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Procedia
Earth and Planetary Science**Water Rock Interaction [WRI 14]****Improving internal consistency of standard state thermodynamic data for sulfate ion, portlandite, gypsum, barite, celestine, and associated ions**D. Kirk Nordstrom^{a*}^aUS Geological Survey, 3215 Marine St., Boulder, CO 80303 USA**Abstract**

Thermochemical measurements in the gypsum-portlandite-water system are actually better than those reflected in the thermodynamic properties of CODATA. It is argued that by careful choice of starting points and pathways and with new data, improvements in standard state properties can achieve improved consistency with solubilities of gypsum, portlandite, barite, witherite, celestine, and strontianite if better entropy estimates of these minerals are made.

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1. Introduction

Probably the most intractable aspect of achieving reliable thermodynamic data is to demonstrate internal consistency for a wide-ranging network of properties. Ruscic et al. [1] consider reliable thermodynamic data the *conditio sine qua non* for most areas of physical chemistry. Internal consistency has been defined [2, 3] as consistency with the basic thermodynamic relationships, a consistent set of fundamental physical constants and atomic weights, a consistent chemical model for aqueous species, consistent pressure- and temperature-dependent models, and an appropriate choice of starting point in the network. The starting point should be a reaction or compound property that is most reliable for the chosen network set, but evaluating the most reliable original measurements can be challenging and laborious.

Wagman et al. [2] also known as the NBS tables, describe two methods that have been used to evaluate data, the sequential method and the simultaneous-fit method. The National Bureau of Standards (NBS, now the National Institute of Standards and Technology, NIST) tables were done with a combination of both techniques although primarily with the sequential method. The Committee on Data for Science and Technology (CODATA) thermodynamic tables' book on Ca [4] simultaneously fit most

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measurements of the major compounds and species of Ca to provide what is probably the most consistent set available for Ca data. Several iterations of simultaneous fits were necessary to screen outliers and to find the best weighting factors for reliable data.

This paper proposes that selecting the best possible starting points and keeping the paths simple with the least amount of assumptions or auxiliary data can lead to highly reliable results which can anchor standard state properties for important minerals and aqueous species at 298.15K and 1 bar and remove inconsistencies. The Ca-SO₄-OH-H₂O system with solubilities of gypsum and portlandite, was chosen for detailed study for several reasons: because of the high quality of data, because the results can be compared with those from the critical evaluation by Garvin et al. [4], and because gypsum solubility is fundamental to many aqueous geochemical systems.

2. Gypsum solubility

Numerous measurements of gypsum solubility in aqueous solutions have been obtained since at least 1874 [5] and have been reviewed by Freyer and Voigt [6]. Averaging a dozen of the most careful measurements at 25°C gives a solubility of $0.01528 \pm 0.000075m$, in which the \pm represents the range from highest to lowest (1 standard deviation is 0.000047). Hence, the solubility is known with greater accuracy and precision than the mean activity coefficient, γ_{\pm} . Using the Pitzer method, Rogers [7] estimated the γ_{\pm} as 0.3369. Lilley and Briggs [8] reported a measurement of $\gamma_{\pm} = 0.3379$. An estimate using the ion association model and the WATEQ4F code gave $\gamma_{\pm} = 0.3315$. The former two estimates were considered more reliable and they were averaged to give $\gamma_{\pm} = 0.3374 \pm 0.0005$, again representing the error by the range of numbers. The mean activity of a solution at equilibrium solubility with gypsum is the square root of the activity for a symmetrical electrolyte and $a_{CaSO_4} = (a_{\pm})^2 = (m_{\pm} \gamma_{\pm})^2 (a_{H_2O})^2 = 2.655 \times 10^{-5}$. From this value the $\log K_{sp} = -4.576 \pm 0.048$ and the standard state Gibbs free energy of the solubility reaction is found to be $26.123 \pm 0.132 \text{ kJ mol}^{-1}$, an error of 0.5%. This value compares to the CODATA value of 26.16 ± 0.35 that was based on fewer data containing a larger variance.

To obtain the standard state Gibbs free energy for the species that make up the solubility reaction, gypsum, $Ca^{2+}_{(aq)}$, $SO_4^{2-}_{(aq)}$, and $H_2O_{(l)}$, three can be obtained directly and the third (sulfate ion) by difference. The heat capacity and entropy for gypsum has been remeasured and re-evaluated by Robie et al. [9] who reported $S^{\circ} = 193.8 \pm 0.3 \text{ J mol}^{-1} \text{ K}^{-1}$, an improvement on the CODATA value of $193.928 \pm 2.092 \text{ J mol}^{-1} \text{ K}^{-1}$. The enthalpy of formation for gypsum is a little more problematic because there are very few measurements primarily dehydration-hydration enthalpies, and dissolution enthalpies. Kelley et al. [10] concluded that $\Delta_f H^{\circ}(\text{gypsum}) = -2005.9 \text{ kJ mol}^{-1}$ based on the heat of hydration of anhydrite. Since that time the enthalpy of anhydrite has been improved [11] and there has been a small change in the enthalpy of $H_2O_{(g)}$ which leads to $-2022.2 \text{ kJ mol}^{-1}$. This value compares well with the CODATA value of $-2022.919 \pm 0.725 \text{ kJ mol}^{-1}$ and the value of $-2023.0 \pm 4.3 \text{ kJ mol}^{-1}$ from Robie and Hemingway [12]. Because the reported error in the CODATA value overlaps with the value calculated from Kelley et al. [10], it is used in the current evaluation. Using the entropies of the elements from CODATA except for the revised value for $Ca_{(cr)}$ from Alcock et al. [13], and using the relation $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$, the Gibbs free energy of formation of gypsum from the elements is $-1797.20 \pm 0.725 \text{ kJ mol}^{-1}$ which compares well with CODATA ($-1797.359 \pm 0.350 \text{ kJ mol}^{-1}$).

Next, a direct estimate of the $\Delta_f G^{\circ}_{(Ca^{2+})}$ is derived from the solubility of portlandite. Portlandite dissolves to just $Ca^{2+}_{(aq)}$ and $OH^{-}_{(aq)}$ ions so that if the thermodynamic properties of portlandite are known, then the $Ca^{2+}_{(aq)}$ can be precisely determined because $OH^{-}_{(aq)}$ is well established.

3. Portlandite solubility

The solubility of portlandite, $\text{Ca}(\text{OH})_2$, has been reviewed and evaluated by Lambert and Clever [14] with a solubility of 0.02028 m at 25°C. Baes and Mesmer [15] calculated a $\log K_{\text{sp}} = -5.19 \pm 0.01$ based on a solubility of 0.0203 m and a reliable activity coefficient. For comparison, the more recent work of Duchesne and Reardon [16] reported $\log K_{\text{sp}} = -5.19 \pm 0.04$. This K_{sp} leads to a $\Delta_f G^\circ$ of $29.629 \pm 0.057 \text{ kJ mol}^{-1}$, using the error from [15]. The entropy, heat capacity, and enthalpy of portlandite have been evaluated by Chase [17] leading to $\Delta_f G^\circ = -898.421 \text{ kJ mol}^{-1}$. Including the slight adjustment by Alcock et al. [13] and using CODATA values for entropies, $\Delta_f G^\circ = -898.201 \text{ kJ mol}^{-1}$. A value of $-898.2 \pm 0.2 \text{ kJ mol}^{-1}$ adequately covers the range of entropies. Combined with the CODATA value for $\Delta_f G^\circ_{(\text{OH}^-)}$, of $-157.2 \pm 0.1 \text{ kJ mol}^{-1}$, $\Delta_f G^\circ_{(\text{Ca}^{2+})} = -554.17 \pm 0.2 \text{ kJ mol}^{-1}$. By comparison, CODATA gives $-552.807 \pm 1.050 \text{ kJ mol}^{-1}$ and Wagman et al. [2] gives $-553.58 \text{ kJ mol}^{-1}$. Now the Gibbs free energy of the sulfate ion can be determined by difference from these data.

4. Standard state Gibbs free energy of the sulfate ion

Substituting the above derived Gibbs free energies into the solubility equilibrium expression for gypsum, the result is $\Delta_f G^\circ_{(\text{SO}_4^{2-})} = -742.628 \text{ kJ mol}^{-1}$ which varies by about 2 kJ mol^{-1} from the CODATA value in Garvin et al. [4] of $-744.588 \text{ kJ mol}^{-1}$ and from the CODATA key value ($-744.00 \text{ kJ mol}^{-1}$) in Cox et al. [18]. A confirmation that the Gibbs free energy for the sulfate ion is more internally consistent can be demonstrated with the revised data for strontianite and witherite solubilities and the well-established solubilities of barite and celestine. The solubilities of strontianite and witherite, respectively, were remeasured [19,20] and revised values for the free energies of the strontium and barium ions, respectively, were recommended. Using these properties along with the K_{sp} values for barite and celestine [3] and the revised enthalpies of formation for barite and celestine [11], the standard state Gibbs free energy for the sulfate ion can be recalculated as $-740.130 \text{ kJ mol}^{-1}$ and $-740.506 \text{ kJ mol}^{-1}$, respectively. These values are more consistent with the combined data for gypsum, barite, witherite, celestine, and strontianite solubilities than those from CODATA but only if the estimated entropies for celestine and barite from [3] are used. The results are shown in table 1. Further work is required to determine consistent values of enthalpy and entropy for sulfate and calcium ions and for celestine and barite.

Table 1. Thermodynamic properties of species at 25°C and 1 bar considered in this evaluation.

Species	$S^\circ \text{ J mol}^{-1} \text{ K}^{-1}$	$\Delta_f H^\circ \text{ kJ mol}^{-1}$	$\Delta_f G^\circ \text{ kJ mol}^{-1}$	Log K_{sp}
$\text{H}_{2(\text{g})}$	130.680	0.0	0.0	–
$\text{O}_{2(\text{g})}$	205.147	0.0	0.0	–
$\text{S}_{(\text{cr})}$	32.056	0.0	0.0	–
$\text{H}_2\text{O}_{(\text{g})}$	188.834	-241.826	-228.582	–
$\text{H}_2\text{O}_{(\text{l})}$	69.95	-285.83	-237.141	–
$\text{OH}^-_{(\text{aq})}$	-10.90	-230.015	-157.244	–
$\text{Ca}^{2+}_{(\text{aq})}$	–	–	-554.17	–
$\text{Ba}^{2+}_{(\text{aq})}$	8.4	-532.50	-555.36	–
$\text{Sr}^{2+}_{(\text{aq})}$	-31.50	-550.90	-563.83	–
$\text{SO}_4^{2-}_{(\text{aq})}$	–	–	-742.628	–
Portlandite	83.387	-986.085	-898.421	-5.19
Gypsum	193.8	-2022.2	-1797.2	-4.576
Barite	128.6	-1464.5	-1352.41	-9.97
Celestine	128.3	-1452.1	-1338.76	-6.62
Witherite	112.13	-1210.85	-1132.21	-8.562
Strontianite	97.2	-1225.77	-1144.73	-9.271

Conclusions

In this paper, the argument is made that by careful selection of highly reliable measurements and by keeping the path through the thermodynamic network as simple and direct as possible the standard state thermodynamic properties of several species of interest to geochemistry can be improved. By comparing the network involving the solubilities of gypsum, portlandite, barite, and witherite, and the calorimetric data for the solid mineral phases, a more internally set of properties can be obtained that indicates the Gibbs free energy for the sulfate ion should be adjusted to a slightly larger quantity. Future work will evaluate the temperature dependence of the solubilities to determine the enthalpy and entropy of the calcium and sulfate ions. This analysis also revealed an inconsistency in that part of the network that involves celestine, and strontianite.

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