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AN UPDATE OF THERMODYNAMIC DATA ON URANIUM AND A COMPARISON OF VARIOUS DATA SOURCES AND DATABASES

PART 1 – INVENTORY AND COMPARISON OF FREE ENERGY VALUES FOR INORGANIC AQUEOUS URANIUM SPECIES AT 25°C *with ASSOCIATED SPREADSHEETS located at*

<http://e2geochemistry.com/PDF/AqueousUraniumDataTables.xls>

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The resurgence of interest in uranium as a commodity brings along renewed interest in exploration and concern about environmental management of uranium. Once again the geochemistry of uranium is in the spotlight and it behooves us to take stock of any new information that has been accumulated and to assess the status of our thermodynamic databases used to perform geochemical calculations.

The geochemistry of uranium is exceedingly complex given that

1. there are nearly 200 minerals containing uranium as an essential constituent,
2. its polyvalent nature,
3. the tendency of uranium to form numerous potentially significant soluble uranyl complexes with common ligands, and
4. the added issues of radioactive decay and the differential mobility of the daughters.

Further, the environmental concerns surrounding uranium stem from both its radioactive aspects and its chemical toxicity, both of which are amplified by public concern that is not always driven by logic. We need not complicate matters with out-of-date or erroneous thermodynamic databases.

Part 1 of this series of presentations is a simple inventory of available thermodynamic data for aqueous uranium compounds that may be used for equilibrium-based calculations, especially by computer codes. The objective is to provide a simple means for comparing various data sources and databases so that users can identify missing aqueous compounds in a given database, add them where appropriate, and determine if the constants being used are consistent with preferred sources. This is not intended to be a critical assessment of the available thermodynamic data – all discovered data was included.

Part 1 presents tabulations of thermodynamic values and a spreadsheet used to calculate consistent ΔG_f° values from equilibrium constants. These tables are contained in an Excel spreadsheet associated with the newsletter and may be accessed at the following address: <http://e2geochemistry.com/PDF/AqueousUraniumDataTables.xls>.

The temptation is nearly irresistible to presume the sufficiency, completeness, applicability, internal consistency and accuracy of thermodynamic databases associated with well-known computer codes. Thermodynamic databases are tedious to be sure and examining them is time-consuming. However, performing calculations with any of the popular computer codes (e.g., PHREEQEC, MINTEQA2, The Geochemist's Workbench, etc.) without first thoroughly investigating the applicable parts of the thermodynamic database is potentially the height of self-delusion.

In addition to being tedious, databases are often not attributed and thus tracing the source of thermodynamic data can be very difficult. Worst of all, databases typically are not directly comparable with each other or their sources without reduction of the critical information to a common variable. For example, most databases rely on K-equilibrium constants to define the stability of aqueous phases and minerals, but the program-specific conventions for writing the reactions for which the K constants are given vary, making the K's cumbersome to compare. The Gibbs free energy of compound formation at 25°C is a far more consistent quantity, but unless provided directly in the database, its calculation requires selection of some ancillary quantities (e.g. the ΔG_f° for H₂O, CO₃⁼ or UO²⁺) that are not specified in the database of concern. Consequently, there is a risk to the internal consistency of the calculated ΔG_f° for other compounds derived from the K values. In addition, the conversion, albeit simple, between kilocalories and kilojoules is cumbersome.

Part 1 strives to survey important recent sources as well as some older but traditional data sources of thermodynamic and equilibrium constant data for aqueous uranium-containing compounds. Popular databases associated with computer codes are also surveyed. The free energy values presented in the various sources and the values used for computation in databases are presented in a consistent manner such that the user can more readily evaluate the comparability between data sources and databases. A table is also presented indicating which data sources and databases include each species so that the completeness of a given databases can be assessed. The ultimate source of free energy or equilibrium data are not identified in each case and the reader is directed to Guillaumont et al (2003) for further information.

Databases and data sources surveyed for this inventory. The following recent collections of data were inventoried for information on aqueous uranium compounds. All data were reduced to standard molar Gibbs free energies of formation (ΔG_f°), standard molar enthalpy of formation (ΔH_f°) and standard molar entropy (S°), all at 298.15 °K (stated in terms of kilocalories/mole, kilocalories/mole and calories/°K/mole, respectively). The specifics of the data reduction used for this work are provided below. However, the reader should be aware that the exact origin of numbers presented in computer databases is not always known and small differences in the calculated ΔG_f° values derived from different databases may result even when the ultimate data source is the same.

SOURCES OF THERMODYNAMIC AND EQUILIBRIUM DATA

A. Guillaumont et al (2003) This volume should probably be regarded as the most comprehensive and authoritative overall source of thermodynamic data on uranium available today. It was edited by the Organization for Economic Co-Operation and Development (OECD) Nuclear Energy Agency (NEA). The uranium portion was produced as an update of the Chemical Thermodynamic of Uranium (Grenthe et al, 1992) which assimilated available data through 1989. The 2003 volume is believed to be inclusive of data through 2001. Tabulated data includes ΔG_f° , ΔH_f° , S° and C_p° for a wide array of aqueous compounds and solids. In addition, $\log_{10} K^\circ$, ΔG_r° , ΔH_r° , and ΔS_r° are provided for selected reactions. All values are provided at 298.15 °K, 0.1 MPa, and $I = 0$, and in terms of joules. All data include estimates of uncertainty.

This volume was cited as the primary source of thermodynamic data by Gustafsson et al (2008), which is consistent with the limited amount of significant new data between 2001 and 2008. The only new data cited by Gustafsson was attributed to Dong and Brooks (2006).

The ISU-based thermodynamic data (kilojoules and joules) abstracted from Guillaumont et al (op. cit.) was converted to kilocalories and calories according to the following exact conversion:

$$1 \text{ (thermochemical) calorie} = 4.184 \text{ joule}$$

Of the several species presented in Guillaumont et al (op. cit) but not appearing in the computer program databases surveyed here, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ may be among the more significant. This complex appears to dominate over the mono- and di-carbonate ($\text{UO}_2\text{CO}_3^\circ$ and $\text{UO}_2(\text{CO}_3)_2^{2-}$, respectively) at neutral and alkaline pHs, as depicted in many prior publications (e.g., Langmuir (1979) and Langmuir 1997)

- B. Dong and Brooks (2006) The data presented in this article addresses a potentially important set of ternary complexes that challenge the long-perceived dominance of binary uranyl-carbonate complexes in the pH range 7.5 to 8.5 and 7.1 to 8.5 for $[\text{Ca}_i] = 40$ and 400 mg/L, respectively ($\log P_{\text{CO}_2} = -3.5$ atm and $[\text{U}_i] = 1 \mu\text{mol/L}$ or 0.24 mg/L). Of potential significance is the dominance of the neutral $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^\circ$ complex in a pH range with elevated Ca where $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ were previously assumed to dominate.
- C. Fujiwara et al. (2003) measured the solubility product of $\text{UO}_2 \cdot x\text{H}_2\text{O}$ and also reported hydrolysis constants for the U(IV) complexes UOH^{3+} , $\text{U}(\text{OH})_2^{2+}$, $\text{U}(\text{OH})_3^+$, and $\text{U}(\text{OH})_4^\circ$ expressed a β_n° values for $I = 0$. ΔG_f° values for this report were calculated as follows $\log \beta_n^\circ = \Delta G_r^\circ / -RT(2.302585)$ where $R = 0.00198719(6)$ kcal/K^o-mol and $T = 298.15$ °K or $\log \beta_n^\circ = \Delta G_r^\circ / -1.364241288$. Good agreement was found with Guillaumont et al (2003).

- D. Fujiwara et al (2005b) measured the hydrolysis constants for $U(OH)_5^-$ and $U(OH)_6^{=}$. β_n° values for $I = 0$ were converted to ΔG_r° values as discussed for Fujiwara et al (2003). The value provided for $U(OH)_5^-$ is not well constrained but does not correspond well with the value presented in MINTEQ.
- E. Fujiwara et al (2005) examined the solubility product of $UO_3 \cdot 2H_2O$ and $UO_2(OH)_2$ and present the pH-dependent U(VI)-OH species distribution based on data in Guillaumont et al (2003).
- F. Shock et al. (1997) Although this article was reviewed by Guillaumont et al (2003) the thermodynamic values presented therein were not incorporated by Guillaumont. The article is noteworthy because at least 13 species presented by Shock et al do not appear in any of the other sources reviewed for this work. These include five species attributed to Grenthe et al (1992) that are not apparent in that document.

DATABASES COMPILED FOR COMPUTER PROGRAMS

G. The Lawrence Livermore National Laboratory (LLNL) databases have been adapted (reformatted) for multiple modeling programs including The Geochemist's Workbench and PhreeqC. In general, these databases appear to be among the most comprehensive with respect to aqueous phases. At least the two following "official" versions exist and there are likely numerous customized versions.

LLNL Thermodynamic Database (August 13, 1986) based on the dataset of T. Wolery et al.: data file data0.3245r46. Reformatted to Geochemist's Workbench format October 1994 as the default thermo.dat database. Rockware (Golden, Colorado, <http://www.rockware.com/product/data.php?id=132>) provides a link to this database at <http://www.geology.uiuc.edu/Hydrogeology/thermo/thermo.dat>

LLNL Extended Thermodynamic Database (December 3, 1996) Rockware (Golden, Colorado, <http://www.rockware.com/product/data.php?id=132>) provides a link to an expanded and updated GWB version of the LLNL dataset at <http://www.geology.uiuc.edu/Hydrogeology/thermo/thermo.com.v8.r6%2B.dat>. The dataset contains additional uranium complexes relative to the default thermo.dat, but many people feel that it is less internally consistent than "thermo.dat", especially with respect to aluminum- and sulfur-bearing species.

Operating data in the LLNL databases is in the form of $\log_{10} K^\circ$ values at 25°C, and other temperatures if available, for the formation reaction written in terms of other species as given. In addition, comment lines associated with individual entries provide ΔG_f° , ΔH_f° , and ΔS_f° (typically in SI units) for the species, and the source of data. For comparison purposes (the objective of this work) the operational $\log_{10} K^\circ$ at 25°C values were converted to ΔG_r° according to $(\log_{10} K^\circ = \Delta G_r^\circ (kcal/mol) / -1.364241288)$ and a ΔG_f° was then calculated for the species of interest.

To calculate the ΔG_f° value of the species of interest it was necessary to select a consistent set of ΔG_f° values for all the other reactants and products in the applicable reaction represented by the given $\log_{10} K^\circ$. For this purpose, the selected auxiliary values

given in Guillaumont et al (2003) were used as shown in Table 1 as input to a simple spreadsheet (see attached). Because of the variety and applicability of methods used to extrapolate $\log_{10} K^{\circ}$ at 25°C to other temperatures, the ΔG_f° value for the species of interest as derived from the $\log_{10} K^{\circ}$ given for 25°C (and used by the program) rarely agrees with the ΔG_f° value stated in the comment lines associated with the species.

H. MINTEQA2

MINTEQA2 Database (associated with Release 4.03, May 2006)

MINTEQA2 is available free directly from U.S. Environmental Protection Agency, Center for Exposure Assessment (CEAM) – Ecosystems Research Division, Office of Research and Development (ORD) at <http://www.epa.gov/ceampubl/mmedia/minteq/>.

Data from the MINTEQA2 database was handled as described for the extended LLNL database. MINTEQA2 does not specify ΔG_f° values but “old” and current $\log K$ ($I = 0$) values and data source citations are provided in the Supplemental User Manual (HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc, 1999)

In order to calculate ΔG_f° values from MINTEQA2 equilibrium constants with the same spreadsheet used to calculate it was necessary to change the sign on the equilibrium constant.

Visual Minteq Visual MINTEQ is a Windows version of MINTEQA2 ver 4.0, which was released by the USEPA in 1999. MINTEQA2 is a chemical equilibrium model for the calculation of metal speciation, solubility equilibria etc. for natural waters. It is probably the most widespread model for these purposes today, and it is renowned for its stability. As the development of a Windows version of MINTEQA2 is being supported by the two Swedish research councils [VR](#) and [MISTRA](#), the program is distributed via Internet from <http://www.lwr.kth.se/English/OurSoftware/vminteq/> free of charge.

The thermodynamic database examined for this work was made available in Geochemist's Workbench format at <http://www.lwr.kth.se/English/OurSoftware/vminteq/> EPA's home page for MINTEQ is reached at <http://www.epa.gov/ceampubl/mmedia/minteq/>

The free energy data for one species in the MINTEQA2 database ($\text{UO}_2\text{S}_2\text{O}_3^{\circ}$) is in distinct conflict with another more recent and documented sources.

I. PHREEQC

Phreeqc (Phreeqc and Phreeqc-orig and Phreeqc.dat for GWB) The first two databases are available from USGS at the following address <ftp://brrftp.cr.usgs.gov/pub/charlton/phreeqc/phreeqc-2.15.0-2697.exe>. The thermodynamic database from PhreeQC release 2.8, for use with the GWB programs. The dataset has been compiled from file phreeqc.dat. Dataset was compiled by Daniel Saalfeld and Craig Bethke, University of Illinois, August 2003. These databases contains no uranium species.

WATEQ4f Database available from USGS at:
ftp://brrftp.cr.usgs.gov/pub/jwball/Wateq4f/Wq4f_Installer.exe

The thermodynamic database from Wateq4F, for use with GWB releases 5.0 and later is also available. This dataset invokes activity coefficient calculations consistent with the implementation in Wateq4F. Can be downloaded at:
<http://www.rockware.com/product/data.php?id=132>

One species in the WATEQ4f data base ($\text{U}(\text{CO}_3)_4^{4-}$) was found to be in conflict with other data.

Table 1 Auxiliary Thermodynamic Data
 from Guillaumont et al (2003)

	ΔG_f° (kJ/mol)	ΔG_f° (kcal/mol)
H2O	-237.14	-56.678
OH -	-157.22	-37.576
O2 (aq) *	-3.9	-16.318
CO3 2-	-527.9	-126.171
HCO3 -	-586.845	-140.259
SO4 2-	-744.004	-177.821
SO3 2-	-487.472	-116.509
F -	-281.523	-67.286
Cl -	-131.217	-31.362
ClO3 -	-7.903	-1.889
NO3 -	-110.794	-26.480
N3 -	348.2	83.222
Br -	-103.85	-24.821
BrO3 -	19.07	4.558
SCN -	92.7	22.156
I -	-51.724	-12.362
IO3 -	-126.338	-30.196
HPO4 2-	-1095.99	-261.948
PO4 3-	-1025.49	-245.098
Mg 2+	-455.375	-108.837
Ca 2+	-552.806	-132.124
Sr 2+	-563.864	-134.767
Ba 2+	-557.656	-133.283
H4SiO4 o	-1307.735	-312.556
H2AsO4 -	-753.203	-180.02

Note: * Value for O2 (aq) taken from Wagman et al (1991) and sourced in National Bureau of Standards Technical Notes 270-3 through 270-8.

REFERENCES

- Bernhard, G., Geipel, G., Brendler, V., and Nitsche, H., 1996, Speciation of uranium in seepage waters of a mine tailings pile studied by time-resolved laser-induced fluorescence spectroscopy: *Radiochim. Acta*, v. 74, p. 87-91.
- Bernhard, G., Geipel, G., Reich, T., Brendler, V., Amayri, S., and Nitsche, H., 2001, Uranyl (VI) carbonate complex formation: Validation of the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (aq) species.: *Radiochimica Acta*, v. 89, p. 511-518.
- Burns, P. C., 1999, The crystal chemistry of uranium, Chap. 2 *in* Burns, P. C., and Finch, R., eds., *Uranium: Mineralogy, Geochemistry and the Environment. Reviews in Mineralogy, Reviews in Mineralogy, Vol. 38: Washington, D.C., Mineralogical Society of America.*
- Dong, W., and Brooks, S. C., 2006, Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) using anion exchange method.: *Env. Sci. & Technology*, v. 40, p. 4689-4695.
- Fujiwara, K., Yamana, H., Fujii, T., and Moriyama, H., 2003, Determination of uranium(IV) hydrolysis constants and solubility product of $\text{UO}_2 \cdot x\text{H}_2\text{O}$: *Radiochim. Acta*, v. 91, p. 345-350.
- Fujiwara, K., Yamana, H., Fujii, T., Kawamoto, K., Sasaki, T., and Moriyama, H., 2005, Solubility product of hexavalent uranium hydrous oxide: *Nuclear Sci. and Technol.*, v. 42, p. 289-294.
- Fujiwara, K., Yamana, H., Fujii, T., Kawamoto, K., Sasaki, T., and Moriyama, H., 2005b, Solubility of uranium (IV) hydrous oxide in high pH solution under reducing condition: *Radiochim. Acta*, v. 93, p. 347-350.
- Grenthe, I., Fuger, J., Konings, R. J. M., Lemire, R. J., Muller, A. B., Nguyen-Trung, C., and Wanner, H., 1992, *Chemical Thermodynamics of Uranium: Issy-les-Moulineaux (France), Nuclear Energy Agency - Organization for Economic Co-Operation and Development*, 715 p.
<http://www.nea.fr/html/dbtdb/pubs/uranium.pdf>
- Guillaumont, R., Fanghanel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D., and Rand, M., 2003, *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium, and Technetium: Amsterdam, Elsevier. ISBN: 0-444-51401-5*
- Gustafsson, J. P., Dassman, E., and Backstrom, M., 2008, Towards a consistent geochemical model for prediction of uranium (VI) removal from groundwater by ferrihydrite: *Appl. Geochem.*, v. 24, p. 454-46
- HydroGeoLogic, Inc., and Allison Geoscience Consultants, Inc., 1999, *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0.*
- Langmuir, D., 1979, Uranium solution-mineral equilibria at low temperature with applications to sedimentary ore deposits, *in* Kimberly, M. M., ed., *Short Course in Uranium Deposits: Their Mineralogy and Origin: Toronto, Mineralogical Association of Canada, University of Toronto Press*, p. 17-56.
- Langmuir, D., 1997, *Aqueous environmental geochemistry: Upper Saddle River, N.J., Prentice Hall*, viii, 600 p. p.
- Shock, E. L., Sassani, D. C., and Betz, H., 1997, Uranium in geologic fluids: Estimates of standard partial molar properties, oxidation potential, and hydrolysis constants at high temperature and pressures: *Geochim. Cosmochim. Acta*, v. 61, p. 4245-4266.
- Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Bailey, S. M., Halow, I., Churney, K. L., and Nuttall, R. L., 1991, Selected values of chemical thermodynamic properties, *in* Lide, D. R., ed., *Handbook of Chemistry and Physics, 71st Edition: Boca Raton, Chemical Rubber Company*, p. 5-16 - 5-59.

