2)4(OH)7+(Ao) + 7 H+(Ao) | DG= | 166.19 | 1.50 | .000 | | -1.0 | | | 75SCH |
| 10 | PuO2+2(Ao) + Cl-(Ao) = PuO2Cl+(Ao) | DG= | 0.0 | 0.5 | .000 | | -1.0 | | | 65MAZ/SEV |
| 11 | PuO2+2(Ao) + 2 Cl-(Ao) = PuO2Cl2(Ao) | DG= | 4.40 | 1.00 | .000 | | -1.0 | | | 65MAZ/SEV |
| 12 | Pu(Cr) + 3 H+(Ao) = Pu+3(Ao) + 1.5 H2(G)<br>Selected value, based on calorim. of redox rxns. in 1 M HClO4, following [66RAN].<br>CONSTRAINT - SOLVED EXACTLY. | DH= | -592.0 | 2.1 | .000 | | INF | | | 76FUG/OET |
| 13 | = Pu+3(Ao)<br>Selected value, based on DH(sol), S and solubility of PuCl3:6H2O. | S= | -184.5 | 8.4 | .000 | | -1.0 | | | 76FUG/OET |
| 14 | Pu+3(Ao) + H+(Ao) = Pu+4(Ao) + 0.5 H2(G)<br>From and analysis in [66RAN], adjusted for hydrolysis. | DH= | 55.6 | 2.1 | .000 | | -1.0 | | | 76FUG/OET |
| 15 | Pu+3(Ao) + H+(Ao) = Pu+4(Ao) + 0.5 H2(G)<br>From EMF meas. of Pu+3/Pu+4 couple in 1 M HClO4, adjusted to the stand. state. | DG= | 97.07 | 0.29 | .000 | | -1.0 | | | 76FUG/OET |
| 16 | Pu+3(Ao) + 2 H2O(L) = PuO2+2(Ao) + H+(Ao) + 1.5 H2(G)<br>Based on calorim. meas. of redox rxn. in aq. HClO4, following [66RAN]. | DH= | 341.4 | 6.3 | .000 | | -1.0 | | | 76FUG/OET |

| NO. | REACTION | PROP. MEAS. | OBSVD. kJ/mol or J/(mol.K) | +- UNC. | RESID. (OB-CAL) | STD. DEV. | AVE. FIT | WT. | STD. RES. | REFERENCE |
|---|---|---|---|---|---|---|---|---|---|---|
| 17 | Pu+3(Ao) + 2 H2O(L) = PuO2+2(Ao) + H+(Ao) + 1.5 H2(G)<br>Combination of DG for Pu+4(ao) = Pu+3(ao) + PuO2+2(ao) with DG for the Pu+3/Pu+4 couple in 1 M HClO4, and assigning the value to the stand. state. | DG= | 295.93 | 0.63 | .000 | | -1.0 | | | 76FUG/OET |
| 18 | Pu(Cr) + O2(G) = PuO2(Cr)<br>Combustion of alpha Pu, based on [58HOL/MUL] and [57POP/IVA]. | DH= | -1055.8 | 0.8 | .000 | | -1.0 | | | 78GUR/VEI |
| 19 | = PuO2(Cr)<br>Low Temp. Cp meas. | S= | 66.13 | 0.26 | .000 | | -1.0 | | | 76FLO/OSB |
| 20 | Pu(Cr) + 1.5 F2(G) = PuF3(Cr)<br>Selected value, based on DH(ppt) of PuF3:0.4H2O | DH= | -1585.7 | 2.9 | .000 | | -1.0 | | | 83FUG/PAR |
| 21 | = PuF3(Cr)<br>Calorimetric, on 242Pu.<br>CONSTRAINT - SOLVED EXACTLY. | S= | 126.11 | 0.38 | .000 | | INF | | | 74OSB/FLO |
| 22 | 4 PuF3(Cr) + O2(G) = 3 PuF4(Cr) + PuO2(Cr)<br>Estim. from equilib. 783-1073 K, following [66RAN]. 2d law analysis (?)<br>LISTED FOR INFORMATION ONLY. | DH= | -190.4 | 20.9 | 61.682 | | .0 | | | 83FUG/PAR |
| 23 | PuF4(Cr) = Pu+4(Ao) + 4 F-(Ao)<br>Estim., assuming same DsolH as for UF4(cr)<br>LISTED FOR INFORMATION ONLY. | DH= | -18.4 | 12.6 | 12.980 | | .0 | | | 83FUG/PAR |
| 24 | PuO2(Cr) + 4 HF(G) = PuF4(Cr) + 2 H2O(G)<br>Based on equilib. at 673-873 K [45JOH].<br>LISTED FOR INFORMATION ONLY. | DH= | -178.2 | 20.9 | 2.813 | | .0 | | | 83FUG/PAR |
| 25 | Pu+4(Ao) + 2 H2(G) + 2 F2(G) = PuF4(Cr) + 4 H+(Ao)<br>Estim. from D(DfH((MF4, cr)-DfH(M+4, ao)) vs. ionic radius for the series Th, U, Pu.<br>LISTED FOR INFORMATION ONLY. | DH= | -1319.6 | 13.0 | -9.623 | | .0 | | | 83FUG/PAR |
| 26 | 2 PuF4(Cr) + SF4(G) = 2 PuF3(Cr) + SF6(G)<br>Estim. from lack of reaction at 773 K [61JOH/FIS]<br>LISTED FOR INFORMATION ONLY. | DH= | -10.5 | 20.9 | -99.705 | | .0 | | | 83FUG/PAR |
| 27 | Pu(Cr) + 2 F2(G) = PuF4(Cr)<br>Selected value, based on estim. from equilib. data, using S(PF4, cr) = 147.2 J/mol.K<br>CONSTRAINT - SOLVED EXACTLY. | DH= | -1846.4 | 2.1 | .000 | | INF | | | 83FUG/PAR |

| NO. | REACTION | PROP. MEAS. | OBSVD. | +- UNC. | RESID. (OB-CAL) | STD. DEV. | AVE. FIT | WT. | STD. RES. | REFERENCE |
|---|---|---|---|---|---|---|---|---|---|---|
| | | kJ/mol or J/(mol.K) | | | | | | | | |
| 28 | = PuF4(Cr)<br>Low temp. Cp meas. | S= | 147.25 | 0.37 | .000 | | -1.0 | | | 75OSB/FLO |
| 29 | Pu(Cr) + 2 F2(G) = PuF4(Cr)<br>Selected value, based on estimate from equilib. data using S(PuF4, cr) = 161.9 J/mol.K est. from PuF4-PuF6 equilib.<br>LISTED FOR INFORMATION ONLY. | DH= | -1778.2 | 1.0 | 68.199 | | .0 | | | 66RAN |
| 30 | PuO2+(Ao) + H+(Ao) = PuO2+2(Ao) + 0.5 H2(G) | DH= | 92.47 | 2.50 | .000 | | -1.0 | | | 76FUG/OET |
| 31 | PuO2+(Ao) + H+(Ao) = PuO2+2(Ao) + 0.5 H2(G)<br>FROM EMF IN 1 M HCLO4, CORR. TO STD. STATE E/V=1.016. NOT USED, NOT CONSISTENT WITH ESTIM. FROM NPO2+ AND THE RXN PU+4 + PUO2+ = PU+3 + PUO2+2.<br>LISTED FOR INFORMATION ONLY. | DG= | 97.91 | 5.00 | 4.958 | | .0 | | | 76FUG/OET |
| | = PuO2+(Ao) | S= | -20.92 | 8.40 | .000 | | -1.0 | | | 76FUG/OET |
| 33 | Pu+3(Ao) + HSO4-(Ao) = PuSO4+(Ao) + H+(Ao) | DG= | -4.64 | 0.10 | .000 | | -1.0 | | | 78VAS/BAG |
| 34 | Pu+3(Ao) + 2 HSO4-(Ao) = Pu(SO4)2-(Ao) + 2 H+(Ao) | DG= | -3.86 | 0.12 | .000 | | -1.0 | | | 78VAS/BAG |
| 35 | Pu+4(Ao) + HSO4-(Ao) = PuSO4+2(Ao) + H+(Ao) | DG= | -16.10 | 0.12 | .000 | | -1.0 | | | 76BAG/RAM |
| 36 | Pu+4(Ao) + 2 HSO4-(Ao) = Pu(SO4)2(Ao) + 2 H+(Ao) | DG= | -26.62 | 0.50 | .000 | | -1.0 | | | 76BAG/RAM |
| 37 | PuO2+2(Ao) + HSO4-(Ao) = PuO2SO4(Ao) + H+(Ao) | DG= | -6.61 | 1.50 | .000 | | -1.0 | | | 76PAT/RAM |
| 38 | Pu+3(Ao) + NO3-(Ao) = PuNO3+2(Ao)<br>From analysis of Pu complexes in nitric acid hydrazine nitrate mixtures (at 20 C). Kaso = 5.9+-0.5 | DG= | -4.57 | 1.20 | .000 | | -1.0 | | | 59SHE/TIM |
| 39 | Pu+3(Ao) + 2 NO3-(Ao) = Pu(NO3)2+(Ao)<br>From analysis of Pu complexes in nitric acid hydrazine nitrate mixtures (at 20 C). Kaso = 14.3+- 0.8 | DG= | -6.85 | 1.70 | .000 | | -1.0 | | | 59SHE/TIM |
| 40 | Pu+3(Ao) + 3 NO3-(Ao) = Pu(NO3)3(Ao)<br>From analysis of Pu complexes in nitric acid hydrazine nitrate mixtures (at 20 C). Kaso = 14.4 +-0.8 | DG= | -6.85 | 2.90 | .000 | | -1.0 | | | 59SHE/TIM |

| NO. | REACTION | PROP. MEAS. | OBSVD. | +- UNC. | RESID. (OB-CAL) | STD. DEV. | AVE. FIT | WT. | STD. RES. | REFERENCE |
|---|---|---|---|---|---|---|---|---|---|---|
| | | kJ/mol or J/(mol.K) | | | | | | | | |
| 41 | Pu+4(Ao) + NO3-(Ao) = PuNO3+3(Ao) | DG= | -3.42 | 0.60 | .000 | | -1.0 | | | 76BAG/RAM |
| 42 | Pu+4(Ao) + 2 NO3-(Ao) = Pu(NO3)2+2(Ao) | DG= | -6.28 | 0.60 | .000 | | -1.0 | | | 76BAG/RAM |
| 43 | PuO2+2(Ao) + NO3-(Ao) = PuO2NO3+(Ao) | DG= | 0.0 | 2.9 | .000 | | -1.0 | | | 65MAZ/SEV |
| 44 | Pu+3(Ao) + Cl-(Ao) = PuCl+2(Ao) | DG= | 0.0 | 1.2 | .000 | | -1.0 | | | 56WAR/WEL |
| 45 | Pu+4(Ao) + 2 F-(Ao) = PuF2+2(Ao) | DG= | -43.43 | 0.20 | .000 | | -1.0 | | | 76BAG/RAM |
| 46 | PuO2+2(Ao) + F-(Ao) = PuO2F+(Ao) | DG= | -6.16 | 0.60 | .000 | | -1.0 | | | 76PAT/RAM |
| 47 | Pu+3(Ao) + H2PO4-(Ao) = PuH2PO4+2(Ao) | DG= | -8.45 | 0.60 | .000 | | -1.0 | | | 71MOS |
| 48 | Pu+3(Ao) + 2 H2PO4-(Ao) = Pu(H2PO4)2+(Ao) | DG= | -12.44 | 0.90 | .000 | | -1.0 | | | 71MOS |
| 49 | Pu(OH)2.5Cl0.5(Cr) = Pu+3(Ao) + 2.5 OH-(Ao) + 0.5 Cl-(Ao) | DG= | 114.37 | 6.00 | .000 | | -1.0 | | | 50BUS/COW |
| | Pu(OH)4(Am) = Pu+4(Ao) + 4 OH-(Ao) | DG= | 315.03 | 6.00 | .000 | | -1.0 | | | 49KAS |
| 51 | PuO2(OH)(Am) = PuO2+(Ao) + OH-(Ao) | DG= | 49.08 | 6.00 | .000 | | -1.0 | | | 49KRA/DAM |
| 52 | Pu(SO4)2(Cr) = Pu+4(Ao) + 2 SO4-2(Ao)<br>Combination of selections for Pu(SO4)2, Pu+4(ao) [76FUG/OET] and SO4-2(ao) [78COD] | DG= | 42.46 | 2.90 | .000 | | -1.0 | | | 78COR/OHA |
| 53 | Pu(HPO4)2(Am) = Pu+4(Ao) + 2 HPO4-2(Ao)<br>Pu(HPO4)2(am) = Pu(HPO4)2:xH2O(gel) | DG= | 154.09 | 2.00 | .000 | | -1.0 | | | 49KIN |
| 54 | Pu(Cs) = Pu+4(Ao)<br>CONSTRAINT - SOLVED EXACTLY. | HGS= | 0.000 | 0.000 | .000 | | INF | | | |
| 55 | Pu(Cs) + O2(Gs) = PuO2+2(Ao)<br>CONSTRAINT - SOLVED EXACTLY. | HGS= | 0.000 | 0.000 | .000 | | INF | | | |
| 56 | Pu(Cs) = Pu+3(Ao)<br>CONSTRAINT - SOLVED EXACTLY. | HGS= | 0.000 | 0.000 | .000 | | INF | | | |
| | Pu(Cs) + O2(Gs) = PuO2(Cr)<br>CONSTRAINT - SOLVED EXACTLY. | HGS= | 0.000 | 0.000 | .000 | | INF | | | |
| 58 | Pu(Cs) + 1.5 F2(Gs) = PuF3(Cr)<br>CONSTRAINT - SOLVED EXACTLY. | HGS= | 0.000 | 0.000 | .000 | | INF | | | |
| 59 | Pu(Cs) + 2 F2(Gs) = PuF4(Cr)<br>CONSTRAINT - SOLVED EXACTLY. | HGS= | 0.000 | 0.000 | .000 | | INF | | | |
| 60 | Pu(Cs) + O2(Gs) = PuO2+(Ao)<br>CONSTRAINT - SOLVED EXACTLY. | HGS= | 0.000 | 0.000 | .000 | | INF | | | |

NOTES ON THE LISTING OF THE REACTIONS

REACTION NOS. MATCH THOSE GIVEN WITH THE SOLUTION FOR FORMATION PROPERTIES. STATISTICS FOR REACTIONS ARE BASED ON THAT SOLUTION.

THE REACTIONS LISTED HERE MAY FORM SEVERAL INDEPENDENT NETWORKS. IF SO, THEY WERE SOLVED SEPARATELY.

PRIOR TO SOLVING THE NETWORK, ALL ENTROPY REACTIONS ARE MULTIPLIED BY T/1000 TO PUT THEM ON THE SAME SCALE AS ENTHALPY AND FREE ENERGY REACTIONS. THIS FACTOR HAS BEEN REMOVED BEFORE PRINTING THE CATALOG OF REACTIONS. SEE ALSO DISCUSSION OF WEIGHTS, BELOW.

DEFINITIONS: NETWORKS CONTAIN ALL PROPERTIES THAT ARE OVERDETERMINED. SIDE CHAINS ARE SINGLE MEASUREMENTS THAT SPECIFY INDIVIDUAL PROPERTIES. CONSTRAINTS ARE EXACT RELATIONS BETWEEN TWO OR MORE PROPERTIES.

UNCERTAINTY SHOWN IN BRACKETS IS MACHINE-ASSIGNED. IT IS EQUAL TO 10 IN THE LEAST SIGNIFICANT DIGIT OF THE OBSERVATION, AND IS SUPPLIED WHEN NO ESTIMATE IS PROVIDED BY THE DATA ANALYST.

WT.= WEIGHT FOR THE REACTION. WT. IS POSITIVE FOR REACTIONS THAT ARE IN A NETWORK, AND IS -1 FOR CONSTRAINTS, SIDE-CHAINS AND UNUSED REACTIONS. WEIGHTS PRINTED ABOVE ARE APPLICABLE DIRECTLY TO ENTHALPY AND FREE ENERGY REACTIONS AND TO ENTROPY REACTIONS MULTIPLIED BY T/1000. FOR WEIGHTED SOLUTIONS, WT. IS LIMITED (USUALLY) TO THE RANGE 0.1 TO 20. IT IS EQUAL TO THE RECIPROCAL OF THE UNCERTAINTY OF THE REACTION AFTER ALLOWING FOR THE UNCERTAINTIES IN THE AUXILIARY DATA. CONSTRAINT REACTIONS ARE TREATED AS HAVING ZERO UNCERTAINTIES. IN THE SPECIAL CASE OF A SEQUENTIAL PAIR OF SOLUTIONS, WT. FOR THE SECOND IS EQUAL TO THE RECIPROCAL OF THE AVERAGE FIT OF THE FIRST.

RESID. = OBSERVED- PREDICTED VALUE.

STD.DEV.= 1 STANDARD DEVIATION FOR THE PREDICTED VALUE. NEITHER THE UNCERTAINTY OF THE REACTION NOR THOSE OF THE AUXILIARY DATA ARE INCLUDED EXCEPT TO THE EXTENT THAT THEY INFLUENCE THE WEIGHT USED IN THE SOLUTION.

AVE. FIT = (RESID. ± UNCERTAINTY)/2, OR, IN SPECIAL CASES, = UNCERTAINTY/2. IT IS A COMBINED MEASURE OF CONSISTENCY AND EXPECTED ACCURACY.

STD. RES. IS THE RESIDUAL NORMALIZED TO UNITY AT ONE STD. DEVIATION (APPROXIMATELY) OF THE NETWORK. A VALUE LESS THAN 0.5 IS VERY GOOD. A VALUE GREATER THAN 2 MEANS A VERY POOR FIT. DEFINITIONS ARE:

STD.RES.(LEAST SUM) = RESID(I)/((SUM(WT(J)*RESID(J))/DF)/WT(I))

STD.RES.(LEAST SQUARES) = RESID(I)/ SQRT((SPR/WT(I)) - SIGMA(I)**2) , WHERE SPR = SUM(WT(J)*RESID(J)**2)/DF.
FOR BOTH CASES J RUNS OVER ALL REACTIONS, AND DF (DEGREES OF FREEDOM) = (NO. OF REACTIONS) - (NO. OF VARIABLES).

REACTIONS LABELED 'CONSTRAINT' ARE SOLVED EXACTLY, PER INSTRUCTIONS FROM THE DATA ANALYST.