

Chemical Modeling of Aqueous Systems II

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Chapter 31

Revised Chemical Equilibrium Data for Major Water—Mineral Reactions and Their Limitations

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A revised, updated summary of equilibrium constants and reaction enthalpies for aqueous ion association reactions and mineral solubilities has been compiled from the literature for common equilibria occurring in natural waters at 0-100°C and 1 bar pressure. The species have been limited to those containing the elements Na, K, Li, Ca, Mg, Ba, Sr, Ra, Fe(II/III), Al, Mn(II,III,IV), Si, C, Cl, S(VI) and F. The necessary criteria for obtaining reliable and consistent thermodynamic data for water chemistry modeling is outlined and limitations on the application of equilibrium computations is described. An important limitation is that minerals that do not show reversible solubility behavior should not be assumed to attain chemical equilibrium in natural aquatic systems.

Chemical modeling results for aqueous systems is dependent on the primary thermodynamic and kinetic data needed to perform the calculations. For aqueous equilibrium computations, a large number of thermodynamic properties of solute-solute, solute-gas and solute-solid reactions are available for application to natural waters and other aqueous systems. Unfortunately, an internally consistent thermodynamic data base that is accurate for all modeling objectives, has not been achieved. Nor is it likely to be achieved in the near future. The best that can be hoped for is a tolerable level of inconsistency, with continuing progress toward the utopian goal through national and international consensus.

An essential attribute of accurate thermodynamic data is its internal consistency (see next section). Another characteristic of such data is that it has been reproduced by different investigators using different techniques and/or methods of evaluation. The tremendous need for such evaluations has been stressed by Stockmayer (1), and Lide (2), because the use of erroneous numerical values can have severe consequences for a highly technological society. Aqueous chemical models, for example, are finding increased use by water quality specialists, geochemists, hydrologists and engineers as an important tool for the interpretation of natural water chemistry.

Research investigators within the Water Resources Division of the U.S. Geological Survey have developed a series of computer

programs that can perform various types of equilibrium computations for chemical reactions in natural waters. Over fifteen years ago the original programs WATCHEM (3), WATEQ (4), and SOLMNEQ (5) were introduced to perform speciation calculations for selected major components in natural waters. Since then, a series of U.S.G.S. reports have provided modifications of the original WATEQ program (6 - 13). The original thermodynamic database for the WATEQ series was published in the first paper (4) as a table of equilibrium constants and enthalpies of reaction. Later reports revised or added selected values to the database but did not reproduce unadjusted numbers. Consequently, no single document contains all values of this extensively revised database. One objective for this paper is to provide such documentation, for both major constituents (Ca, Mg, Na, K, HCO₃, CO₃, Cl, SO₄, F, Si(OH)₄, H and OH) and selected minor and trace elements (Ba, Sr, Ra, Li, Al, Fe(II), Fe(III) and Mn). Further revisions are being planned to include more trace elements. The experience gained from numerous applications of the WATEQ series of programs has affected earlier decisions regarding which components (and reactions should be in the program and how the reactions should be portrayed. Furthermore, progress in thermodynamic data evaluation, and in understanding the behavior of mineral dissolution/precipitation reactions and of redox species, has affected not only the values in the database but also how they are used. The main objectives of this paper are: (1) to document the revised equilibrium constants and their temperature dependencies found most reliable for applications to natural waters; (2) to explain why some mineral reactions are best left out of routine applications of chemical modeling; (3) to explain some of the difficulties inherent in the interpretation of aquatic geochemical processes; and (4) to describe examples of the difficulty of achieving thermodynamic consistency in equilibrium data (e.g., calorimetric vs. solubility data).

REQUIREMENTS FOR THERMODYNAMIC CONSISTENCY

Thermodynamic consistency is achieved when the following criteria are met (14):

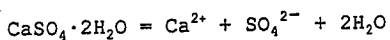
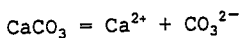
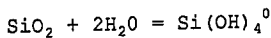
- The fundamental thermodynamic relationships and their consequences are obeyed. This criterion permits the comparison of calorimetric and solubility data.
- Common scales are used for temperature, energy, atomic mass and the fundamental physical constants.
- Conflicts and inconsistencies among measurements are resolved.
- An appropriate mathematical model is chosen to fit all the temperature and pressure dependent data.
- An appropriate aqueous chemical model is chosen to fit all aqueous solution data.
- An appropriate choice of standard states is made and applied to all similar substances.

Numerous discrepancies can be found in the literature when comparing measurements of the same system reported by different investigators or when comparing solubility data with calorimetric, electrochemical or vapor pressure data, etc. There is no universally-accepted aqueous chemical model. There is no universally-accepted model for temperature or pressure dependence of thermodynamic functions. Often the only available measurement

of some property does not adequately characterize the solid or the aqueous phase. Inconsistencies are common among aqueous chemical models and they can be very difficult to resolve. One inconsistency is that non-ideality can be interpreted using different electrolyte theories such as the ion-association theory (15), the specific-ion interaction theory (16, 17), or the ion hydration theory (18). Further inconsistency can arise from neglecting to fit simultaneously all types of solution data (heat measurements, vapor pressure measurements, density measurements, electrochemical measurements, freezing and boiling point measurements) with a single, reliable model utilizing the best available data for the density and dielectric constant of the solvent. An excellent example of a comprehensive approach to resolving such inconsistencies is given in papers by Ananthaswamy and Atkinson (19, 20), in their evaluation of the properties of aqueous calcium chloride. Similar evaluations need to be done for other solutes relevant to natural water chemistry and then correlated where common ions occur. Evaluated aqueous solute data must also be fitted together with solubility and solid phase data in a thermodynamic network (21, 22). In fact, this is the approach used by the Committee on Data for Science and Technology (CODATA). After this evaluation has been done, the entire thermodynamic network must be refitted if a new value of an important property is reported. As a result progress is slow and only a tolerable level of inconsistency can be hoped for. Fortunately, many equilibrium constants reported for the same reaction can be in good agreement in spite of these inconsistencies. All of these inconsistencies need not be totally resolved for the objectives of chemical modeling, although no one has really defined how well thermodynamic properties must be known. The ion-pair data presented in this paper is restricted to the ion-association model which is limited to an upper concentration of about 1 molal because it uses a modified, extended Debye-Hückel expression for the activity coefficients (4). The advantage of this approach is that much more data are available for use in multicomponent, multiphase systems of interest to geochemists and the precision of the data is often better for low ionic strength solutions -- the majority of natural waters.

THE USE OF FREE ENERGIES VS EQUILIBRIUM CONSTANTS

The thermodynamic database for an aqueous chemical model is generally presented as a tabulation of free energies or equilibrium constants. The use of free energies both for the database and to calculate equilibrium constants has been avoided as much as possible in the present compilation because such an approach can introduce much larger errors than the use of equilibrium constants. As examples, free energy-based solubility product constants, for the common minerals quartz, calcite and gypsum, will be compared to values for the same constants based on highly reliable solubility data. Free energy data for these minerals and their associated solutes in the dissolution reactions:



are shown in Table 1, obtained from six important sources: The National Bureau of Standards (NBS, 23); three U.S. Geological Survey (USGS) sources in which the data on quartz are from the recent evaluation by Hemingway (24), the data on calcite are from Robinson *et al.* (25) and the remaining USGS data are from Robie *et*

Table 1. Gibbs free energies of formation from the elements for species in the dissolutions of quartz, calcite and gypsum, and derived solubility product constants at 298.15 K

Species	G_f° (kJ/mol)		
	CODATA	NBS	USGS
Quartz	---	-856.64	-856.288
Calcite	-1129.074	-1128.79	-1130.610
Gypsum	-1797.359	-1797.28	-1797.197
Si(OH) ₄ (aq)	---	-1316.6	-1308.0
Ca ²⁺ ₂ (aq)	-552.803	-553.58	-553.54
CO ₃ ²⁻ (aq)	-527.898	-527.81	-527.90
SO ₄ ²⁻ (aq)	-744.002	-744.53	-744.630
H ₂ O _(l)	-237.141	-237.129	-237.141
logK _{sp} Quartz	---	-2.51	-3.95
logK _{sp} Calcite	-8.47	-8.30	-8.61
logK _{sp} Gypsum	-4.60	-4.36	-4.34

al. (26); and two CODATA Recommended Key Values sources in which the data on calcite and gypsum are from Garvin *et al.* (27) and the remaining CODATA values are from Cox *et al.* (28).

Comparison of the NBS and the USGS log K_{sp} values shows that quartz solubility is discrepant by more than an order of magnitude. The generally accepted solubility at 298.15 K is about 6 mg/L, equivalent to log K_{sp} = -3.98 (29), if we make the safe assumptions that no activity coefficient corrections are needed and that molarity equals molality. Although several percent error may be attached to this solubility value, it cannot possibly be as high as the NBS data implies. The main source of error is the free energy value for silicic acid. The value, discussed in Hemingway (30), must be considered the more reliable because the resulting log K is closer to the measured value.

Calcite solubility product constants range over 0.3 log units. The major tabulated differences are in the free energies of calcite and of the calcium ion. The most reliable measurement and evaluation of calcite solubility is that of Plummer and Busenberg (31). They found log K_{sp} = -8.48(± 0.02) at 298.15 K which agrees excellently with the CODATA value of -8.47. The main source of error can be traced to a 2 kJ/mol difference between the CODATA and USGS values for the enthalpy of formation of calcite from the elements. The recent CODATA revisions of the calcium ion and calcite values take into account many different properties including the Plummer and Busenberg solubility value (31). Hence, they are the most reliable values for this system.

The gypsum solubility product constant, log K_{sp} = -4.58(± 0.015), is known with high precision and accuracy at 298.15 K due to the careful measurements of Lilley and Briggs (32), as well as good agreement with many other measurements (cf. 33). The CODATA free energies are the only ones compatible with the solubility determinations since they were based on several high-quality solubility experiments and on calorimetric data. The USGS free energies are based on NBS data that pre-dates the Wagman *et al.* (23) and CODATA revisions.

The main point of these examples is that the most reliable thermodynamic property is the one obtained by the most direct path, i.e. the one closest to the actual measurement. Free energies of individual phases or species are always derived values, never directly measured ones. Only certain properties, such as heat capacities, heat contents, entropies and volumes are directly measured for a single species or phase. Free energy measurements are measurements of processes and reactions. Reported free energies of individual species are nearly always derived from free

energy measurements of processes such as an EMF measurement or a solubility measurement. Reversing the calculation to obtain a solubility product constant from free energies can introduce additional errors. Hence, the best data for use in chemical modeling will be those values based on reaction equilibria and not those based on free energies of individual reactants and products. When individual free energies have to be used (i.e. when no reaction equilibria data exist) then it becomes very important to tie the values to reaction equilibria that are well-established, as Cox et al. (28) have done. This is not to say that errors and inconsistencies don't appear when interpreting solubility data, especially reducing data from high ionic concentrations, but just that the more direct the measurement, the more reliable the thermodynamic properties are likely to be.

DEBYE-HÜCKEL SOLVENT PARAMETERS

The calculation of activity coefficients for aqueous species requires Debye-Hückel theory to represent long-range electrostatic interactions among ions. These interactions are a function of the density, ρ , the dielectric constant, ϵ , and the temperature of the solvent. All other parameters are either fundamental physical constants or empirical fitting parameters. For example, the Debye-Hückel solvent parameters, A and B, appear in the extended Debye-Hückel equation (14). A and B are both a function of the ρ and ϵ of water. New data and recent evaluations for water and revisions in the fundamental physical constants postdate the original values used in the WATEQ program. Gildseth et al. (34) have evaluated the density of water, from both their measurements (5-80°C) and those of others, to an accuracy of 3 ppm. The function that gives the best fit is:

$$\rho = 1 - \frac{(t - 3.9863)^2(t + 288.9414)}{508929.2(t + 68.12963)} + 0.011445e^{-374.3/t}$$

where t is in degrees Celsius. Uncertainties in this function, over the range 0-100°C, are overshadowed by uncertainties in the value of ϵ .

There have been four recent evaluations of the dielectric constant for water. The earliest is that of Helgeson and Kirkham (35), who fit a single equation to measurements for the pressure and temperature ranges of 1-5000 bars and 0-600°C. Bradley and Pitzer (36) developed an equation for the dielectric constant up to 350°C and 500 bars. The most comprehensive evaluation appears to be that of Uematsu and Franck (37), in which errors were weighted according to temperature range for the total range of 0-350°C and up to 5 kbar. Finally, Khodakovskiy and Dorofeyeva (38) evaluated the dielectric constant from 0-300°C and up to 5 kbar. Ananthaswamy and Atkinson (19) point out that the Bradley and Pitzer (36) equation agrees excellently with the IUPAC recommended values (39), it does not depend on the density or saturation pressure of water as do other equations, and seems a reasonable compromise compared to other values. On the other hand, comparing results from the four procedures over the range of 0-100°C, deviations are not greater than 0.1%. All of these equations are quite lengthy because of the large range of temperature and pressure to which they have been fitted. The temperature range is limited to 0-100°C in this paper and we have chosen the Uematsu and Franck (37) equation, modified as follows:

$$\epsilon = 2727.586 + 0.6224107T - 466.9151 \ln T - 52000.87/T$$

This fits to within 0.01 units of the empirical dielectric constant

(about 0.013%) up to 100°C and agrees quite well with the results of other published evaluations.

REVISED EQUILIBRIUM DATA

The thermodynamic data cited in Table 2 (at the end of this discussion) are restricted to 0-100°C and 1 bar (100 kPa) pressure, standard state conditions for solids and infinite dilution reference state for aqueous species. The mineral and aqueous species have been limited to those applicable to natural waters that contain the following elements: Na, K, Li, Ca, Mg, Ba, Sr, Ra, Fe, Al, Mn, Si, C, Cl, S and F. Only sulfate is considered for sulfur species, but both Fe(II) and Fe(III) species are tabulated. No solid solution models are considered. A range of solubility product constants is given for minerals whose solubilities depend significantly on the "degree of crystallinity," i.e. particle size effects, order-disorder phenomena and defect structures. These minerals are dolomite, siderite, rhodocrosite, gibbsite, ferrihydrite/goethite and quartz/chalcedony. [It now appears that the reported range of solubilities for quartz and chalcedony (microcrystalline quartz) reflects crystal ordering and particle size effects for the same basic structure (S.R. Gislason and R.O. Fournier, pers. comm.)]. Kaolinite, sepiolite and kerolite are also expected to be affected by the degree of crystallinity, but inadequate data exist to describe these effects at this time. Enthalpies of reaction are given in kcal/mol because the programs were originally set up with these units. Equilibrium constants are generally given to one more figure than is significant for purposes of avoiding round-off errors.

In the past, speciation computations applied to water analyses often included ion activity product (IAP) values and saturation indices for minerals that have never displayed reversible solubility behavior either in laboratory studies or in natural waters. Some of these minerals are unstable at 298 K and 1 bar, others dissolve incongruently, and still others are not thermodynamically identifiable phases in the traditional phase rule sense. If reversibility has never been shown and there is good reason to believe that they do not attain equilibrium solubility, they should be deleted from equilibrium-based modeling computations and from the interpretation of low-temperature equilibrium mineral assemblages (41). For example, mineral groups such as smectites, illites and micas have never been shown to control water composition as reflected by a constant IAP for a known composition of that mineral in an aquifer where water composition has significantly varied. Such demonstrations, however, are plentiful for minerals such as gypsum and calcite. Consequently, the following minerals or mineral groups are being deleted from the present compilation: smectites, illites, chlorites, micas, feldspars, amphiboles, pyroxenes and pyrophyllite. Talc also is deleted because it is only known to form in brines at low temperatures and such high ionic strength solutions are outside of the range of applicability of the chosen chemical model. It is important to remember that although natural water systems may not achieve equilibrium saturation with respect to this list of silicates, these minerals may still affect the overall water-rock mass balance relationship along a flow path, as might be described by the models developed by Garrels and Mackenzie (42) and Parkhurst et al. (43). Important chemical components can always be added or removed from a water body without achieving reversible solubility control. This partial equilibrium condition exists when the chemical potentials of some components in a system reach equilibrium while others do not (e.g. calcite and barite may reach equilibrium solubility but co-existing biotite or plagioclase may never reach this state). The advantages of both approaches should

Table 2. Summary of Revised Thermodynamic Data. I. Fluoride and Chloride Species

Reaction	ΔH_f^0 (kcal/mol)	log K	Ref.	Reaction	ΔH_f^0 (kcal/mol)	log K	Ref.
$H^+ + F^- = HF^0$	3.18	3.18	(a)	$Al^{3+} + F^- = AlF^{2+}$	1.06	7.0	(54)
$H^+ + 2F^- = HF_2^-$	4.55	3.76	(7)	$Al^{3+} + 2F^- = AlF_2^+$	1.98	12.7	(54)
$Na^+ + F^- = NaF^0$	----	-0.24	(49)	$Al^{3+} + 3F^- = AlF_3^0$	2.16	16.8	(54)
$Ca^{2+} + F^- = CaF^+$	4.12	0.94	(50)	$Al^{3+} + 4F^- = AlF_4^-$	2.20	19.4	(54)
$Mg^{2+} + F^- = MgF^+$	3.2	1.82	(b)	$Al^{3+} + 5F^- = AlF_5^{2-}$	1.84	20.6	(54)
$Mn^{2+} + F^- = MnF^+$	----	0.84	(23)	$Al^{3+} + 6F^- = AlF_6^{3-}$	-1.67	20.6	(54)
$Fe^{2+} + F^- = FeF^+$	---	1.0	(c)				
$Fe^{3+} + F^- = FeF^{2+}$	2.7	6.2	(50)	$Si(OH)_4 + 4H^+ + 6F^-$	-16.26	30.18	(55)
$Fe^{3+} + 2F^- = FeF_2^+$	4.8	10.8	(50)	$= SiF_6^{2-} + 4H_2O$			
$Fe^{3+} + 3F^- = FeF_3^0$	5.4	14.0	(50)	$Fe^{2+} + Cl^- = FeCl^+$	----	0.14	(d)
$Mn^{2+} + Cl^- = MnCl^+$	----	0.61	(23)	$Fe^{3+} + Cl^- = FeCl^{2+}$	5.6	1.48	(52)
$Mn^{2+} + 2Cl^- = MnCl_2^0$	----	0.25	(23)	$Fe^{3+} + 2Cl^- = FeCl_2^+$	----	2.13	(52)
$Mn^{2+} + 3Cl^- = MnCl_3^-$	----	-0.31	(23)	$Fe^{3+} + 3Cl^- = FeCl_3^0$	----	1.13	(56)

Mineral	Reaction	ΔH_f^0 (kcal/mol)	log K	Ref.
Cryolite	$Na_3AlF_6 = 3Na^+ + Al^{3+} + 6F^-$	9.09	-33.84	(e)
Fluorite	$CaF_2 = Ca^{2+} + 2F^-$	4.69	-10.6	(f)

Redox Potentials	ΔH_f^0 (kcal/mol)	E^0 (volts)	log K	Ref.
$Fe^{2+} = Fe^{3+} + e^-$	9.68	-0.770	-13.02	(g)
$Mn^{2+} = Mn^{3+} + e^-$	25.8	-1.51	-25.51	(h)

Reaction	Analytical Expressions for Temperature Dependence	Ref.
$H^+ + F^- = HF^0$	$\log K_{HF} = -2.033 + 0.012645T + 429.01/T$	(a)
$CaF_2 = Ca^{2+} + 2F^-$	$\log K_{FLUORITE} = 66.348 - 4298.2/T - 25.271 \log T$	(f)

References for fluoride and chloride species

a.) log K, ΔH_f° and temperature dependence from Naumov *et al.* (47) in agreement with the critical evaluations by Bond and Hefter (48) and Garvin *et al.* (27); b.) log K from Sillen and Martell (51), ΔH_f° from Smith and Martell (52); c.) estimated from a measurement of 0.83 at I = 1 M and the tendency for divalent fluorides to have log K \approx 1 (53); d.) based on Davison (108) which agrees well with Turner *et al.* (109); e.) log K from Roberson and Hem (57) and ΔH_f° from (58) for cryolite and from (28) for ions; f.) based on reference (50) but forced to go through log K = -10.6 at 298.15 K to be in agreement with the solubility data of Macaskill and Bates (59) and Brown and Roberson (60); g.) E^0 and log K from Whittemore and Langmuir (61), ΔH_f° from V. Parker, personal communication; h.) based on (23) in agreement with Bard *et al.* (62).

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Table 2. Summary of Revised Thermodynamic Data. II. Oxide and Hydroxide Species

Reaction	ΔH_f° (kcal/mol)	log K	Ref.	Reaction	ΔH_f° (kcal/mol)	log K	Ref.
$H_2O = H^+ + OH^-$	13.362	-14.000	(a)	$Fe^{3+} + H_2O = FeOH^{2+} + H^+$	10.4	-2.19	(65)
$Li^+ + H_2O = LiOH^0 + H^+$	0.0	-13.64	(65)	$Fe^{3+} + 2H_2O = Fe(OH)_2^+ + 2H^+$	17.1	-5.67	(c)
$Na^+ + H_2O = NaOH^0 + H^+$	0.0	-14.18	(65)	$Fe^{3+} + 3H_2O = Fe(OH)_3^0 + 3H^+$	24.8	-12.56	(c)
$K^+ + H_2O = KOH^0 + H^+$	---	-14.46	(65)	$Fe^{3+} + 4H_2O = Fe(OH)_4^- + 4H^+$	31.9	-21.6	(c)
$Ca^{2+} + H_2O = CaOH^+ + H^+$	---	-12.78	(b)	$2Fe^{3+} + 2H_2O = Fe_2(OH)_4^{2+} + 2H^+$	13.5	-2.95	(65)
$Mg^{2+} + H_2O = MgOH^+ + H^+$	---	-11.44	(65)	$3Fe^{3+} + 4H_2O = Fe_3(OH)_4^{5+} + 4H^+$	14.3	-6.3	(65)
$Sr^{2+} + H_2O = SrOH^+ + H^+$	---	-13.29	(65)	$Al^{3+} + H_2O = AlOH^{2+} + H^+$	11.49	-5.00	(54)
$Ba^{2+} + H_2O = BaOH^+ + H^+$	---	-13.47	(65)	$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+$	26.90	-10.1	(54)
$Ra^{2+} + H_2O = RaOH^+ + H^+$	---	-13.49	(66)	$Al^{3+} + 3H_2O = Al(OH)_3^0 + 3H^+$	39.89	-16.9	(54)
$Fe^{2+} + H_2O = FeOH^+ + H^+$	13.2	-9.5	(65)	$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$	42.30	-22.7	(54)
$Mn^{2+} + H_2O = MnOH^+ + H^+$	14.4	-10.59	(65)				

Mineral	Reaction	ΔH_f° (kcal/mol)	log K	Ref.
Portlandite	$Ca(OH)_2 + 2H^+ = Ca^{2+} + 2H_2O$	-31.0	22.8	(65)
Brucite	$Mg(OH)_2 + 2H^+ = Mg^{2+} + 2H_2O$	-27.1	16.84	(65)
Pyrolusite	$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	-65.11	41.38	(d)
Hausmanite	$Mn_3O_4 + 8H^+ + 2e^- = 3Mn^{2+} + 4H_2O$	-100.64	61.03	(d)
Manganite	$MnOOH + 3H^+ + e^- = Mn^{2+} + 2H_2O$	----	25.34	(23)
Pyrochroite	$Mn(OH)_2 + 2H^+ = Mn^{2+} + 2H_2O$	----	15.2	(65)
Gibbsite (crystalline)	$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	-22.8	8.11	(69)
Gibbsite(microcrystalline)	$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	(-24.5)	9.35	(e)
Al(OH) ₃ (amorphous)	$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	(-26.5)	10.8	(f)
Goethite	$FeOOH + 3H^+ = Fe^{3+} + 2H_2O$	----	-1.0	(72)
Ferrihydrite(amorphous to microcrystalline)	$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$	----	3.0 to 5.0	(g)

Reaction	Analytical Expressions for Temperature Dependence	Ref.
$H_2O = H^+ + OH^-$	$\log K_w = -283.9710 + 13323.00/T - 0.05069842T + 102.24447 \log T - 1119669/T^2$	(a)
$Al^{3+} + H_2O = AlOH^{2+} + H^+$	$\log K_1 = -38.253 - 656.27/T + 14.327 \log T$	(54)
$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+$	$\log \beta_2 = 88.500 - 9391.6/T - 27.121 \log T$	(54)
$Al^{3+} + 3H_2O = Al(OH)_3^0 + 3H^+$	$\log \beta_3 = 226.374 - 18247.8/T - 73.597 \log T$	(54)
$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$	$\log \beta_4 = 51.578 - 11168.9/T - 14.865 \log T$	(54)

References for oxide and hydroxide species

a.) refitted from Olafsson and Olafsson (63), in good agreement with Marshall and Franck (64); b.) CODATA compatible (27), in good agreement with (65); c.) log K from (65) except log β_3 is corrected to I = 0 from Kester *et al.* (67) and enthalpies are estimated from free energies of reaction and entropies estimated from a correlation plot; d.) Robie and Hemingway (68) using ion values from (23); e.) Hem and Roberson (70) for log K and enthalpy estimated by assuming that it changes by the same amount as the free energy; f.) Feitknecht and Schindler (71) for log K and enthalpy derived as above and considered highly uncertain; g.) data based on the range of reported values from (72), Schwertmann and Taylor (73) and Norvell and Lindsay (74).

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Table 2. Summary of Revised Thermodynamic Data. III. Carbonate Species

Reaction	ΔH_f° (kcal/mol)	log K	Ref.	Reaction	ΔH_f° (kcal/mol)	log K	Ref.
$\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq})$	-4.776	-1.468	(31)	$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3^0$	3.545	3.224	(31)
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-$	2.177	-6.352	(31)	$\text{Mg}^{2+} + \text{CO}_3^{2-} = \text{MgCO}_3^0$	2.713	2.98	(80)
$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	3.561	-10.329	(31)	$\text{Sr}^{2+} + \text{CO}_3^{2-} = \text{SrCO}_3^0$	5.22	2.81	(76)
$\text{Ca}^{2+} + \text{HCO}_3^- = \text{CaHCO}_3^+$	2.69	1.106	(31)	$\text{Ba}^{2+} + \text{CO}_3^{2-} = \text{BaCO}_3^0$	3.55	2.71	(77)
$\text{Mg}^{2+} + \text{HCO}_3^- = \text{MgHCO}_3^+$	0.79	1.07	(75)	$\text{Mn}^{2+} + \text{CO}_3^{2-} = \text{MnCO}_3^0$	---	4.90	(81)
$\text{Sr}^{2+} + \text{HCO}_3^- = \text{SrHCO}_3^+$	6.05	1.18	(76)	$\text{Fe}^{2+} + \text{CO}_3^{2-} = \text{FeCO}_3^0$	---	4.38	(53)
$\text{Ba}^{2+} + \text{HCO}_3^- = \text{BaHCO}_3^+$	5.56	0.982	(77)	$\text{Na}^+ + \text{CO}_3^{2-} = \text{NaCO}_3^-$	8.91	1.27	(82)
$\text{Mn}^{2+} + \text{HCO}_3^- = \text{MnHCO}_3^+$	---	1.95	(78)	$\text{Na}^+ + \text{HCO}_3^- = \text{NaHCO}_3^-$	---	-0.25	(15)
$\text{Fe}^{2+} + \text{HCO}_3^- = \text{FeHCO}_3^+$	---	2.0	(79)	$\text{Ra}^{2+} + \text{CO}_3^{2-} = \text{RaCO}_3^0$	1.07	2.5	(66)
Mineral	Reaction	ΔH_f° (kcal/mol)	log K	Ref.			
Calcite	$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-2.297	-8.480	(31)			
Aragonite	$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-2.589	-8.336	(31)			
Dolomite(Ordered)	$\text{CaMg}(\text{CO}_3)_2 = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$	-9.436	-17.09	(a)			
Dolomite(Disordered)	$\text{CaMg}(\text{CO}_3)_2 = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$	-11.09	-16.54	(b)			
Strontianite	$\text{SrCO}_3 = \text{Sr}^{2+} + \text{CO}_3^{2-}$	-0.40	-9.271	(76)			
Siderite(crystalline)	$\text{FeCO}_3 = \text{Fe}^{2+} + \text{CO}_3^{2-}$	-2.48	-10.89	(c)			
Siderite(precipitated)	$\text{FeCO}_3 = \text{Fe}^{2+} + \text{CO}_3^{2-}$	---	-10.45	(d)			
Witherite	$\text{BaCO}_3 = \text{Ba}^{2+} + \text{CO}_3^{2-}$	0.703	-8.562	(77)			
Rhodocrosite(crystalline)	$\text{MnCO}_3 = \text{Mn}^{2+} + \text{CO}_3^{2-}$	-1.43	-11.13	(e)			
Rhodocrosite(synthetic)	$\text{MnCO}_3 = \text{Mn}^{2+} + \text{CO}_3^{2-}$	---	-10.39	(e)			
Reaction	Analytical Expressions for Temperature Dependence						Ref.
$\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq})$	$\log K_H = 108.3865 + 0.01985076T - 6919.53/T - 40.45154 \log T + 669365/T^2$						(31)
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-$	$\log K_1 = -356.3094 - 0.06091964T + 21834.37/T + 126.8339 \log T - 1684915/T^2$						(31)
$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	$\log K_2 = -107.8871 - 0.03252849T + 5151.79/T + 38.92561 \log T - 563713.9/T^2$						(31)
$\text{Ca}^{2+} + \text{HCO}_3^- = \text{CaHCO}_3^+$	$\log K_{\text{CaHCO}_3^+} = 1209.120 + 0.31294T - 34765.05/T - 478.782 \log T$						(31)
$\text{Mg}^{2+} + \text{HCO}_3^- = \text{MgHCO}_3^+$	$\log K_{\text{MgHCO}_3^+} = -59.215 + 2537.455/T + 20.92298 \log T$						(75)
$\text{Sr}^{2+} + \text{HCO}_3^- = \text{SrHCO}_3^+$	$\log K_{\text{SrHCO}_3^+} = -3.248 + 0.014867T$						(76)
$\text{Ba}^{2+} + \text{HCO}_3^- = \text{BaHCO}_3^+$	$\log K_{\text{BaHCO}_3^+} = -3.0938 + 0.013669T$						(77)
$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3^0$	$\log K_{\text{CaCO}_3^0} = -1228.732 - 0.299444T + 35512.75/T + 485.818 \log T$						(31)
$\text{Mg}^{2+} + \text{CO}_3^{2-} = \text{MgCO}_3^0$	$\log K_{\text{MgCO}_3^0} = 0.9910 + 0.00667T$						(80)
$\text{Sr}^{2+} + \text{CO}_3^{2-} = \text{SrCO}_3^0$	$\log K_{\text{SrCO}_3^0} = -1.019 + 0.012826T$						(76)
$\text{Ba}^{2+} + \text{CO}_3^{2-} = \text{BaCO}_3^0$	$\log K_{\text{BaCO}_3^0} = 0.113 + 0.008721T$						(77)
$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$	$\log K_{\text{CALCITE}} = -171.9065 - 0.077993T + 2839.319/T + 71.595 \log T$						(31)
$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$	$\log K_{\text{ARAGONITE}} = -171.9773 - 0.077993T + 2903.293/T + 71.595 \log T$						(31)
$\text{SrCO}_3 = \text{Sr}^{2+} + \text{CO}_3^{2-}$	$\log K_{\text{STRONTIANITE}} = 155.0305 - 7239.594/T - 56.58638 \log T$						(76)
$\text{BaCO}_3 = \text{Ba}^{2+} + \text{CO}_3^{2-}$	$\log K_{\text{WITHERITE}} = 607.642 + 0.121098T - 20011.25/T - 236.4948 \log T$						(77)

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Table 2. Summary of Revised Thermodynamic Data. IV. Silicate Species

Reaction	ΔH_r° (kcal/mol)	log K	Ref.
$\text{Si}(\text{OH})_4^0 = \text{SiO}(\text{OH})_3^- + \text{H}^+$	6.12	-9.83	(87)
$\text{Si}(\text{OH})_4^0 = \text{SiO}_2(\text{OH})_2^{2-} + 2\text{H}^+$	17.6	-23.0	(88)

Mineral	Reaction	ΔH_r° (kcal/mol)	log K	Ref.
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 2\text{Al}^{3+} + 2\text{Si}(\text{OH})_4^0 + \text{H}_2\text{O}$	-35.3	7.435	(a)
Chrysotile	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 3\text{Mg}^{2+} + 2\text{Si}(\text{OH})_4^0 + \text{H}_2\text{O}$	-46.8	32.20	(b)
Sepiolite	$\text{Mg}_2\text{Si}_4\text{O}_{15}(\text{OH})_2 \cdot 3\text{H}_2\text{O} + 4\text{H}^+ + 0.5 \text{H}_2\text{O} = 2\text{Mg}^{2+} + 3\text{Si}(\text{OH})_4^0$	-10.7	15.76	(c)
Kerolite	$\text{Mg}_5\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot \text{H}_2\text{O} + 6\text{H}^+ + 3\text{H}_2\text{O} = 3\text{Mg}^{2+} + 4\text{Si}(\text{OH})_4^0$	---	25.79	(90)
Quartz	$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{Si}(\text{OH})_4^0$	5.99	-3.98	(29)
Chalcedony	$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{Si}(\text{OH})_4^0$	4.72	-3.55	(29)
Amorphous Silica	$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{Si}(\text{OH})_4^0$	3.34	-2.71	(29)

Reaction	Analytical Expressions for Temperature Dependence	Ref.
$\text{Si}(\text{OH})_4^0 = \text{SiO}(\text{OH})_3^- + \text{H}^+$	$\log K_1 = -302.3724 - 0.050698T + 15669.69/T + 108.18466 \log T - 1119669/T^2$	(87)
$\text{Si}(\text{OH})_4^0 = \text{SiO}_2(\text{OH})_2^{2-} + 2\text{H}^+$	$\log \beta_2 = -294.0184 - 0.072650T + 11204.49/T + 108.18466 \log T - 1119669/T^2$	(88)
$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 3\text{Mg}^{2+} + 2\text{Si}(\text{OH})_4^0 + \text{H}_2\text{O}$	$\log K_{\text{CHRYSTILE}} = 13.248 + 10217.1/T - 6.1894 \log T$	(b)
$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{Si}(\text{OH})_4^0$	$\log K_{\text{QUARTZ}} = 0.41 - 1309/T$	(29)
$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{Si}(\text{OH})_4^0$	$\log K_{\text{CHALCEDONY}} = -0.09 - 1032/T$	(29)
$\text{SiO}_2 + 2\text{H}_2\text{O} = \text{Si}(\text{OH})_4^0$	$\log K_{\text{AMORPHOUS SILICA}} = -0.26 - 731/T$	(29)

References for silicate species

a.) (41) for log K, (26) for enthalpy; b.) log K, obtained from (89) data after conversion using our K_e equation and least squares fitting, is consistent with (26) data; c.) log K from (90); ΔH_r° obtained from 273-373 K fit of (90) data.

References for carbonate species

a.) (26), using ion values from (23); b.) from Helgeson et al. (83) using ion values of (23); c.) log K of Smith (84) recalculated using the present aqueous model at 303 K, adjusted to 298 K using ΔH_r° calculated using ion values from (23) and Robie et al. (85) for solid; d.) Singer and Stumm (86) recalculated to be consistent with the present aqueous model; e.) log K from Garrels et al. (82) and ΔH_r° from (23) and Robie et al. (85) for the solid.

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Table 2. Summary of Revised Thermodynamic Data. V. Sulfate Species

Reaction	ΔH_r° (kcal/mol)	log K	Ref.	Reaction	ΔH_r° (kcal/mol)	log K	Ref.
$H^+ + SO_4^{2-} = HSO_4^-$	3.85	1.988	(91)	$Mn^{2+} + SO_4^{2-} = MnSO_4^0$	3.37	2.25	(99)
$Li^+ + SO_4^{2-} = LiSO_4^-$	----	0.64	(52)	$Fe^{2+} + SO_4^{2-} = FeSO_4^0$	3.23	2.25	(c)
$Na^+ + SO_4^{2-} = NaSO_4^-$	1.12	0.70	(a)	$Fe^{2+} + HSO_4^- = FeHSO_4^+$	---	1.08	(102)
$K^+ + SO_4^{2-} = KSO_4^-$	2.25	0.85	(b)	$Fe^{2+} + SO_4^{2-} = FeSO_4^+$	3.91	4.04	(c)
$Ca^{2+} + SO_4^{2-} = CaSO_4^0$	1.65	2.30	(96)	$Fe^{2+} + 2SO_4^{2-} = Fe(SO_4)_2^-$	4.60	5.38	(c)
$Mg^{2+} + SO_4^{2-} = MgSO_4^0$	4.55	2.37	(97)	$Fe^{2+} + HSO_4^- = FeHSO_4^{2+}$	---	2.48	(102)
$Sr^{2+} + SO_4^{2-} = SrSO_4^0$	2.08	2.29	(98)	$Al^{3+} + SO_4^{2-} = AlSO_4^+$	2.15	3.02	(54)
$Ba^{2+} + SO_4^{2-} = BaSO_4^0$	---	2.7	(52)	$Al^{3+} + 2SO_4^{2-} = Al(SO_4)_2^-$	2.84	4.92	(54)
$Ra^{2+} + SO_4^{2-} = RaSO_4^0$	1.3	2.75	(66)	$Al^{3+} + HSO_4^- = AlHSO_4^{2+}$	---	0.46	(104)

Mineral	Reaction	ΔH_r° (kcal/mol)	log K	Ref.
Gypsum	$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$	-0.109	-4.58	(d)
Anhydrite	$CaSO_4 = Ca^{2+} + SO_4^{2-}$	-1.71	-4.36	(d)
Celestite	$SrSO_4 = Sr^{2+} + SO_4^{2-}$	-1.037	-6.63	(106)
Barite	$BaSO_4 = Ba^{2+} + SO_4^{2-}$	6.35	-9.97	(d)
Radium sulfate	$RaSO_4 = Ra^{2+} + SO_4^{2-}$	9.40	-10.26	(66)
Melanterite	$FeSO_4 \cdot 7H_2O = Fe^{2+} + SO_4^{2-} + 7H_2O$	4.91	-2.209	(107)
Alunite	$KAl_3(SO_4)_2(OH)_6 + 6H^+ = K^+ + 3Al^{3+} + 2SO_4^{2-} + 6H_2O$	-50.25	-1.4	(e)

Reaction	Analytical Expressions for Temperature Dependence	Ref.
$H^+ + SO_4^{2-} = HSO_4^-$	$\log K_2 = -56.889 + 0.006473T + 2307.9/T + 19.8858 \log T$	(91)
$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$	$\log K_{\text{GYPSUM}} = 68.2401 - 3221.51/T - 25.0627 \log T$	(d)
$CaSO_4 = Ca^{2+} + SO_4^{2-}$	$\log K_{\text{ANHYDRITE}} = 197.52 - 8669.8/T - 69.835 \log T$	(d)
$SrSO_4 = Sr^{2+} + SO_4^{2-}$	$\log K_{\text{CELESTITE}} = -14805.9622 - 2.4660924T + 756968.533/T$ $- 40553604/T^2 + 5436.3588 \log T$	(106)
$BaSO_4 = Ba^{2+} + SO_4^{2-}$	$\log K_{\text{BARITE}} = 136.035 - 7680.41/T - 48.595 \log T$	(d)
$RaSO_4 = Ra^{2+} + SO_4^{2-}$	$\log K_{\text{RaSO}_4} = 137.98 - 8346.87/T - 48.595 \log T$	(66)
$FeSO_4 \cdot 7H_2O = Fe^{2+} + SO_4^{2-} + 7H_2O$	$\log K_{\text{MELANTERITE}} = 1.447 - 0.004153T - 214949/T^2$	(107)

References for sulfate species

a.) log K from Rhigaletto and Davies (92), ΔH_r° from Austin and Mair (93); b.) log K from Truesdell and Hostetler (94), ΔH_r° from Siebert and Christ (95) refitting of (94); c.) log K values are in good agreement between (52), (95) and Stupp (103); enthalpies are derived from the Fuoss fitting method of Siebert and Christ (95) except for the iron(III) sulfate ion triplet which assumes a value equivalent to that for the aluminum sulfate ion triplet; d.) Langmuir and Melchior (33), where the gypsum data is refitted from Blount and Dickson (105) and is in excellent agreement with the highly precise data of Lilley and Briggs (32) at 298 K; e.) log K from Adams and Rawajfeh (100) and ΔH_r° calculated from enthalpies of formation found in Kelley et al. (101) and Robie et al. (26).

be clear -- one is needed to determine the tendency for mineral solubility constraints on water composition and the other is needed to describe mass transfer sources and sinks in a geochemically reacting flow system (44).

It may also be argued that the simulation of water-rock interactions should allow for solubility equilibria involving feldspars, micas, etc. For such studies the choice of solubility product constants and free energies must and should be made by the investigators. We cannot propose such values here when an enormous range of values and properties (solid-solutions, interlayering, defects, surface areas, etc.) is known to exist for these minerals and reversible solubility behavior has not been demonstrated.

A brief summary of the status of the thermodynamic properties for water-mineral reactions using the ion-association theory and revised data is:

1. These computations are reliable for the range 0-100°C and up to 1 molal ionic strength for major univalent and divalent ions, a limited set of minor and trace elements, and iron and manganese redox species.
2. Major carbonate mineral solubilities and their associated ion pairs are reliable except for dolomite, siderite and rhodocrosite, for which ranges of Ksp values are estimated.
3. Oxide and hydroxide solubilities are generally reliable for calcium, magnesium, aluminum and iron, but the Ksp values can range over several orders of magnitude depending on degree of crystallinity, especially particle size affects. There are continuing controversies regarding the actual reactive phases being measured in solubility studies, and further refinements have been proposed (45), 46).
4. Quartz, kaolinite, chrysotile, sepiolite and kerolite solubilities are reliable for estimates in chemical modeling at low temperatures. Ksp values for these minerals are also strongly influenced by degree of crystallinity. Other silicate mineral solubilities are either unreliable, or do not describe the behavior of these minerals in natural waters.
5. Common sulfate mineral solubilities and their associated ion pairs are reliable within other restrictions of the model.

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