

535813



Sandia National Laboratories

Operated for the U.S. Department of Energy by
Sandia Corporation

Carlsbad Programs Group
4100 National Parks Highway
Carlsbad, NM 88220

date: June 8, 2004

to: Larry Brush, Repository Performance Dept. 6822 (MS-1395)
Carlsbad Programs Group

from: Yongliang Xiong, Repository Performance Dept. 6822 (MS-1395)
Carlsbad Programs Group

subject: A Correction of the Molecular Weight of Oxalate in FMT_021120.CHEMDAT, and
Incorporation of Calcium Oxalate Monohydrate (Whewellite) into CHEMDAT with Its
Recommended Dimensionless Standard Chemical Potential Value

1. A Correction of the Molecular Weight of Oxalate ($C_2O_4^{2-}$, abbreviated as Ox^{2-}) in
FMT_021120.CHEMDAT

In the FMT database, i.e., FMT_021120.CHEMDAT (Giambalvo, 2003), an error occurs for the molecular weight of oxalate ($C_2O_4^{2-}$). The molecular weight is listed as 28.84000 g. The correct value should be 88.0196 g. The error was caused when the space for the pseudo-element 'air' in the original version of CHEMDAT (Babb and Novak, 1995) was taken by oxalate in the development of FMT_970407.CHEMDAT, FMT_970407_HMAG4323.CHEMDAT, FMT_970407_HMAG5424.CHEMDAT, FMT_970407_NESQ.CHEMDAT (Novak, 1997), and FMT_021120.CHEMDAT (Giambalvo, 2003). The molecular weight for the pseudo-element 'air' (28.84000 g) was never updated to the molecular weight of oxalate (88.0196 g). However, this error would not have impact on the calculations under AP-098.

2. Recommended Dimensionless Standard Chemical Potential (μ^0/RT) of Calcium Oxalate Monohydrate (Whewellite)

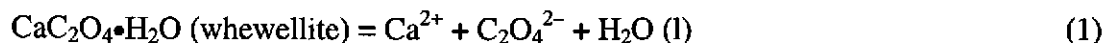
In the FMT_021120.CHEMDAT (Giambalvo, 2003), only three oxalate solid phases, i.e., $H_2C_2O_4 \cdot H_2O$, $NaHC_2O_4 \cdot H_2O$ and $Na_2C_2O_4$, were included (Giambalvo, 2002). However, there are three calcium oxalate hydrates, including calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$; COM; whewellite), calcium oxalate dihydrate ($CaC_2O_4 \cdot 2H_2O$; COD; weddellite), and calcium oxalate trihydrate ($CaC_2O_4 \cdot 3H_2O$; COT) (Streit and others, 1998). Among them, whewellite is the stable phase, whereas weddellite and COT are metastable (Streit and others, 1998). Whewellite and weddellite are the major components of most of the urinary calculi (Streit and others, 1998). The phase whewellite, $CaC_2O_4 \cdot H_2O$, which has much lower solubility than sodium oxalates, is not in the FMT_021120.CHEMDAT database. It has been well known that the solid phase that has the lowest solubility in a system controls the solubility of relevant species; therefore, the absence of whewellite from the current FMT database will certainly overpredict the concentrations of oxalate species.

WIPP:1.4.2.2:SFT:QA-L:210790

Exceptional Service in the National Interest

Information Only

Nancollas and Gardner (1974) determined the solubility product constants for whewellite at 25 °C for the following reaction in the ionic strength ranging from 0.02 to 0.20 M:



They extrapolated the K_{sp} to infinite dilution by using the Davies equation. The K_{sp} at the infinite dilution obtained by them is 2.00×10^{-9} ($\log K_{\text{sp}} = -8.70$, see Table 1).

Tomažič and Nancollas (1979) also determined the K_{sp} at 25 °C at the ionic strength of 0.15 M. The K_{sp} at the infinite dilution, determined by employing the Davies equation for extrapolation, is 1.66×10^{-9} ($\log K_{\text{sp}} = -8.78$, Table 1).

Most recently, Streit and others (1998) determined the K_{sp} of whewellite at 25 °C at the ionic strength of 0.02 m. They also extrapolated the K_{sp} to infinite dilution by using the Davies equation. The K_{sp} at the infinite dilution is 1.70×10^{-9} ($\log K_{\text{sp}} = -8.77$, Table 1).

As the K_{sp} determined by these three independent studies are consistent, an average value is recommended by this study. The recommended $\log K_{\text{sp}}$ for whewellite is -8.75 ± 0.07 (2σ) (Table 1).

According to the $\log K_{\text{sp}}$ recommended above for reaction (1), the free energy of change ($\Delta_r G^\circ$) for reaction (1) at reference state (25 °C and 1 bar) is derived by employing the equation:

$$\Delta_r G^\circ = -2.303 \times R \times T \times \log K_{\text{sp}} \quad (2)$$

where R is the gas constant ($8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is absolute temperature in K ($T = 298.15 \text{ K}$ at 25 °C). Based upon the free energy of change for reaction (1) derived above in conjunction with the free energies of formation for Ca^{2+} , $\text{C}_2\text{O}_4^{2-}$ and $\text{H}_2\text{O} \text{ (l)}$ (Table 2), the free energy of formation for whewellite can be derived. To derive the free energy of formation for whewellite consistent with the current FMT_021120.CHEMDAT database, all the auxiliary thermodynamic data for Ca^{2+} , $\text{C}_2\text{O}_4^{2-}$ and $\text{H}_2\text{O} \text{ (l)}$ are taken from FMT_021120.CHEMDAT (Table 2). The derived value for whewellite and relevant auxiliary thermodynamic data are listed in Table 2. The recommended dimensionless standard chemical potential (μ^0/RT) for whewellite is -326.0981 (Table 2).

References

- Babb, S.C., and Novak, C.F. 1995. "WIPP PA User's Manual for FMT, Version 2.0." Albuquerque, NM: Sandia National Laboratories. ERMS 228119.
- Giambalvo, E.R. 2002. "Recommended μ^0/RT Values for Modeling the Solubility of Oxalate Solids in WIPP Brines." Memorandum to L.H. Brush, July 31, 2002. Carlsbad, NM: Sandia National Laboratories. ERMS 523057.
- Giambalvo, E.R. 2003. "Release of FMT Database FMT_021120.CHEMDAT." Memorandum to L.H. Brush, March 10, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 526372.
- Nancollas, G.H., and G.L. Gardner. 1974. "Kinetics of Crystal Growth of Calcium Oxalate," *Journal of Crystal Growth*. Vol. 21, 267–276.
- Novak, C.F. 1997. "Calculation of Actinide Solubilities in WIPP SPC and ERDA-6 Brines under MgO Backfill Scenarios Containing either Nesquehonite or Hydromagnesite as the Mg-CO₃ Solubility-Limiting Phase." Memorandum to R.V. Bynum, April 21, 1997. Carlsbad, NM: Sandia National Laboratories. ERMS 246124.
- Streit, J., L.-C. Tran-Ho, and E. Konigsberger. 1998. "Solubility of the Three Calcium Oxalate Hydrates in Sodium Chloride Solutions and Urine-Like Liquors," *Monatsheft für Chemie*. Vol. 129, 1225–1236.
- Tomažič, B., and G.H. Nancollas. 1979. "The Kinetics of Dissolution of Calcium Oxalate Hydrates," *Journal of Crystal Growth*. Vol. 46, 355–361.

Table 1. Solubility Product Constant ($\log K_{sp}$) of Whewellite
($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) at Infinite Dilution and at 25 °C and 1 bar.

References	$\log K_{sp}$
Nancollas & Gardner, 1974	-8.70
Tomazic & Nancollas, 1979	-8.78
Streit and others, 1998	-8.77
Recommended value, this study	-8.75 ± 0.07 (2σ)
Recommended $\Delta_f G^\circ$	49.954 ± 0.799 (2σ) kJ mol^{-1}

Table 2. Derived Free Energy of Formation ($\Delta_f G^\circ$) and Dimensionless Standard Chemical Potential (μ°/RT) of Whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) at 25 °C and 1 bar, and Associated Auxiliary Thermodynamic Properties of Relevant Species.

Species	$\Delta_f G^\circ$ (kJ mol^{-1})	μ°/RT	References
Whewellite	-808.378	-326.0981	This Study
H_2O (l)	-237.144	-95.6635	FMT_021120.CHEMDAT
Ca^{2+}	-553.548	-223.3000	FMT_021120.CHEMDAT
$\text{C}_2\text{O}_4^{2-}$	32.268	13.0170	FMT_021120.CHEMDAT