Redox calculations with Visual Minteq:

Redox calculations in Minteq, Visual Minteq, etc., are a problem for the programmers and for the software to handle. The problem is that you don’t want the program automatically adjusting the various oxidation states of species and water all the time, because in fact most redox is not at equilibrium. For example, if the solution were at equilibrium, you would not normally have organic matter and oxygen in the solution at the same time, but in fact you do, all the time and it is often necessary to model the specific equilibrium. For example, you often have acetic acid, HAc, or alcohol in water and the water is aerated, but each of these would always react thermodynamically to consume all the oxygen or all the organic compound, yet this does not normally happen. To overcome these problems has caused programmers quite a bit of trouble.

For each redox couple that you want to be “turned on,” or operative in the calculation a new hypothetical species is defined mathematically, as illustrated below. The concentration of this imaginary species is always set to 1.00 and therefore is serves only as a “place holder.” If you click on Redox in the Main menu and look at the sulfide/sulfate couple, as in the following figure:

\[
\begin{align*}
\text{SO}_4^{2-} + 9\text{H}^+ + 8\text{e}^- & \rightarrow \text{HS}^- + 4\text{H}_2\text{O} & \text{pE}^0 = \log K = 33.66 \\
\frac{1}{8}\text{SO}_4^{2-} + \frac{9}{8}\text{H}^+ + \text{e}^- & \rightarrow \frac{1}{8}\text{HS}^- + \frac{1}{2}\text{H}_2\text{O} & \text{pE}^0(1\text{e}^-) = \log K(1\text{e}^-) = 4.21
\end{align*}
\]

This is for the half reaction:
The values in the Redox screen can be interpreted as follows:

\[
[\text{HS}^-/\text{SO}_4^{2-} - 2] = 10^{33.66}[\text{SO}_4^{2-}] [\text{H}^+] [e^-]^8 [\text{H}_2\text{O}]^{-4}
\]

rearranging:

\[
10^{33.66} = \frac{[\text{HS}^-/\text{SO}_4^{2-} - 2][\text{HS}^-]^4 [\text{H}_2\text{O}]^4}{[\text{SO}_4^{2-}]^4 [\text{H}^+]^9 [e^-]^8}
\]

With: \([\text{HS}^-/\text{SO}_4^{2-} - 2] = 1.00; [\text{H}_2\text{O}] = 1.00\) the above equation becomes:

\[
10^{33.66} = \frac{[\text{HS}^-]^4}{[\text{SO}_4^{2-}]^4 [\text{H}^+]^9 [e^-]^8}
\]

This is the equation used by Visual Minteq, of course after inserting activities \{\} for the concentrations [ ]. The activity of the electron is taken to be the same as the concentration, \([e^-] = \{e^-\}\).

**Redox 1 fixed pe.VDA** If you fix the pe value in Visual Minteq, then all the sulfur in the form of S(-II) and SO\(_4\) will be combined and reapportioned between the two forms so that the pe is calculated. To do this all other speciation is done at the same time. For example, if you set pe = -4.00; and TotHS = 0.001 and TotSO\(_4\) = 0.001 and pH = 5.5 and Ionic strength = 0.00.

1. Open Visual Minteq, which initializes all settings. Set the pH fixed at 5.50 and the ionic strength to 0.00. Select HS-1 on the main menu and set equal to 0.001 M; do the same thing for SO\(_4\)-2 = 0.001 M.
2. Select Redox
3. Select the HS-/SO\(_4\)-2 redox couple, as follows, and click on Add and Back to main menu.

**Visual MINTEQ**

3. Select the HS-/SO\(_4\)-2 redox couple, as follows, and click on Add and Back to main menu.
4. In the Main menu select Parameters, at the top. Then, select Specify pe and Eh. Select Fixed pe and type –4, and Save and Back to main menu.

5. On the main menu select Run Minteq and the Output screen will look like this:
Using these values of concentration the log $K = pE^0$ can be calculated to check on internal consistency:

$$\frac{[\text{HS}^-]^{1/8}}{[\text{SO}_4^{2-}]^{1/8}[\text{H}^+]^{9/8}[e^{-pe}]^{1}} = \frac{(5.8629\times10^{-5})^{1/8}}{(4.0556\times10^{-21})^{1/8}(10^{-5.5})^{9/8}(10^{pE})^{1}} = 10^{4.21}$$

as expected.

6. Select Equilibrated mass distribution:

<table>
<thead>
<tr>
<th>Component</th>
<th>Total dissolved</th>
<th>% dissolved</th>
<th>Total sorbed</th>
<th>% sorbed</th>
<th>Total precipitated</th>
<th>% precipitated</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1</td>
<td>1.9445E-3</td>
<td>100.000</td>
<td>0</td>
<td>0.000</td>
<td>0</td>
<td>0.000</td>
</tr>
<tr>
<td>HS-1</td>
<td>2.0000E-3</td>
<td>100.000</td>
<td>0</td>
<td>0.000</td>
<td>0</td>
<td>0.000</td>
</tr>
<tr>
<td>SO4-2</td>
<td>4.0556E-21</td>
<td>100.000</td>
<td>0</td>
<td>0.000</td>
<td>0</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Note that nearly all of the sulfur is in the form of S(-II) oxidation state($1.9414E-3 + 5.8629E-5 = 2.000E-3$), as expected since the $pe = -4$ which is a reducing condition.

**Redox 2 calculate pe.VDA:** Alternatively, if you had specified the concentration of HS- and of SO42- and instructed the program to calculate the pe value, the total at each oxidation state is constant, but the speciation is still done and then the pe is calculated.

1. Open Visual Minteq, which initializes all settings. Set the pH fixed at 5.50 and the ionic strength to 0.00. Select HS-1 on the main menu and set equal to 0.001 M; do the same thing for SO4-2 = 0.001 M.
2. Select Redox on the main menu.
3. Select the HS-/SO4-2 redox couple and click on Add and Back to main menu.
4. In the Main menu select Parameters. Then, select Specify pe and Eh. Select pe/Eh computed; supply a guess for pe to 10. Often, the program will not converge with redox calculations; when this occurs it is typically necessary to change the initial guess of pe and try again (values might be 10, 0, -4, -10). Save and Back to main menu.
5. On the main menu select Run Minteq and the Output screen will look like this:

Notice that the computed $\text{pe} = -1.788$. Using these values of concentration the log $K = pE^o$ can be calculated to check on internal consistency:

$$\frac{[\text{HS}^-]^{1/8} \cdot [\text{H}^+]^{9/8} \cdot [e^{-\text{pe}}]}{[\text{SO}_4^{2-}]^{1/8} \cdot [\text{H}_2\text{O}]^{9/8}} = \frac{(2.9314 \times 10^{-5})^{1/8}}{(9.9969 \times 10^{-4})^{1/8} (10^{-5.5})^{9/8} (10^{+1.788})^{1/8}} = 10^{4.21}$$

again, as expected.

7. Select Equilibrated mass distribution:
Note that the TotHS-1 and TotSO4-2 = 0.001, still.

**Redox 3 FeS Fe(OH)3 –4 pe pH sweep.VDA:** Add 1 gram of solid FeS (Mackinawite) to system at pe = -4 (anaerobic) and permit Fe(OH)3 (ferrihydrate) to precipitate if possible from 4 to 12 pH.

1. Open Visual Minteq
2. Set pe to -4
3. Fixed pH = 4; Ionic strength = 0.00;
4. Select Solid phases and excluded species, Specify finite solid phases, select Mackinawite, 0.01138 M (1 g of FeS), back to main menu.

5. Select Solid phases and excluded species, Possible solid phases, Ferrihydrite, Add, Back to main menu. This will permit Fe(OH)3 precipitation, if by redox the solution becomes supersaturated with ferrihydrite.
6. Select Multi problem sweep, pH, 19 pts, 4 to 12 pH by 0.50 pH, and output TotFe(III), TotFe(II), TotHS-1, TotSO4-2, and H2Saq. Save and back to main menu:
7. Select Run Minteq and obtain the following output on step No. 10:
8. Select Sweep results and print to Excel and after a bit of formatting:

Notice that at pH = 4 nearly all the FeS is dissolved and it precipitates steadily to about 7.5 pH where the redox of (HS⁻ → SO₄²⁻) becomes predominant and by 8 pH the oxidation of (Fe²⁺ → Fe³⁺) becomes important and builds up TotFe³⁺ in solution until at about 8.5 pH Fe(OH)₃ begins to precipitate and all the sulfur is in solution in the form of SO₄²⁻. The slow rise in TotFe³⁺ in solution above 9 pH is due to increased formation
of Fe(OH)$_4^-$ complexes. This is exactly what can happen in a natural bog that contains FeS (acid volatile sulfides) as it becomes aerated or the pH changes due to algae growth, or to nutrient changes, or physical chemical alterations from pollution. In natural environments the pH can easily vary from 4 to 10 pH, causing enormous changes in the sulfide/sulfate ratios…