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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\textsubscript{2}O\textsubscript{4}\textsuperscript{2-}, abbreviated as Ox\textsuperscript{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\textsubscript{2}O\textsubscript{4}\textsuperscript{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 (\mu\textsuperscript{0}/RT) of Calcium Oxalate Monohydrate (Whewellite)

In the FMT_021120.CHEMDAT (Giambalvo, 2003), only three oxalate solid phases, i.e., H\textsubscript{2}C\textsubscript{2}O\textsubscript{4}\textcdot H\textsubscript{2}O, NaHC\textsubscript{2}O\textsubscript{4}\textcdot H\textsubscript{2}O and Na\textsubscript{2}C\textsubscript{2}O\textsubscript{4}, were included (Giambalvo, 2002). However, there are three calcium oxalate hydrates, including calcium oxalate monohydrate (CaC\textsubscript{2}O\textsubscript{4}\textcdot H\textsubscript{2}O; COM; whewellite), calcium oxalate dihydrate (CaC\textsubscript{2}O\textsubscript{4}\textcdot 2H\textsubscript{2}O; COD; weddellite), and calcium oxalate trihydrate (CaC\textsubscript{2}O\textsubscript{4}\textcdot 3H\textsubscript{2}O; 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\textsubscript{2}O\textsubscript{4}\textcdot H\textsubscript{2}O, 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.
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:

$$\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O (whewellite)} = \text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} + \text{H}_2\text{O (l)}$$  \hspace{1cm} (1)

They extrapolated the $K_{sp}$ to infinite dilution by using the Davies equation. The $K_{sp}$ at the infinite dilution obtained by them is $2.00 \times 10^{-9}$ (log $K_{sp} = -8.70$, 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 $1.66 \times 10^{-9}$ (log $K_{sp} = -8.78$, 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 $1.70 \times 10^{-9}$ (log $K_{sp} = -8.77$, 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 $K_{sp}$ for whewellite is $-8.75 \pm 0.07$ (2σ) (Table 1).

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

$$\Delta_f G^\circ = -2.303 \times R \times T \times \log K_{sp}$$  \hspace{1cm} (2)

where R is the gas constant (8.31441 J mol$^{-1}$ K$^{-1}$), and T is absolute temperature in K ($T = 298.15$ 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$^{2+}$, C$_2$O$_4^{2-}$ and H$_2$O (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$^{2+}$, C$_2$O$_4^{2-}$ and H$_2$O (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 ($\mu^0$/RT) for whewellite is $-326.0981$ (Table 2).
References


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

<table>
<thead>
<tr>
<th>References</th>
<th>log $K_{sp}$</th>
</tr>
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<tbody>
<tr>
<td>Nancollas &amp; Gardner, 1974</td>
<td>−8.70</td>
</tr>
<tr>
<td>Tomazic &amp; Nancollas, 1979</td>
<td>−8.78</td>
</tr>
<tr>
<td>Streit and others, 1998</td>
<td>−8.77</td>
</tr>
<tr>
<td>Recommended value, this study</td>
<td>−8.75 ± 0.07 (2σ)</td>
</tr>
</tbody>
</table>

Recommended $\Delta G^\circ$  49.954 ± 0.799 (2σ) kJ mol$^{-1}$

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

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta_f G^\circ$ (kJ mol$^{-1}$)</th>
<th>$\mu^o$/RT</th>
<th>References</th>
</tr>
</thead>
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<tr>
<td>Whewellite</td>
<td>−808.378</td>
<td>−326.0981</td>
<td>This Study</td>
</tr>
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<td>H$_2$O (l)</td>
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<td>−95.6635</td>
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<td>Ca$^{2+}$</td>
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<td>−223.3000</td>
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<tr>
<td>C$_2$O$_4^{2-}$</td>
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<td>13.0170</td>
<td>FMT_021120.CHEMDAT</td>
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