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# Evaluation of Thermodynamic Data

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**Used Fuel Disposition Campaign**

**Generic Engineered Barrier System Evaluations**

**(Work Package FT-13LL080603)**

**Evaluation of Thermodynamic Data**

**(M4FT-13LL08060325)**

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## Thermodynamic Data: Progress

Thermodynamic data are essential for understanding and evaluating geochemical processes, as by speciation-solubility calculations, reaction-path modeling, or reactive transport simulation. These data are required to evaluate both equilibrium states and the kinetic approach to such states (via the affinity term or its equivalent in commonly used rate laws). These types of calculations and the data needed to carry them out are a central feature of geochemistry in many applications, including water-rock interactions in natural systems at low and high temperatures. Such calculations are also made in engineering studies, for example studies of interactions involving man-made materials such as metal alloys and concrete. They are used in a fairly broad spectrum of repository studies where interactions take place among water, rock, and man-made materials (e.g., usage on YMP and WIPP). Waste form degradation, engineered barrier system performance, and near-field and far-field transport typically incorporate some level of thermodynamic modeling, requiring the relevant supporting data.

The development of thermodynamic databases has a long history in geochemistry (e.g., Garrels and Christ, 1965; Helgeson et al., 1969; Helgeson et al., 1978; Johnson et al., 1992; Robie and Hemingway, 1995), paralleled by related and applicable work in the larger scientific community (e.g., Wagman et al., 1982, 1989; Cox et al., 1989; Barin and Platzki, 1995; Binneweis and Milke, 1999). Unfortunately, the National Bureau of Standards (now the National Institutes of Science and Technology) no longer generally addresses thermodynamic data pertaining to aqueous, mineral, and gas species, its last work being the compilation of Wagman et al. (1982) and the errata published in 1989. IUPAC, whose efforts in this area were generally limited to data pertaining to key species only (a small subset), has not done much in this area since the publication of the Cox et al. (1989) report. The standards organizations have been basically inactive regarding thermodynamic data of interest to geochemical and repository studies for over twenty years. For radionuclide elements, much of this void has been filled by the European Nuclear Energy Agency (NEA), which has sponsored a series of review volumes (e.g., Grenthe et al., 1992 [1: uranium]; Silva et al., 1995 [2: americium]; Rard et al., 1999 [3: technetium]; Lemire et al., 2001 [4: neptunium and plutonium]; Guillaumont et al., 2003 [5: update on uranium, neptunium, plutonium americium, and technetium]; Gamsjäger et al., 2005 [6: nickel]; and Olin et al., 2005 [7: selenium]).

The YMP dilute systems database is widely used in the geochemistry community for a variety of applications involving rock/water interactions. It builds on the work of Prof. Helgeson and his students (see BSC, 2007a for many applicable references, including ones to the SUPCRT92 code and associated database), and covers a significant range of temperature (25-300°C). The last version (data0.ymp.R5) covers 86 chemical elements, 1219 aqueous species, 1156 minerals and other solids species, and 128 gas species. Many data for actinide species have been adopted from the Nuclear Energy Agency (NEA) series of volumes on actinide thermodynamics (see references given in BSC, 2007a), and the appropriate temperature extrapolations have been applied.

Progress in FY13 has continued to focus on the basic foundation of a thermodynamic database, namely values for *key data* associated with specific chemical species (solid, gas, aqueous) on which data for other species depend. This direction was taken after generating new estimates of

thermodynamic properties of various complex clays and related sheet silicates. At that time, it was noted that some of the inputs derived from the mineral data of Helgeson et al. (1978) either needed correction or seemed weakly supported. This further suggested the likelihood of necessary wholesale correction to the Helgeson et al. (1978) in regard to the aluminosilicate minerals. This sort of correction would affect the calculated relationships of clay minerals and related sheet silicates, including the illites and chlorite, among themselves and with other silicates and aluminosilicates. Also, understanding the needed corrections is required to evaluate the possible benefit of replacing the Helgeson et al. (1978) dataset with the similar but more modern one of Holland and Powell (2011). At this time we believe that it is necessary to settle various key data issues in order to properly move forward with either one. Once the key data issues are resolved, corrections would be needed to either for use in UFD applications. These corrections are needed to assure accurate calculation of solubilities and mineral phase relationships, particularly in the relative low temperature range (<300°C).

It is infeasible to re-do the many thousands, if not tens of thousands of experiments that contribute to the existing literature on thermodynamic data of potential significance to the UFD and similar geochemical applications. Therefore, it is necessary to re-evaluate a large body of historical data collected in a timespan of about a century and only do new experiments as absolutely required, not only to fill gaps but to resolve discrepancies in the data that cannot otherwise be resolved. Therefore, this is mostly a task of re-evaluating existing data.

A major problem with thermodynamic data is that data are typically dependent on other data. For example, Gibbs energies and enthalpies cannot be measured absolutely. The convention is to define them in terms of formation from the chemical elements in their standard reference forms. The standard reference forms are usually the thermodynamically stable forms at 298.15K and 1 bar pressure. An exception is white phosphorus, which in modern work is mostly used in place of the stable red form.

The Gibbs energy of formation is related to the enthalpy of formation is:

$$\Delta G_{f,i}^o = \Delta H_{f,i}^o - T\Delta S_{f,i}^o$$

where  $\Delta G_{f,i}^o$  is the (standard molar) Gibbs energy of formation,  $\Delta H_{f,i}^o$  is the (standard molar) enthalpy of formation,  $T$  is the absolute temperature, and  $\Delta S_{f,i}^o$  is the (standard molar) entropy of formation. The Gibbs energy and enthalpy of formation are generally tabulated along with the absolute (standard molar) entropy ( $S^o$ ), not the entropy of formation. The entropy of formation of a chemical substance is related to the absolute entropy of the substance by:

$$\Delta S_{f,i}^o = S_i^o - \sum_{\epsilon} \nu_{\epsilon,i} S_{\epsilon}^o$$

where  $\epsilon$  denotes a chemical element,  $\nu_{\epsilon,i}$  is the stoichiometric coefficient of the element in the  $i$ -th chemical substance, and  $S_{\epsilon}^o$  is the absolute (standard molar) entropy of the element in its reference state.

The use of two reference forms for phosphorus has caused trouble. Consider two USGS compilations of thermodynamic data. Robie and Hemingway (1995) give the same

thermodynamic data for  $\text{PO}_4^{3-}$  (within precision) as the earlier compilation of Robie et al. (1978) [See Table 8 of the present report]. However, the earlier work uses *red* phosphorus as the reference form for P (entropy of 22.85 J/mol-K), while the later one uses the *white* form (41.09 J/mol-K). Something is clearly wrong here.

Recommended values for elemental entropies have varied somewhat over time. Table 1 lists the recommended values from nine relatively modern authoritative sources. Problem areas are noted in this table. One can see that discrepancies do exist, but most are relatively small. Older sets of recommended values are given in Tables 2 and 3. In Table 1, the units are modern (Joule units, not calorie units) and the standard pressure is one bar. In Table 2, the values are given in calorie units and the standard pressure is 1 atm (1.013 bar). In Table 3, the values are given in Joule units but the standard pressure is again 1 atm. The difference in standard pressure causes no discrepancies for condensed phases, but does matter for gases.

The importance of elemental entropies in relating Gibbs energies to enthalpies clearly defines these entropies as the first group of key data. One would think that every compilation of thermodynamic data would begin with a selection and presentation of these data. However, that is generally not the case, and the elemental reference forms are more often treated as ordinary chemical species and scattered about the data tables following whatever general arrangement of chemical species is employed. As many of even the modern data compilations do not exist in computerized or other searchable form, this creates something of an impediment to making corrections to data that one may wish to adopt in one's own work. Many of the compilations do include words to the effect that corrections have been made where necessary. However, there is no objective evidence as to how rigorously this may have been practiced.

Tables 1-3 were created in part to look at trends and gaps in the available data for elemental entropies. However, they were also created to serve as an easy reference in evaluating whether or not such corrections may have been made or to make such corrections if needed.

In general, we prefer the NEA-TDB values (included in Table 1) for future thermodynamic database work. These include the data from Cox et al. (1989) [the last CODATA report]. However, there are still a fair number of gaps; only 50 elements are covered. Barin and Platzki (1995) covers many more elements (89). It is probably a good place to start in filling gaps for a UFD thermodynamic database. However, direct evaluation of original sources should be made, along with a search for and evaluation of any data in the newer literature.

Entropy values are generally easy to obtain by calorimetry. Usually the sample remains intact. Other means of obtaining values are possible, but this is the most common. The situation is more challenging for obtain Gibbs energy data or enthalpy data. To obtain Gibbs energy data, a system of chemical components must be in equilibrium and one of these must be the chemical species of interest. To obtain enthalpy data, the idea is to completely react the sample, producing other chemical species. Gibbs energies and enthalpies both may be sensitive to the exact nature of the chemical species of interest, and in the case of minerals, there are often issues of proper characterization of chemical composition, crystallinity, particle size, etc.

In theory, one could just obtain enthalpy of formation data or everything of interest and then calculate the corresponding Gibbs energies. One could then just use equilibrium measurements as a means of test. However, it has been found that Gibbs energies can often give higher accuracy (cf. Helgeson et al., 1978). This is particularly important because what geochemists and others are more often trying to do is calculate equilibria or reaction rates that depend on distances from equilibria. The reality is that what we have today is a mixed set of results. It is somewhat unfortunate that both Gibbs energies and enthalpies are tied to elemental reference forms, as those reference forms are tied to a particular oxidation state (zero), while the oxidation states in chemical species of interest may be different. Much of the uncertainty associated with a given Gibbs energy of formation or enthalpy of formation may be associated with relating the elemental reference forms to forms that represent the oxidation states in the species of interest. This appears to be a problem with aluminum, in regard to the relation of Al metal (the reference form) to the form common in minerals (Al[III]). Again, however, establishing the appropriate key data is the way to proceed. Such a key datum might be the Gibbs energy or enthalpy of corundum (Al<sub>2</sub>O<sub>3</sub>).

Table 4 shows a selection of key data for aqueous species and minerals taken from the slop98.dat datafile associated with SUPCRT92. This includes the mineral data of Helgeson et al. (1978), with corrections in the case of Ca-bearing aluminosilicates performed in March, 1990. SUPCRT92 is very important to the UFD because it (along with the NEA-TDB database as developed at the time) were used to develop the Yucca Mountain Project dilute systems database. Table 5 shows the slop98.dat (SUPCRT92) key data converted to Joule units alongside the corresponding data from NEA-TDB (through volume 12). Various discrepancies are marked. The NEA-TDB data for the aqueous phosphate species were validated by Rard and Wolery (2007). The corresponding slop98.dat data are incorrect, and in fact were superseded in a SUPCRT92 data file used to update the Yucca Mountain Project dilute systems thermodynamic database. We note that SiO<sub>2</sub>(aq) (used in slop98.dat) and Si(OH)<sub>4</sub>(aq) (used in NEA-TDB) are in fact the same species, just differing in formally assigned H<sub>2</sub>O. Correcting for this, the two value sets are copacetic. However, in the development of the Yucca Mountain Project dilute systems database, different data were assigned that correspond to the “Rimstidt” paradigm, which is consistent with modern thinking among most geochemists (cf. BSC, 2007a). These data are shown in Table 6.

Table 7 similar shows the same key data from the last two NBS compilations, the NBS 270 series and Wagman et al. (1982). The first uses *calorie* units, the second, *Joule* units. Table 8 similar shows the same key data from the last two USGS compilations, Robie et al., 1978) and Robie and Hemingway (1995). Both use Joule units.

Tables 4-8 are intended to support further UFD thermodynamic database development by providing ready access to key data from important compilations, and thus to assist in developing a single set of key data to use in further development of the UFD thermodynamic database. One would think, as for the entropies of the elements, that such key data would be identified and presented in one place in any compilation. However, that is, again, not generally the case. It may be necessary to refer to these older key data sets in evaluating other, non-key data, as they may depend on data in these sets.



A major problem of concern is aluminum, because Helgeson et al. (1978) after careful consideration of a body of conflicting data obtained one resolution, while USGS investigators (e.g., Robie and Hemingway, 1995) came to a different resolution. The main problem seems to be relating Al[III] in some form to Al metal (the elemental reference form).

A closer look at the Helgeson et al. (1978) paper (supported by discussions with Dr. K.J. Jackson, one of Prof. Helgeson's former students) indicates that in building most of the aluminosilicate data from mineral-mineral phase equilibrium data, kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) was used as an anchor mineral for the  $\text{Al}_2\text{O}_3$  component. However, Helgeson et al. did not use calorimetric data for the Gibbs energy of kaolinite. Instead, they estimated the Gibbs energy from a solubility ( $\log K$ ) approach. The solubility data were taken from a natural system, in which groundwater was assumed to be in equilibrium with kaolinite and gibbsite. This is not an approach that most investigators today (if not then) would prefer. The resulting Gibbs energy for kaolinite was used to derive Gibbs energies for some other aluminosilicates, and so forth in a somewhat complex chain. We are engaged in attempting corrections to the Helgeson et al. (1978) approach to deriving kaolinite data, which of course depends on gibbsite data. We are also looking at the USGS approach to this issue. Holland and Powell (1985) developed their database using corundum as the key aluminum mineral, so that needs to be looked at as well.

## Recommendations for Future Database Development

The following are recommendations for future thermodynamic database development and improvements:

- Continue evaluation of a large body of historical data reported over the last century
- Future database should use NEA-TBD data where feasible (post-Nickel volume)
- Consider Barin and Platzki a source of thermodynamic data to backfill NEA-TBD gaps
- Perform experiments to populate unknown data and resolve discrepancies only when absolutely required
- Establish key data for aluminum using Gibbs energy or enthalpy of corundum ( $\text{Al}_2\text{O}_3$ ) to resolve discrepancies between Helgeson (1978) and Robie/Hemingway (1995), also incorporating Holland/Powell (1985) data
- Update SUPCRT92 mineral data for consistency with desired key data
- Maybe replace the SUPCRT92 mineral data with the Holland and Powell (2011) data, adjusting for consistency with the desired key data
- Put the SUPCRT92 functionality for calculating thermodynamic properties as a function of temperature and pressure into Cantera
- Collaborate with European investigators (Therada, Pitzer, benchmarking)
- Fully update working databases at opportune times (e.g., do official releases)
- Take another look at temperature and pressure extrapolation of data for aqueous species for which HKF EOS data are not available
- Address high-ionic strength model data (Pitzer model, others)
- Include surface complexation modeling improvements as well as chemical thermodynamic data improvements

Additionally, other than work on Yucca Mountain dilute and concentrated solution databases, the US has largely abandoned thermodynamic database development. Some of the last collections of U.S. thermodynamic data are from Bureau of Mines (no longer an entity) in 1995, USGS in 1995 and NBS (now NIST) in 1982. International efforts have continued, including those of France (2007), Belgium (2007), Sweden (2006), Finland (2007), Spain (2003), Japan (2005) with many of these relying heavily on the Swiss Nagra/PSI data, and the NEA-TDB program performs critical review on data.

A DOE thermodynamic database would be of interest to many DOE programs, including those in DOE-NE, DOE-EM, DOE-FE and Office of Science. Since several international repository programs have made progress on the development of thermodynamic data in parallel to US efforts, it would be beneficial for DOE to integrate international thermodynamic data into a multi-program DOE database. Specific guidance on the creation, population and review of such a database would be required. Requirements for a DOE thermodynamic database should include:

- QA/QC – traceable, reproducible, consistent, uncertainty
- Integration with other national and international programs
- Benchmarking (possibly against NEA-TDB)
- Include geochemical reactions, redox, sorption, ion exchange
- Ability to handle both dilute and concentrated systems strengths (pitzer, debye-huckel, etc.)
- Data for elevated temperature and pressure
- Portability to multiple systems, programs, countries
- Open source format

Table 1. Entropies of the Chemical Elements in Their Standard Reference Forms. The data shown here represent “modern” era values characterized by the use of Joule units and a standard pressure of 1.0 bar. NEA-TDB data (light green) are generally preferred over values from other sources, but only cover a limited number of elements. Light orange background marks problematic or potentially problematic values. This table is taken from workbook TDProperties\_Rev0\_u3.xlsx.

Handle	USGS 1452	NBS 82	JANAF 3rd	CODATA 89	NEA TDB	Barin	NIST-JANAF	USGS 2131	Lange's
Element	Robie et al. 1978 J/mol-K	Wagman et al. 1982 J/mol-K	Chase et al. 1985 J/mol-K	Cox et al. 1989 J/mol-K	NEA TDB Series 1992- J/mol-K	Barin and Platzki 1995 J/mol-K	Chase (ed.) 1998 J/mol-K	Robie and Hemingway 1995 J/mol-K	Lange's Handbook 2005 J/mol-K
Ac		56.5							56.5
Ag	42.55	42.55		42.55	42.550	42.677		42.55	42.55
Al	28.35	28.33	28.275	28.30	28.300	28.275	28.275	28.30	28.30
Am					55.400	54.488			62.7
Ar	154.84	154.843	154.845	154.846	154.846	154.845	154.845		154.846
As	35.69	35.1			35.100	35.706		35.69	35.1
At2									121.3
Au	47.49	47.40				47.497		47.49	47.4
B	5.90	5.86	5.834	5.90	5.900	5.830	5.834	5.83	5.90
Ba	64.42	62.8	62.475		62.420	62.417	62.475	62.42	62.48
Be	9.54	9.50	9.440	9.50	9.500	9.440	9.440	9.50	9.50
Bi	56.74	56.74			56.740	56.735		56.74	56.7
Bk									
Br2	152.32	152.231	152.206	152.210	152.210	152.210	152.206	152.20	152.21
C	5.74	5.740	5.740	5.74	5.740	5.740	5.740	5.74	5.74
Ca	41.63	41.42	41.588	41.59	41.590	41.422	41.588	42.90	41.59
Cd	51.80	51.76		51.80	51.800	51.798		51.80	51.8
Ce	69.46	72.0				69.454		72.0	72.0
Cf									
Cl2	223.08	223.066	223.079	223.081	223.081	223.117	223.079	223.08	233.08
Cm									
Co	30.04	30.04	30.067			30.041	30.067	30.04	30.0
Cr	23.64	23.77	23.618			23.640	23.618	23.62	23.8
Cs	85.23	85.23	85.147	85.23	85.230	85.147	85.147	85.23	85.23
Cu	33.15	33.150	33.164	33.15	33.150	33.164	33.164	33.14	33.15

Table 1 (continued)

Handle	USGS 1452	NBS 82	JANAF 3rd	CODATA 89	NEA TDB	Barin	NIST-JANAF	USGS 2131	Lange's
Element	Robie et al. 1978 J/mol-K	Wagman et al. 1982 J/mol-K	Chase et al. 1985 J/mol-K	Cox et al. 1989 J/mol-K	NEA TDB Series 1992- J/mol-K	Barin and Platzki 1995 J/mol-K	Chase (ed.) 1998 J/mol-K	Robie and Hemingway 1995 J/mol-K	Lange's Handbook 2005 J/mol-K
Dy	74.89	74.77				74.894			75.6
Er	73.18	73.18				73.178			73.18
Es									
Eu	80.79	77.78				77.822			77.78
F2	202.79	202.78	202.789	202.791	202.791	202.795	202.789	202.79	202.791
Fe	27.28	27.28	27.321			27.280	27.321	27.09	27.32
Fm									
Fr		95.4							95.40
Ga	40.83	40.88	40.838			40.828	40.838		40.8
Gd	68.45	68.07				67.948			68.07
Ge	31.09	31.09		31.09	31.090	31.087		31.09	31.09
H	130.68	130.684	130.680	130.680	130.680	130.680	130.680	130.68	130.680
He	126.15	126.150	126.152	126.153	126.153	126.148	126.152		126.153
Hf	43.56	43.56	43.560			43.555	43.560		43.56
Hg	75.90	76.02	76.028	75.90	75.900	75.898	76.028	75.90	75.90
Ho	75.02	75.3				75.019			75.3
I2	116.15	116.135	116.142	116.140	116.140	116.142	116.142	116.14	116.14
In	57.84	57.82				57.823			57.8
Ir	35.48	35.48				35.505			35.48
K	64.68	64.18	64.670	64.68	64.680	64.670	64.670	64.67	64.68
Kr	164.08	164.082	164.084	164.085	164.085	164.085	164.084		164.085
La	56.90	56.9				56.902			56.9
Li	29.12	29.12	29.085	29.12	29.120	29.080	29.085	29.09	29.12
Lr									
Lu	50.96	50.96				50.961			50.96
Md									
Mg	32.68	32.68	32.671	32.67	32.670	32.677	32.671	32.67	32.67
Mn	32.01	32.01	32.010			32.008	32.010	32.01	32.01
Mo	28.66	28.66	28.605			28.593	28.605	28.66	28.71

Table 1 (continued)

Handle	USGS 1452	NBS 82	JANAF 3rd	CODATA 89	NEA TDB	Barin	NIST-JANAF	USGS 2131	Lange's
Element	Robie et al. 1978 J/mol-K	Wagman et al. 1982 J/mol-K	Chase et al. 1985 J/mol-K	Cox et al. 1989 J/mol-K	NEA TDB Series 1992- J/mol-K	Barin and Platzki 1995 J/mol-K	Chase (ed.) 1998 J/mol-K	Robie and Hemingway 1995 J/mol-K	Lange's Handbook 2005 J/mol-K
N2	191.61	191.61	191.609	191.609	191.609	191.609	191.609	191.61	191.609
Na	51.30	51.21	51.455	51.30	51.300	51.455	51.455	51.46	51.30
Nb	36.40	36.40	36.464			36.401	36.464		36.4
Nd	71.09	71.5				71.086			7.16
Ne	146.32	146.328	146.327	146.328	146.328	146.324	146.327		146.328
Ni	29.87	29.87	29.870		29.870	29.874	29.87	29.87	29.87
No									
Np					50.460	50.459			
O2	205.15	205.138	205.147	205.152	205.152	205.147	205.147	205.15	205.152
Os	32.64	32.6				32.635			32.6
P	22.85	41.09	41.077	41.09	41.090	41.070	41.077	41.09	41.09
Pa		51.9				51.882			51.8
Pb	65.06	64.81	64.785	64.80	64.800	64.785	64.785	64.8	64.80
Pd	37.82	37.57				37.823			37.61
Pm									
Po									62.8
Pr	73.93	73.2				73.931			73.2
Pt	41.63	41.63				41.631		41.63	41.63
Pu	51.46				54.460	51.463			51.5
Ra		71							71
Rb	76.78	76.78	76.778	76.78	76.780	76.780	76.778		76.78
Re	36.53	36.86				36.526			36.9
Rh	31.54	31.51				31.505			31.51
Rn	176.23	176.21	176.235			176.231	176.235		176.235
Ru	28.53	28.53				28.535			28.53
S	31.80	31.80	32.056	32.054	32.054	32.056	32.056	32.05	32.054
Sb	45.52	45.69			45.520	45.522		45.52	45.7
Sc	34.64	34.64				34.644			34.64
Se	42.27	42.442			42.090	42.258		42.27	41.97

Table 1 (continued)

Handle	USGS 1452	NBS 82	JANAF 3rd	CODATA 89	NEA TDB	Barin	NIST-JANAF	USGS 2131	Lange's
Element	Robie et al. 1978 J/mol-K	Wagman et al. 1982 J/mol-K	Chase et al. 1985 J/mol-K	Cox et al. 1989 J/mol-K	NEA TDB Series 1992- J/mol-K	Barin and Platzki 1995 J/mol-K	Chase (ed.) 1998 J/mol-K	Robie and Hemingway 1995 J/mol-K	Lange's Handbook 2005 J/mol-K
Si	18.81	18.83	18.820	18.81	18.810	18.820	18.820	18.81	18.81
Sm	69.50	69.58				69.496			69.58
Sn	51.20	51.55		51.18	51.180	51.195		51.18	51.08
Sr	55.40	52.3	55.694		55.700	55.690	55.694	55.69	55.0
Ta	41.51	41.51	41.471			41.505	41.471		41.47
Tb	73.70	73.22				73.304			73.22
Tc					32.506	33.472			33.47
Te	49.50	49.71			49.221	49.497		49.71	49.70
Th	53.39	53.39		51.8	51.800	53.388		51.83	51.8
Ti	30.63	30.63	30.759	30.72	30.720	30.759	30.759	30.76	30.72
Tl	64.18	64.18				64.183			64.18
Tm	74.01	74.01				74.015			74.01
U	50.29	50.21		50.20	50.200	50.292		50.2	50.20
V	28.91	28.91	28.936			28.911	28.936	28.94	28.94
W	32.64	32.64	32.660			32.660	32.660	32.65	32.6
Xe	169.68	169.683	169.684	169.685	169.685	169.683	169.684		169.685
Y	44.43	44.43				44.434			44.4
Yb	59.83	59.87				59.831			59.87
Zn	41.63	41.63	41.717	41.63	41.630	41.631	41.717	41.63	41.63
Zr	38.99	38.99	38.869		39.080	38.869	38.869	38.87	39.0
Count	85	88	47	37	50	89	47	50	93

Notes: The Lange's Handbook value for Cl<sub>2</sub> of 233.08 J/mol-K is possibly a typo where the actual value should be 223.08 J/mol-K. The value for P given by Robie et al. (1978) differs because they use red phosphorus as the reference form instead of the now generally accepted white form. The NEA-TDB value for Pu is notably higher than the values given by other sources.

Table 2. Entropies of the Chemical Elements in Their Standard Reference Forms. The data shown here represent older historical era values characterized by the use of calorie units (1 cal = 4.184 joule) and a standard pressure of 1.0 atm (1.013 bar). This table is taken from workbook TDProperties\_Rev0\_u3.xlsx. Still earlier data compilations by Lewis and Gibson (1917) and Lewis et al. (1922), which appear to be the earliest such compilations, are not included here, though they are given in the spreadsheet. Also in the spreadsheet is a small compilation that was included in the International Critical Tables of 1929 (which gave the data in Joule units, for 1 bar pressure). The data included here, though historical, is often found cited in later literature or in tracing the origin of data presented in later literature. Note that some sources use red phosphorus as the reference form for P instead of the now commonly accepted white form.

Handle	USBM 350	NBS 500	ACS 18	USBM 592	USGS 1259	NBS 270	JANAF 2nd	USBM 672
Element	Kelly 1932 cal/mol-K	Rossini et al. 1952 cal/mol-K	Stull and Sinke 1956 cal/mol-K	Kelley and King 1961 cal/mol-K	Robie and Waldbaum 1968 cal/mol-K	NBS 270-3 to 270-8 1968-1981 cal/mol-K	Stull and Prophet 1971 cal/mol-K	Pankratz 1982 cal/mol-K
Ac			15.00	15.0		13.5		
Ag	10.15	10.206	10.20	10.20	10.20	10.17		10.170
Al	6.75	6.769	6.77	6.77	6.77	6.77	6.769	6.776
Am								13.023
Ar	36.8	36.983	36.98	36.98		36.9822		36.983
As	8.4	8.4	8.40	8.4	8.40	8.4		8.534
At2			29.00	29.0				
Au	11.4	11.4	11.32	11.31	11.31	11.33		11.330
B		1.56	1.4	1.403	1.403	1.40	1.403	1.410
Ba		16	15.50	16.0	16.0	15.0		14.918
Be	2.14	2.28	2.28	2.28	2.28	2.27	2.280	2.270
Bi	13.8	13.6	13.58	13.5	13.56	13.56		13.560
Bk								
Br2	36.6	36.4	36.25	36.4	36.384	36.384	36.384	36.379
C	1.3	1.3609	1.37	1.36	1.372	1.372	1.359	1.372
Ca	9.95	9.95	9.95	9.95	9.95	9.90	9.932	9.940
Cd	12.30	12.3	12.37	12.37	12.38	12.37		12.380
Ce	13.80	13.8	16.64	16.6	15.3	17.2		17.200
Cf								
Cl2	53.8	53.286	53.29	53.29	53.288	53.288	53.2890	53.290
Cm								17.200
Co	6.8	6.8	7.18	7.18	7.18	7.18	7.180	7.180
Cr	5.6	5.68	5.70	5.68	5.65	5.68		5.650

Table 2 (continued)

Handle	USBM 350	NBS 500	ACS 18	USBM 592	USGS 1259	NBS 270	JANAF 2nd	USBM 672
Element	Kelly 1932 cal/mol-K	Rossini et al. 1952 cal/mol-K	Stull and Sinke 1956 cal/mol-K	Kelley and King 1961 cal/mol-K	Robie and Waldbaum 1968 cal/mol-K	NBS 270-3 to 270-8 1968-1981 cal/mol-K	Stull and Prophet 1971 cal/mol-K	Pankratz 1982 cal/mol-K
Cs		19.8	20.16	20.1		20.37	20.351	20.370
Cu	7.92	7.96	7.97	7.7	7.97	7.923	7.913	7.924
Dy			17.87	17.9		18.0		17.900
Er			17.48	17.5		17.49		17.490
Es								
Eu			17.00	17.0		18.59		18.600
F2		48.6	48.45	48.49	48.44	48.44	48.447	48.443
Fe	6.47	6.49	6.49	6.49	6.52	6.52	6.529	6.520
Fm								
Fr			22.50	22.5		22.8		
Ga	10.2	10.2	9.82	9.77		9.77		9.758
Gd		14	15.77	16.2		16.27		16.240
Ge		10.14	7.43	7.43		7.43		7.430
H2	31.23	31.211	27.39	31.21	31.208	31.208	31.208	31.207
He	30.13	30.126	30.13	30.13		30.1244		30.125
Hf		13.1	10.91	10.91	10.41	10.41		10.410
Hg	18.5	18.5	18.19	18.17	18.17	18.17	18.171	18.140
Ho			17.77	18.0		18.0		17.930
I2	27.90	27.90	27.90	27.76	27.757	27.757	27.758	27.758
In		12.5	13.82	13.9		13.82		13.820
Ir	8.7	8.7	8.70	8.48		8.48		8.481
K	15.2	15.2	15.39	15.34	15.48	15.34	15.457	15.457
Kr	39.17	39.19	39.19	39.19		39.1905		39.191
La	13.7	13.7	13.60	13.6		13.6		13.600
Li	7.6	6.70	6.75	6.70	6.95	6.96	6.954	6.954
Lr								
Lu			11.75	11.8		12.18		12.180
Md								
Mg	7.77	7.77	7.81	7.81	7.81	7.81	7.814	7.810
Mn	7.3	7.59	7.65	7.64	7.65	7.65		7.650



Table 2 (continued)

Handle	USBM 350	NBS 500	ACS 18	USBM 592	USGS 1259	NBS 270	JANAF 2nd	USBM 672
Element	Kelly 1932 cal/mol-K	Rossini et al. 1952 cal/mol-K	Stull and Sinke 1956 cal/mol-K	Kelley and King 1961 cal/mol-K	Robie and Waldbaum 1968 cal/mol-K	NBS 270-3 to 270-8 1968-1981 cal/mol-K	Stull and Prophet 1971 cal/mol-K	Pankratz 1982 cal/mol-K
Mo	6.83	6.83	6.83	6.82	6.85	6.85	6.837	6.850
N2	45.8	45.767	45.77	45.77	45.77	45.77	45.77	45.770
Na	12.2	12.2	12.21	12.24	12.24	12.24	12.298	12.298
Nb		8.3	8.73	9.0	8.70	8.70		8.700
Nd			17.50	17.5		17.1		17.100
Ne	35.0	34.948	34.95	34.95		34.9471		34.947
Ni	7.12	7.20	7.14	7.14	7.14	7.14		7.140
No								
Np								12.060
O2	49.03	49.003	49.01	49.01	48.996	49.003	49.004	49.005
Os	7.8	7.8	7.80	7.8		7.8		7.800
P		10.6	(red) 5.46	9.80	(red)5.45	9.82	(red)5.450	9.820
Pa			12.40	12.4		12.4		12.400
Pb	15.63	15.51	15.49	15.49	15.55	15.49	15.484	15.490
Pd	8.9	8.9	9.05	9.06		8.98		9.013
Pm			17.21	17.2				
Po			15.00	15.0				
Pr			17.45	17.6		17.5		17.670
Pt	10.0	10.0	10.00	9.95	9.95	9.95		9.950
Pu								13.420
Ra		17	17.00	17.0		17		
Rb		16.6	18.22	18.1		18.35		18.350
Re		10	8.89	8.89		8.81		8.730
Rh	7.6	7.6	7.60	7.53		7.53		7.542
Rn	42.10	42.10	42.10	42.10		42.09		
Ru	6.9	6.9	6.90	6.82		6.82		6.839
S	7.6	7.62	7.62	7.62	7.60	7.60	7.631	7.661
Sb	10.5	10.5	10.92	10.92	10.92	10.92		10.880
Sc			9.00	9.0		8.28		8.280
Se		10.0	10.15	10.14	10.144	10.144		10.144

Table 2 (continued)

Handle	USBM 350	NBS 500	ACS 18	USBM 592	USGS 1259	NBS 270	JANAF 2nd	USBM 672
Element	Kelly 1932 cal/mol-K	Rossini et al. 1952 cal/mol-K	Stull and Sinke 1956 cal/mol-K	Kelley and King 1961 cal/mol-K	Robie and Waldbaum 1968 cal/mol-K	NBS 270-3 to 270-8 1968-1981 cal/mol-K	Stull and Prophet 1971 cal/mol-K	Pankratz 1982 cal/mol-K
Si	4.50	4.47	4.53	4.51	4.50	4.50	4.498	4.500
Sm			16.28	16.3		16.63		16.630
Sn	12.3	12.3	12.29	12.29	12.32	12.32		12.236
Sr		13.0	12.50	12.5	12.5	12.5		12.500
Ta	9.4	9.9	9.90	9.92		9.92		9.920
Tb			17.46	17.5		17.50		17.520
Tc		9	8.00	8.0				
Te		11.88	11.88	11.88	11.88	11.88		11.880
Th	13.6	13.6	12.76	12.8	12.76	12.76		12.760
Ti	6.6	7.24	7.33	7.30	7.32	7.32	7.325	7.320
Tl	15.5	15.4	15.35	15.35		15.34		15.340
Tm			17.06	17.1		17.69		17.690
U	11.1	12.03	12.03	12.03	12.00	12.00		12.000
V		7.05	7.01	7.02	6.91	6.91		6.915
W	8.0	8.0	8.04	7.80	7.80	7.80	7.806	7.800
Xe	40.51	40.53	40.53	40.53		40.529		40.530
Y			11.00	11.0		10.62		10.62
Yb			15.00	15.0		14.31		14.300
Zn	9.95	9.95	9.95	9.95	9.95	9.95		9.950
Zr	9.5	9.18	9.29	9.32	9.31	9.32	9.314	9.320
Count	55	73	92	92	50	88	29	88

Table 3. Entropies of the Chemical Elements in Their Standard Reference Forms. The data shown here represent late historical reports from CODATA in the 1970s. They are characterized by the use of Joule units in combination with a standard pressure of 1.0 atm (1.013 bar). This table is taken from workbook TDProperties\_Rev0\_u3.xlsx. Though superseded by the CODATA 1989 report, these data are occasionally cited in the later literature or in tracing the origin of data presented in later literature.

Handle	CODATA 71	CODATA 73	CODATA 75	CODATA 76	CODATA 77
Element	CODATA 1972 J/mol-K	CODATA 1975 J/mol-K	CODATA 1976 J/mol-K	CODATA 1977 J/mol-K	CODATA 1978 J/mol-K
Ac					
Ag		42.55	42.55	42.55	42.55
Al			28.35	28.35	28.35
Am					
Ar	154.732	154.732	154.732	154.732	154.732
As					
At2					
Au					
B			5.90	5.90	5.90
Ba					
Be				9.50	9.50
Bi					
Bk					
Br2	152.210	152.210	152.210	152.210	152.210
C	5.74	5.74	5.74	5.74	5.74
Ca				41.6	41.6
Cd					51.80
Ce					
Cf					
Cl2	222.965	222.965	222.965	222.965	222.965
Cm					
Co					
Cr					
Cs		85.23	85.23	85.23	85.23
Cu			33.15	33.15	33.15
Dy					
Er					
Es					
Eu					
F2			202.685	202.685	202.685
Fe					
Fm					
Fr					
Ga					
Gd					
Ge					31.09
H2	130.570	130.570	130.570	130.570	130.570
He	126.039	126.039	126.039	126.039	126.039

Table 3 (continued)

Handle	CODATA 71	CODATA 73	CODATA 75	CODATA 76	CODATA 77
Element	CODATA 1972 J/mol-K	CODATA 1975 J/mol-K	CODATA 1976 J/mol-K	CODATA 1977 J/mol-K	CODATA 1978 J/mol-K
Hf					
Hg					75.90
Ho					
I2	116.139	116.139	116.139	116.139	116.139
In					
Ir					
K		64.68	64.68	64.68	64.68
Kr	163.971	163.971	163.971	163.971	163.971
La					
Li		29.12	29.12	29.12	29.12
Lr					
Lu					
Md					
Mg				32.68	32.68
Mn					
Mo					
N2	191.502	191.502	191.502	191.502	191.502
Na		51.30	51.30	51.30	51.30
Nb					
Nd					
Ne	146.214	146.214	146.214	146.214	146.214
Ni					
No					
Np					
O2	205.037	205.037	205.037	205.037	205.037
Os					
P				41.09	41.09
Pa					
Pb					64.80
Pd					
Pm					
Po					
Pr					
Pt					
Pu					
Ra					
Rb		76.78	76.78	76.78	76.78
Re					
Rh					
Rn					
Ru					
S					32.054
Sb					

Table 3 (continued)

Handle	CODATA 71	CODATA 73	CODATA 75	CODATA 76	CODATA 77
Element	CODATA 1972 J/mol-K	CODATA 1975 J/mol-K	CODATA 1976 J/mol-K	CODATA 1977 J/mol-K	CODATA 1978 J/mol-K
Sc					
Se					
Si			18.81	18.81	18.81
Sm					
Sn					51.18
Sr					
Ta					
Tb					
Tc					
Te					
Th				53.39	53.39
Ti					
Tl					
Tm					
U				50.20	50.20
V					
W					
Xe	169.573	169.573	169.573	169.573	169.573
Y					
Yb					
Zn		41.63	41.63	41.63	41.63
Zr					
Count	12	19	24	30	36

Table 4. Key Thermodynamic Data from SUPCRT92 as Represented by the slop98.dat Data File. These data are in calorie units and correspond to a standard pressure of 1 bar. This table is taken from workbook TDProperties\_Rev0\_u3.xlsx. The data shown for H<sub>2</sub>O(l) (light blue background) are not in the data file, but generated by a model built into the SUPCRT92 software. Light orange background marks items of concern. The data here for SiO<sub>2</sub>(aq) were superseded in the construction of the first Yucca Mountain Project database

<b>SUPCRT92 (slop98.dat, 1998)</b>			
<b>Species</b>	<b>ΔG°<sub>f</sub> kcal/mol</b>	<b>ΔH°<sub>f</sub> kcal/mol</b>	<b>S° cal/mol-K</b>
O2(g)	0.0	0.0	49.029
H+	0.	0.	0.
OH-	-37.595	-54.977	-2.56
H2O(l)	-56.688	-68.317	16.7
F-	-67.340	-80.150	-3.15
Cl-	-31.379	-39.933	13.56
Br-	-24.870	-29.040	19.80
I-	-12.410	-13.600	25.50
SO4--	-177.930	-217.400	4.50
HS-	2.860	-3.850	16.3
NO3-	-26.507	-49.429	35.12
NH3(aq)	-6.383	-19.440	25.770
NH4+	-18.990	-31.850	26.57
PO4---	-243.500	-305.300	-53.0
HPO4--	-260.310	-308.815	-8.0
H2PO4-	-270.140	-309.820	21.6
H3PO4(aq)	-273.100	-307.920	38.000
CO2(aq)	-92.250	-98.900	28.100
CO3--	-126.191	-161.385	-11.95
HCO3-	-140.282	-164.898	23.53
SiO2(aq)	-199.190	-209.775	18.000
B(OH)3(aq)	-231.540	-256.820	37.000
BO2-	-162.240	-184.600	-8.9
Al+++	-115.609	-126.834	-77.7
AlO2-	-198.693	-222.125	-7.22
Pb++	-5.710	0.220	4.2
Zn++	-35.200	-36.660	-26.2
Cu+	11.950	17.132	9.7
Cu++	15.675	15.700	-23.2
Ni++	-10.900	-12.900	-30.8
Co++	-13.000	-13.900	-27.0
Fe++	-21.870	-22.050	-25.3
Fe+++	-4.120	-11.850	-66.3
Mn++	-55.100	-52.900	-16.2
Mg++	-108.505	-111.367	-33.00
Ca++	-132.120	-129.800	-13.50
Sr++	-134.760	-131.670	-7.53
Ba++	-134.030	-128.500	2.3
Ra++	-134.200	-126.100	12.9

Table 4 (continued)

SUPCRT92 (slop98.dat, 1998)			
Species	$\Delta G^\circ_f$ kcal/mol	$\Delta H^\circ_f$ kcal/mol	$S^\circ$ cal/mol-K
Li+	-69.933	-66.552	2.70
Na+	-62.591	-57.433	13.96
K+	-67.510	-60.270	24.15
Rb+	-67.800	-60.020	28.8
Cs+	-69.710	-61.670	31.75

P(white)			
P(red)			
Quartz	-204.646	-217.650	9.880
Corundum	-374.824	-397.145	12.180
Gibbsite	-276.168	-309.065	16.750
AlCl <sub>3</sub> .6H <sub>2</sub> O			
Andalusite	-580.587	-615.866	22.200
Kyanite	-580.956	-616.897	20.000
Sillimanite	-580.091	-615.099	23.130
Calcite	-269.880	-288.552	22.150

Table 5. Key Thermodynamic Data from SUPCRT92 (as represented by the *slop98.dat* data file but converted to Joule units) and from NEA-TDB. This table is taken from workbook *TDProperties\_Rev0\_u3.xlsx*. Light orange background marks items of concern (including discrepant values). The SUPCRT92 data for aqueous phosphate species (red background) have been discredited.

SUPCRT92 ( <i>slop98.dat</i> , 1998)				NEA-TDB (through vol. 12)			
Species	$\Delta G^\circ_f$ kJ/mol	$\Delta H^\circ_f$ kJ/mol	$S^\circ$ J/mol-K	Species	$\Delta G^\circ_f$ kJ/mol	$\Delta H^\circ_f$ kJ/mol	$S^\circ$ J/mol-K
O2(g)	0.000	0.000	205.137	O2(g)	0.000	0.000	205.152
H+	0.000	0.000	0.000	H+	0.000	0.000	0.000
OH-	-157.297	-230.024	-10.711	OH-	-157.220	-230.015	-10.900
H2O(l)	-237.183	-285.838	69.873	H2O(l)	-237.140	-285.830	69.950
F-	-281.751	-335.348	-13.180	F-	-281.523	-335.350	-13.800
Cl-	-131.290	-167.080	56.735	Cl-	-131.217	-167.080	56.600
Br-	-104.056	-121.503	82.843	Br-	-103.850	-121.410	82.550
I-	-51.923	-56.902	106.692	I-	-51.724	-56.780	106.450
SO4--	-744.459	-909.602	18.828	SO4--	-744.004	-909.340	18.500
HS-	11.966	-16.108	68.199	HS-	12.243	-16.300	67.000
NO3-	-110.905	-206.811	146.942	NO3-	-110.794	-206.850	146.700
NH3(aq)	-26.706	-81.337	107.822	NH3(aq)	-26.673	-81.170	109.040
NH4+	-79.454	-133.260	111.169	NH4+	-79.398	-133.260	111.170
PO4--	-1018.804	-1277.375	-221.752	PO4--	-1025.491	-1284.400	-220.970
HPO4--	-1089.137	-1292.082	-33.472	HPO4--	-1095.985	-1299.000	-33.500
H2PO4-	-1130.266	-1296.287	90.374	H2PO4-	-1137.152	-1302.600	92.500
H3PO4(aq)	-1142.650	-1288.337	158.992	H3PO4(aq)	-1149.367	-1294.120	161.912
CO2(aq)	-385.974	-413.798	117.570	CO2(aq)	-385.970	-413.260	119.360
CO3--	-527.983	-675.235	-49.999	CO3--	-527.900	-675.230	-50.000
HCO3-	-586.940	-689.933	98.450	HCO3-	-586.845	-689.930	98.400
SiO2(aq)	-833.411	-877.699	75.312	Si(OH)4(aq)	-1307.735	-1456.960	189.973
B(OH)3(aq)	-968.763	-1074.535	154.808	B(OH)3(aq)	-969.268	-1072.800	162.400
BO2-	-678.812	-772.366	-37.238	B(OH)4-			
Al+++	-483.708	-530.673	-325.097	Al+++	-491.507	-538.400	-325.000
AlO2-	-831.332	-929.371	-30.208	Al(OH)4-			
Pb++	-23.891	0.920	17.573	Pb++	-24.238	0.920	18.500
Zn++	-147.277	-153.385	-109.621	Zn++	-147.203	-153.390	-109.800
Cu+	49.999	71.680	40.585	Cu+			
Cu++	65.584	65.689	-97.069	Cu++	65.040	64.900	-98.000
Ni++	-45.606	-53.974	-128.867	Ni++	-45.773	-55.012	-131.800
Co++	-54.392	-58.158	-112.968	Co++			
Fe++	-91.504	-92.257	-105.855	Fe++			
Fe+++	-17.238	-49.580	-277.399	Fe+++			
Mn++	-230.538	-221.334	-67.781	Mn++			
Mg++	-453.985	-465.960	-138.072	Mg++	-455.375	-467.000	-137.000
Ca++	-552.790	-543.083	-56.484	Ca++	-552.806	-543.000	-56.200
Sr++	-563.836	-550.907	-31.506	Sr++	-563.864	-550.900	-31.500
Ba++	-560.782	-537.644	9.623	Ba++	-557.656	-534.800	8.400
Ra++	-561.493	-527.602	53.974	Ra++			
Li+	-292.600	-278.454	11.297	Li+	-292.918	-278.470	12.240
Na+	-261.881	-240.300	58.409	Na+	-261.953	-240.340	58.450



Table 5 (continued)

SUPCRT92 (slop98.dat, 1998)			
Species	$\Delta G^\circ_f$ kJ/mol	$\Delta H^\circ_f$ kJ/mol	$S^\circ$ J/mol-K
K+	-282.462	-252.170	101.044
Rb+	-283.675	-251.124	120.499
Cs+	-291.667	-258.027	132.842

NEA-TDB (through vol. 12)			
Species	$\Delta G^\circ_f$ kJ/mol	$\Delta H^\circ_f$ kJ/mol	$S^\circ$ J/mol-K
K+	-282.510	-252.140	101.200
Rb+			
Cs+	-291.456	-258.000	132.100

P(white)			
P(red)			
Quartz	-856.239	-910.648	41.338
Corundum	-1568.264	-1661.655	50.961
Gibbsite	-1155.487	-1293.128	70.082
AlCl <sub>3</sub> .6H <sub>2</sub> O			
Andalusite	-2429.176	-2576.783	92.885
Kyanite	-2430.720	-2581.097	83.680
Sillimanite	-2427.101	-2573.574	96.776
Calcite	-1129.178	-1207.302	92.676

P(white)	0.000	0.000	41.090
P(red)		-7.500	
Quartz	-856.287	-910.700	41.460
Corundum	-1582.257	-1675.700	50.920
Gibbsite			
AlCl <sub>3</sub> .6H <sub>2</sub> O			
Andalusite			
Kyanite			
Sillimanite			
Calcite			

Table 6. Correction of Data for SiO<sub>2</sub>(aq) and Quartz from the “Fournier” Paradigm to the “Rimstidt” Paradigm. The correction for quartz is quite small. This correction was made in the construction of the first Yucca Mountain Project database. R =Rimstidt, F = Fournier.

		$\Delta G^{\circ}_f$ kcal/mol	$\Delta H^{\circ}_f$ kcal/mol	$S^{\circ}$ cal/mol-K
"Fournier"	SiO <sub>2</sub> (aq)	-199.190	-209.775	18.000
"Rimstidt"	SiO <sub>2</sub> (aq)	-199.540	-212.179	11.128
	$\Delta(R-F)$	-0.350	-2.404	-6.872

		$\Delta G^{\circ}_f$ kJ/mol	$\Delta H^{\circ}_f$ kJ/mol	$S^{\circ}$ J/mol-K
	SiO <sub>2</sub> (aq)	-833.411	-877.699	75.312
	SiO <sub>2</sub> (aq)	-834.875	-887.757	46.560
	$\Delta(R-F)$	-1.464	-10.058	-28.752

"Fournier"	Quartz	-204.646	-217.650	9.880
"Rimstidt"	Quartz	-204.656	-217.663	9.904
	$\Delta(R-F)$	-0.010	-0.013	0.024

	Quartz	-856.239	-910.648	41.338
	"Rimstidt"	-856.281	-910.702	41.438
	Quartz	-0.042	-0.054	0.100

Table 7. Key Thermodynamic Data from the Last Two NBS Efforts (as Represented by the slop98.dat Data File). This table is taken from workbook TDProperties\_Rev0\_u3.xlsx. Data for the preceding and first NBS effort (NBS 500, Rossini et al., 1952) are included in the spreadsheet. The aqueous phosphate species data have been discredited. The Gibbs energy value for  $H_2PO_4^-$  from the NBS 270 series (red background) is likely a typo. Some calorie-Joule units conversions are shown between the left and right tables.

NBS 270-(3-8), Wagman et al. (1968) and others				NBS, Wagman et al. (1982)			
Species	$\Delta G^\circ_f$ kcal/mol	$\Delta H^\circ_f$ kcal/mol	$S^\circ$ cal/mol-K		$\Delta G^\circ_f$ kJ/mol	$\Delta H^\circ_f$ kJ/mol	$S^\circ$ J/mol-K
O2(g)	0	0	49.003		0	0	205.138
H+	0	0	0		0	0	0
OH-	-37.594	-54.970	-2.57		-157.244	-229.994	-10.75
H2O(l)	-56.687	-68.315	16.71		-237.129	-285.830	69.91
F-	-66.64	-79.50	-3.3		-278.79	-332.63	-13.8
Cl-	-31.372	-39.952	13.5		-131.228	-167.159	56.5
Br-	-24.85	-29.05	19.7		-103.96	-121.55	82.4
I-	-12.33	-13.19	26.6		-51.57	-55.19	111.3
SO4--	-177.97	-217.32	4.8		-744.53	-909.27	20.1
HS-	2.88	-4.2	15.0		12.08	-17.6	62.8
NO3-	-26.61	-49.56	35.0		-108.74	-205.0	146.4
NH3(aq)	-6.35	-19.19	26.6		-26.50	-80.29	111.3
NH4+	-18.97	-31.67	27.1	<-----	-79.31	-132.51	113.4
PO4---	-243.5	-305.3	-53.	-243.475	-1018.7	-1277.4	-222.
HPO4--	-260.34	-308.83	-8.0	-260.313	-1089.15	-1292.14	-33.5
H2PO4-	-260.17	-309.82	21.6	-270.143	-1130.28	-1296.29	90.4
H3PO4(aq)	-273.10	-307.92	37.8	-273.074	-1142.54	-1288.34	158.2
CO2(aq)	-92.26	-98.90	28.1		-385.98	-413.80	117.6
CO3--	-126.17	-161.84	-13.6		-527.81	-677.14	-56.9
HCO3-	-140.26	-165.39	21.8		-586.77	-691.99	91.2
H4SiO4(aq)	-314.7	-351.0	43.		-1316.6	-1468.6	180.
H3BO3(aq)	-231.56	-256.29	38.8		-968.75	-1072.32	162.3
B(OH)4-	-275.65	-321.23	24.5		-1153.17	-1344.03	102.5
Al+++	-116.	-127.	-76.9		-485.	-531.	-321.7
Al(OH)4-	-310.2	-356.2	28.		-1305.3	-1502.5	102.9
Pb++	-5.83	-0.4	2.5		-24.43	-1.7	10.5
Zn++	-35.14	-36.78	-26.8		-147.06	-153.89	-112.1
Cu+	11.95	17.13	9.7		49.98	71.67	40.6

Table 7 (continued)

NBS 270-(3-8), Wagman et al. (1968) and others			
Species	$\Delta G^\circ_f$ kcal/mol	$\Delta H^\circ_f$ kcal/mol	$S^\circ$ cal/mol-K
Cu <sup>++</sup>	15.66	15.48	-23.8
Ni <sup>++</sup>	-10.9	-12.9	-30.8
Co <sup>++</sup>	-13.0	-13.9	-27.
Fe <sup>++</sup>	-18.85	-21.3	-32.9
Fe <sup>+++</sup>	-1.1	-11.6	-75.5
Mn <sup>++</sup>	-54.5	-52.76	-17.6
Mg <sup>++</sup>	-108.7	-111.58	-33.0
Ca <sup>++</sup>	-132.30	-129.74	-12.7
Sr <sup>++</sup>	-133.71	-130.45	-7.8
Ba <sup>++</sup>	-134.02	-128.50	2.3
Ra <sup>++</sup>	-134.2	-126.1	13.
Li <sup>+</sup>	-70.10	-66.56	3.2
Na <sup>+</sup>	-62.593	-57.39	14.1
K <sup>+</sup>	-67.70	-60.32	24.5
Rb <sup>+</sup>	-67.87	-60.03	29.04
Cs <sup>+</sup>	-69.79	-61.73	31.80

NBS, Wagman et al. (1982)			
Species	$\Delta G^\circ_f$ kJ/mol	$\Delta H^\circ_f$ kJ/mol	$S^\circ$ J/mol-K
Cu <sup>++</sup>	65.49	64.77	-99.6
Ni <sup>++</sup>	-45.6	-54.0	-128.9
Co <sup>++</sup>	-54.4	-58.2	-113.
Fe <sup>++</sup>	-78.90	-89.1	-137.7
Fe <sup>+++</sup>	-4.7	-48.5	-315.9
Mn <sup>++</sup>	-228.1	-220.75	-73.6
Mg <sup>++</sup>	-454.8	-466.85	-138.1
Ca <sup>++</sup>	-553.58	-542.83	-53.1
Sr <sup>++</sup>	-559.48	-545.80	-32.6
Ba <sup>++</sup>	-560.77	-537.64	9.6
Ra <sup>++</sup>	-561.5	-527.6	54.
Li <sup>+</sup>	-283.98	-278.49	13.4
Na <sup>+</sup>	-261.905	-240.12	59.0
K <sup>+</sup>	-283.27	-252.38	102.5
Rb <sup>+</sup>	-283.98	-251.17	121.50
Cs <sup>+</sup>	-292.02	-258.28	133.05

P(white)	0	0	9.82
P(red)	-2.9	-4.2	5.45
Quartz	-204.75	-217.72	10.00
Corundum	-378.2	-400.5	12.17
Gibbsite	-546.7	-612.5	33.51
AlCl <sub>3</sub> .6H <sub>2</sub> O		-643.3	
Andalusite	-620.8	-655.9	22.28
Kyanite	-620.5	-656.4	20.03
Sillimanite	-627.6	-662.6	22.99
Calcite	-269.80	-288.46	22.2

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-  
1582.389  
-  
2287.393  
-  
2597.427  
-  
2596.172  
-  
2625.878

P(white)	0	0	41.09
P(red)	-12.1	-17.6	22.80
Quartz	-856.64	-910.94	41.84
Corundum	-1582.3	-1675.7	50.92
Gibbsite	-2310.21	-2586.67	136.90
AlCl <sub>3</sub> .6H <sub>2</sub> O	-2261.1	-2691.6	318.0
Andalusite	-2442.66	-2590.27	93.22
Kyanite	-2443.88	-2594.29	83.81
Sillimanite	-2440.99	-2587.76	96.11
Calcite	-1128.79	-1206.92	92.9

Table 8. Key Thermodynamic Data from the Last Two USGS Efforts as Represented by the slop98.dat Data File. This table is taken from workbook TDProperties\_Rev0\_u3.xlsx. Data for the preceding and first USGS effort (Robie and Waldbaum, 1968) are included in the spreadsheet. The aqueous phosphate species data shown here have been discredited. Red background marks known erroneous values. Light orange background marks items of concern.

USGS: Robie et al. (1978)			
Species	$\Delta G^\circ_f$ kJ/mol	$\Delta H^\circ_f$ kJ/mol	$S^\circ$ J/mol-K
O2(g)	0.	0.	205.15
H+	0.	0.	0.
OH-	-157.328	-230.025	-10.71
H2O(l)	-237.141	-285.830	69.95
F-	-281.705	-335.350	-13.18
Cl-	-131.270	-167.080	56.73
Br-	-104.010	-121.500	82.84
I-	-51.915	-56.900	106.70
SO4--	-744.630	-909.270	20.00
HS-	12.100	-16.999	62.80
NO3-	-111.500	-207.400	146.94
NH3(aq)	-26.600	-80.2990	111.00
NH4+	-79.457	-133.260	111.17
PO4---	-1001.550	-1259.550	-222.00
HPO4--			
H2PO4-			
H3PO4(aq)			
H2CO3(aq)	-623.170	-699.650	187.00
CO3--	-527.900	-677.140	-56.90
HCO3-	-586.850	-691.990	91.20
H4SiO4(aq)	-1308.000	-1460.000	180.00
H3BO3(aq)			
H2BO3-			
Al+++	-489.400	-531.000	-308.00
Al(OH)4-			
Pb++	-24.400	-1.700	10.00
Zn++	-147.260	-153.390	-109.60
Cu+	50.000	71.670	41.00

USGS: Robie and Hemingway (1995)			
Species	$\Delta G^\circ_f$ kJ/mol	$\Delta H^\circ_f$ kJ/mol	$S^\circ$ J/mol-K
O2(g)	0.0	0.0	205.15
H+	0.0	0.0	0.00
OH-	-157.3	-230.0	-10.7
H2O(l)	-237.1	-285.8	70.0
F-	-281.5	-335.4	-13.8
Cl-	-131.2	-167.1	56.60
Br-	-103.8	-121.4	82.55
I-	-51.7	-56.8	106.45
SO4--	-744.0	-909.3	18.5
HS-	44.8	16.3	67.0
NO3-	-110.8	-206.9	146.7
NH3(aq)			
NH4+	-79.4	-133.3	111.17
PO4---	-1001.6	-1259.6	-222.0
HPO4--			
H2PO4-			
H3PO4(aq)			
H2CO3(aq)	-623.2	-699.7	184.7
CO3--	-527.0	-675.2	-50.0
HCO3-	-586.8	-689.9	98.4
H4SiO4(aq)	-1307.8	-1460.0	180.0
H3BO3(aq)			
B(OH)4-			
Al+++	-489.4	-538.4	-332.
Al(OH)4-			
Pb++	-24.2	0.9	18.5
Zn++	-147.3	-153.4	-109.8
Cu+	50.0	71.7	40.60

Table 8 (continued)

USGS: Robie et al. (1978)			
Species	$\Delta G^\circ_f$ kJ/mol	$\Delta H^\circ_f$ kJ/mol	$S^\circ$ J/mol-K
Cu <sup>++</sup>	65.520	64.770	-99.60
Ni <sup>++</sup>	-45.600	-54.000	-129.00
Co <sup>++</sup>	-54.400	-58.200	-113.00
Fe <sup>++</sup>	-78.870	-89.100	-138.00
Fe <sup>+++</sup>	-4.600	-48.500	-316.00
Mn <sup>++</sup>	-228.00	-220.700	-73.60
Mg <sup>++</sup>	-454.800	-466.850	-138.00
Ca <sup>++</sup>	-553.540	-542.830	-53.10
Sr <sup>++</sup>	-559.440	-545.800	-33.00
Ba <sup>++</sup>	-560.740	-537.640	9.60
Ra <sup>++</sup>			
Li <sup>+</sup>	-292.620	-278.455	11.30
Na <sup>+</sup>	-261.900	-240.300	58.41
K <sup>+</sup>	-282.490	-252.170	101.04
Rb <sup>+</sup>	-291.715	-251.120	120.46
Cs <sup>+</sup>	-283.625	-258.040	132.84

P(white)			
P(red)	0.	0.	22.85
Quartz	-856.288	-910.700	41.46
Corundum	-1582.228	-1675.700	50.92
Gibbsite	-1154.889	-1293.128	68.44
AlCl <sub>3</sub> .6H <sub>2</sub> O			
Andalusite	-2439.892	-2587.525	93.22
Kyanite	-2441.276	-2591.730	83.76
Sillimanite	-2438.988	-2585.760	96.11
Calcite	-1128.842	-1207.370	91.71

USGS: Robie and Hemingway (1995)			
Species	$\Delta G^\circ_f$ kJ/mol	$\Delta H^\circ_f$ kJ/mol	$S^\circ$ J/mol-K
Cu <sup>++</sup>	65.1	64.9	-98.0
Ni <sup>++</sup>	-45.6	-54.0	-128.9
Co <sup>++</sup>			
Fe <sup>++</sup>	-90.0	-91.1	-107.1
Fe <sup>+++</sup>	-16.7	-49.9	-280.0
Mn <sup>++</sup>	-228.1	-220.8	-73.60
Mg <sup>++</sup>	-455.4	-467.0	-137.0
Ca <sup>++</sup>	-553.6	-543.0	-56.2
Sr <sup>++</sup>	-563.8	-550.9	-31.5
Ba <sup>++</sup>	-555.4	-532.5	8.40
Ra <sup>++</sup>			
Li <sup>+</sup>	-292.9	-278.5	12.24
Na <sup>+</sup>	-261.5	-240.3	58.45
K <sup>+</sup>	-282.5	-252.1	101.20
Rb <sup>+</sup>			
Cs <sup>+</sup>	-291.5	-258.0	132.1

P(white)	0.0	0.0	41.09
P(red)			
Quartz	-856.3	-910.7	41.5
Corundum	-1582.3	-1675.7	50.9
Gibbsite	-1154.9	-1293.1	68.4
AlCl <sub>3</sub> .6H <sub>2</sub> O			
Andalusite	-2441.8	-2589.9	91.4
Kyanite	-2443.1	-2593.8	82.8
Sillimanite	-2439.1	-2586.1	95.4
Calcite	-1128.5	-1207.4	91.7

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