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Research Article

Accuracy of Thermodynamic Databases for Hydroxyapatite Dissolution Constant

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Abstract

Discrepancies have been noted in the solubility constant values of calcium phosphate minerals between various databases employed in widely used aqueous speciation calculation software programs. This can cause serious errors in the calculated speciation of waters when using these software programs. The aim of this communication was to bring to light these discrepancies. Experimental determinations of the hydroxyapatite (HAP) solubility product vary by as much as 10 orders of magnitude as a result of experimental challenges related to the presence of impurities in the HAP used, incongruent dissolution, and the contamination of solutions with dissolved carbon dioxide. It is suggested that the value used in the database Thermo.dat is consistent with experimental data devoid of common experimental problems, whereas other common databases use values that lead to a vastly overestimated solubility of HAP. Key Words: Aqueous speciation—Calcium—Phosphate—Thermodynamic database—Hydroxyapatite solubility—Phosphate availability—Prebiotic synthesis. Astrobiology 20, xxx–xxx.

1. Introduction

The accuracy of thermodynamic databases employed in aqueous speciation codes is critical to obtaining reliable results from the codes. Some widely used software and thermodynamic databases in the fields of aqueous geochemistry and environmental chemistry are the EQ3/EQ6 (Wolery, 1992), Geochemists' Workbench® (Bethke *et al.*, 2019), and PHREEQC (Parkhurst and Apello, 1999). The original database, Thermo.dat, was developed at Lawrence Livermore National Laboratory and used in the pioneering code, EQ3/EQ6 (Wolery, 1992). This database was subsequently updated by Lawrence Livermore National Laboratory and referred to with the name Thermo.com.V8.R6+ PHREEQC uses its own database. All three databases are available as options in Geochemist's Workbench. We recently became interested in calculating the speciation of calcium and phosphate, among other ions, in a specific research context. Therefore, we undertook a comparison of the solubility constants (K_{sp}s) for calcium phosphate minerals in these three thermodynamic databases. We were surprised to discover that wide discrepancies exist in the values reported for calcium phosphate minerals, such as hydroxyapatite ($Ca_5(PO_4)_3OH$; HAP), fluorapatite ($Ca_5(PO_4)_3F$), and whitlockite ($Ca_3(PO_4)_2$) between the three databases. We, therefore, became concerned with determining which database had the accurate K_{sp} values. The goal of this short communication is to share the results of our investigation.

2. Methods

2.1. Determining the accurate solubility constant of HAP

We chose to use HAP (note that the mineral is referred to as hydroxylapatite in Thermo.dat and Thermo.com .V8.R6+) as the case mineral to determine which thermodynamic database reports the accurate values of solubility products. We subsequently compared this value with those reported in the various thermodynamic databases.

2.2. Speciation calculations

We also ran a speciation calculation on Geochemist's Workbench for a system in which 5 g of HAP is equilibrated with 1 kg pure water at 298°K using the three databases and compared the output in terms of calcium and phosphate speciation.

3. Results and Discussion

3.1. Determining the accurate solubility constant of HAP

We first calculated the standard Gibb's free energy of reaction (ΔG^0_r) for dissolution of HAP. Since all three databases in Geochemist's Workbench use a stoichiometry for HAP that is $Ca_5(PO_4)_3OH$, we write the dissolution equation using this stoichiometry:

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$$Ca_5(PO_4)_3OH = 5\ Ca^{2+}{}_{(aq)} + 3(PO_4)^{3-}{}_{(aq)} + OH^-{}_{(aq)} \quad (1)$$

using the standard Gibb's free energy of formation of the *i-th* reactants and products ($\Delta G^0_{f,\ i}$), according to:

$$\Delta G^0_r = 5\Delta G^0_{f,\ Ca^{2+}} + 3\Delta G^0_{f,\ PO_4^{3-}} + \Delta G^0_{f,\ OH^-} - \Delta G^0_{f,\ HAP}. \quad (2)$$

Using standard Gibb's free energy of formation from Faure (1998) (Table 1), we obtain

$$\Delta G^0{}_r = 84.4\ \text{kcal/mol}. \quad (3)$$

Relating $\Delta G^0{}_r$ to the equilibrium constant, K_{sp}, we obtain

$$logK_{sp} = \frac{-\Delta G^0_r}{2.303RT} = -61.9, \quad (4)$$

where R is the ideal gas constant $= 1.987 \times 10^{-3}$ kcal/(mol·K) and T is the absolute temperature (K).

The equation for solubility of HAP in Thermo.dat with the corresponding log K value is

$$Ca_5(PO_4)_3OH\ +\ 4H^+{}_{(aq)} = 5Ca^{2+}{}_{(aq)} + \ 3(HPO_4)^{2-}{}_{(aq)} + H_2O_{(aq)}\ \log K = -11.5. \quad (5)$$

To make the right-hand side of Eq. (5) consistent with the presence of $OH^-{}_{(aq)}$ as in Eq. (1), we add

$$H_2O_{(aq)} = H^+{}_{(aq)} + OH^-{}_{(aq)}\ \log K = -13.9 \quad (6)$$

to yield

$$Ca_5(PO_4)_3OH + 3H^+{}_{(aq)} = 5Ca^{2+}{}_{(aq)} + 3(HPO_4)^{2-}{}_{(aq)} + OH^-{}_{(aq)}\ \log K = -25.4. \quad (7)$$

To make the right-hand side of Eq. (7) consistent with the presence of PO_4^{3-} in Eq. (1), we add

$$3(HPO_4)^{2-}{}_{(aq)} = 3(PO_4)^{3-}{}_{(aq)} + 3H^+{}_{(aq)}\ \log K = -37 \quad (8)$$

to obtain

$$Ca_5(PO_4)_3OH = 5Ca^{2+}{}_{(aq)} + 3(PO_4)^{3-}{}_{(aq)} + OH^-{}_{(aq)}\ \log K_{sp} = -62.4. \quad (9)$$

Table 1. Standard Gibbs Free Energy of Formation of the *i-th* Species (Faure, 1998)

Species	$\Delta G^0{}_{f,i}$ *(kcal/mol)*
Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$	–3030
$Ca^{2+}{}_{(aq)}$	–132.5
$PO_4^{3-}{}_{(aq)}$	–243.5
$OH^-{}_{(aq)}$	–37.6

The log K value in Eq. (9) is similar (within 0.5 log units) to that obtained from the standard Gibbs' free energies of formation [Eq. (4)]. This suggests that the value in Thermo.dat is accurate.

The equation for solubility of HAP in Thermo.com .V8.R6+ with the corresponding log K value is

$$Ca_5(PO_4)_3OH + 4H^+{}_{(aq)} = 5Ca^{2+}{}_{(aq)} + 3(HPO_4)^{2-}{}_{(aq)} + H_2O_{(aq)}\ \log K = -3.0. \quad (10)$$

To make the right-hand side of Eq. (10) consistent with the presence of $OH^-{}_{(aq)}$ as in Eq. (1), we add

$$H_2O_{(aq)} = H^+{}_{(aq)} + OH^-{}_{(aq)}\ \log K = -13.9 \quad (11)$$

to yield

$$Ca_5(PO_4)_3OH + 3H^+{}_{(aq)} = 5Ca^{2+}{}_{(aq)} + 3(HPO_4)^{2-}{}_{(aq)} + OH^-{}_{(aq)}\ \log K = -16.9. \quad (12)$$

To make the right-hand side of Eq. (12) consistent with the presence of PO_4^{3-} as in Eq. (1), we add

$$3(HPO_4)^{2-}{}_{(aq)} = 3(PO_4)^{3-}{}_{(aq)} + 3H^+{}_{(aq)}\ \log K = -37 \quad (13)$$

to obtain

$$Ca_5(PO_4)_3OH = 5Ca^{2+}{}_{(aq)} + 3(PO_4)^{3-}{}_{(aq)} + OH^-{}_{(aq)}\ \log K_{sp} = -53.9. \quad (14)$$

The log K_{sp} value in Eq. (14) is dissimilar to that obtained from standard Gibbs' free energies of formation [Eq. (4)] or to the value in Thermo.dat [Eq. (9)]. The value in Thermo.com.V8.R6+ differs from the accurate value obtained from Gibb's free energies of formation by –8 log units.

The equation for solubility of HAP in PHREEQC with the corresponding log K value is

$$Ca_5(PO_4)_3OH + H^+{}_{(aq)} = 5Ca^{2+}{}_{(aq)} + 3(PO_4)^{3-}{}_{(aq)} + H_2O_{(aq)}\ \log K = -39.6. \quad (15)$$

To make the right-hand side of Eq. (15) consistent with the presence of $OH^-{}_{(aq)}$ as in Eq. (1), we add

$$H_2O_{(aq)} = H^+{}_{(aq)} + OH^-{}_{(aq)}\ \log K = -13.9 \quad (16)$$

to yield

$$Ca_5(PO_4)_3(OH) = 5Ca^{2+}{}_{(aq)} + 3(PO_4)^{3-}{}_{(aq)} + OH^-{}_{(aq)}\ \log K_{sp} = -53.5. \quad (17)$$

The log K_{sp} value in Eq. (17) is dissimilar to that obtained from standard Gibbs' free energies of formation [Eq. (4)] or to the value in Thermo.dat [Eq. (9)], but is identical to the value obtained from Thermo.com.V8.R6+ [Eq. (14)].

Table 2. Results of Speciation Calculations for the Solubility of HAP in Water Using the Three Thermodynamic Databases in Geochemist's Workbench

Aqueous species	*Thermo.dat (molal)*	*Thermo.com.V8.R6+ (molal)*	*PHREEQC (molal)*
$Ca^{2+}_{(aq)}$	2.968 e-06	1.512 e-05	1.408 e-05
$OH^{-}_{(aq)}$	2.416 e-06	1.214 e-05	1.131 e-05
$HPO_4^{2-}{}_{(aq)}$	1.703 e-06	8.879 e-06	8.27 e-06
$H_2PO_4^{-}{}_{(aq)}$	1.157 e-07	1.167 e-07	1.161 e-07
$P_{tot,\ (aq)}$	1.819 e-06	8.996 e-06	8.386 e-06
pH	8.368	9.076	9.049

3.2. Speciation calculations

Table 2 and Fig. 1 show the results of the speciation calculation for the solubility of HAP in water. The results from using the Thermo.com.V8.R6+ and the PHREEQC databases are similar to each other but different from those obtained by using the Thermo.dat database. The concentrations of Ca^{2+} and total PO_4 ($\sim = H_2PO_4^- + HPO_4^{2-}$) are overpredicted by a factor of 4.5 to 5 when using either the Thermo.com.V8.R6+ or the PHREEQC database compared with that predicted by Thermo.dat. The pH of the solution is also overpredicted by 0.7 units.

3.3. Comparison with experimental K_{sp} values

The experimental measurement of K_{sp} values for a mineral such as HAP that is so highly insoluble is a challenging task. Various values have been reported in the literature for K_{sp} of HAP, including −58.5 (Avnimelech *et al.*, 1973; McDowell *et al.*, 1977), −57.5 (Bell *et al.*, 1978), −56.2 (Jaynes *et al.*, 1999), and −53.3 (Zhu *et al.*, 2009) to state a few. With the exception of the value reported by Zhu *et al.* (2009), which is consistent with the values in the Thermo .com.V8.R6+ or the PHREEQC database, all the remaining values are similar and suggest a more negative value of K_{sp}. The challenge of determining an accurate value of K_{sp} for calcium phosphate phases was discussed in detail by Pan and Darvell (2009). These authors noted that the conventional method of determining the K_{sp} of HAP is by the ''large excess of solid'' method, wherein a large amount of HAP is added to a solution and the analyzed solution concentration is combined with ionic speciation calculations to obtain K_{sp}. Pan and Darvell (2009) noted in detail that incongruent dissolution, phase transformation, inaccurate speciation calculations, and contamination by ions, especially CO_2, lead to the large variation in reported K_{sp} values. In particular, the presence of CO_2 in the initially synthesized solid, which is subsequently used for the dissolution experiment, increases the solubility of HAP. A value of −57.5 was obtained by Bell *et al.* (1978) by strict elimination of CO_2 contamination, whereas similar precautions were not stated in the study by Zhu *et al.* (2009). Pan and Darvell (2009) suggested an alternative method to determine the K_{sp} of calcium phosphate phases, which is the ''solid titration'' method. This method eliminates the errors introduced by the phenomena already listed. Using the solid titration method, Pan and Darvell (2009) determined a K_{sp} of HAP = −63, which is even more negative than the values determined by previous workers (Avnimelech *et al.*, 1973; McDowell *et al.*, 1977; Bell *et al.*, 1978) and close to but also more negative than the theoretical value of −61.9 obtained in this study from free energies of formation [Eq. (4)]. The value of −63 is very close to the value of −62.4 used in Thermo.dat. Therefore, based on the discussion, it is concluded that the value reported in Thermo.dat is the most accurate of the three databases.

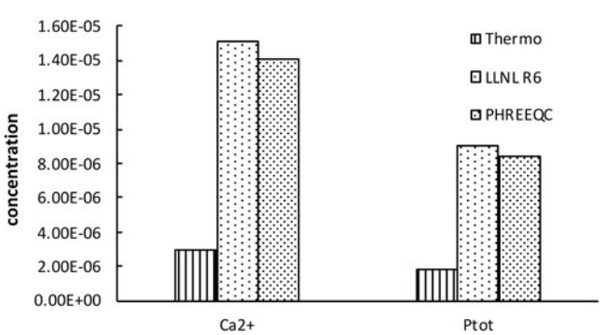

FIG. 1. Concentrations of calcium ion and total dissolved phosphate in equilibrium with HAP in water using the three thermodynamic databases available in Geochemist's Workbench®. LLNL R6 = Thermo.com.V8.R6+.

4. Conclusions

Combining our result for the K_{sp} value calculated from Gibbs free energies of formation and the experimental K_{sp} value of −63 obtained by the solid titration method, the Thermo.dat value is deemed to be consistent with the best available experimental data, whereas the values reported in Thermo.com.V8.R6+ and PHREEQC are not correct. Although we have not conducted a similar analysis for other metal phosphate minerals, discrepancies exist in the K_{sp} values for the calcium phosphate minerals, fluorapatite and whitlockite, between the three databases. Based on the analysis for HAP, we believe that the K_{sp} values for the other calcium phosphate minerals in Thermo.dat will be accurate.

Author Disclosure Statement

No competing financial interests exist.

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Abbreviation Used

HAP = hydroxyapatite