Ion Pair or Complex Formation Equilibria

Dozens of Ion Pairs form in SW & even more complexes – deal with them the same way

\[ \text{Mg}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} \rightleftharpoons \text{MgSO}_4_{(aq)} \]

\[ K_f = \frac{a_{\text{MgSO}_4}}{a_{\text{Mg}} a_{\text{SO}_4}} \]

Larger $K_f =$ stronger formation – reaction
Typical Problem in SW
Find Various Forms or Species

Given total concentration data for certain constituents in SW, find % of species

Example: If total Mg is $C_{Mg} = 5.28 \times 10^{-2} \text{ mol/kg}$
and total SO$_4$ is $C_{SO_4} = 2.82 \times 10^{-2} \text{ mol/kg}$

knowing that

$$\text{Mg}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} \rightleftharpoons \text{MgSO}_4_{(aq)}$$

and the value of the $K_f$ or $K_{MgSO_4} = 2.29 \times 10^2$
Steps in the Manual Solution of Simple Equilibrium Problems

1) Start with a recipe: $C_{Mg} = 5.28 \times 10^{-2} \text{ mol/kg}$
   
   $C_{SO4} = 2.82 \times 10^{-2} \text{ mol/kg}$

2) List the species: $\text{Mg}^{2+}$, $\text{SO}_4^{2-}$, $\text{MgSO}_4$

3) List reaction(s): $\text{Mg}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{MgSO}_4$

4) Write Mass Balance equations:

   $C_{Mg} = [\text{Mg}^{2+}] + [\text{MgSO}_4] = 5.28 \times 10^{-2} \text{ mol/kg}$

   $C_{SO4} = [\text{SO}_4^{2-}] + [\text{MgSO}_4] = 2.82 \times 10^{-2} \text{ mol/kg}$
Steps in the Manual Solution of Simple Equilibrium Problems

5) Write a Charge Balance equation:

\[ Z_{i+}[^{\text{i}^+}] = Z_{i-}[^{\text{i}^-}] \]

6) Write equilibrium constant expression(s):

\[
K_f = \frac{\text{a}_{\text{MgSO}_4}}{\text{a}_{\text{Mg}} \text{a}_{\text{SO}_4}} \quad \text{or} \quad \frac{[\text{MgSO}_4]}{[\text{Mg}^{2+}] [\text{SO}_4^{2-}]} \]

There are 3 species or 3 unknown concentrations

There are also 3 equations (actually 4) to solve
We can solve the 3 equations simultaneously to get an answer

Solve for free Mg concentration first = $[\text{Mg}^{2+}]$

Rearrange the mass balance equations:

$$C_{\text{Mg}} = [\text{Mg}^{2+}] + [\text{MgSO}_4]$$ rearranges to give

$$[\text{MgSO}_4] = C_{\text{Mg}} - [\text{Mg}^{2+}]$$

$$C_{\text{SO}_4} = [\text{SO}_4^{2-}] + [\text{MgSO}_4]$$ rearranges giving

$$[\text{SO}_4^{2-}] = C_{\text{SO}_4} - [\text{MgSO}_4]$$

We must also substitute the 1st into the 2nd
\[ C_{Mg} = [Mg^{2+}] + [MgSO_4] \text{ rearranges} \]

to give \[ [MgSO_4] = C_{Mg} - [Mg^{2+}] \]

\[ C_{SO4} = [SO_4^{2-}] + [MgSO_4] \text{ rearranges} \]

giving \[ [SO_4^{2-}] = C_{SO4} - [MgSO_4] \]

Substituting the 1\textsuperscript{st} into the 2\textsuperscript{nd} for \([MgSO_4]\)

Gives \[ [SO_4^{2-}] = C_{SO4} - (C_{Mg} - [Mg^{2+}]) \]

Now we can \[ K_f = \frac{[MgSO_4]}{[Mg^{2+}][SO_4^{2-}]} \]

Substitute into \(K\)
Our resulting equation looks like

\[
K_{\text{MgSO}_4} = \frac{C_{\text{Mg}} - [\text{Mg}^{2+}]}{[\text{Mg}^{2+}] (C_{\text{SO}_4} - (C_{\text{Mg}} - [\text{Mg}^{2+}]))}
\]

Be careful of signs in denominator

\[
K_{\text{MgSO}_4} = \frac{C_{\text{Mg}} - [\text{Mg}^{2+}]}{[\text{Mg}^{2+}] (C_{\text{SO}_4} - C_{\text{Mg}} + [\text{Mg}^{2+}])}
\]

Cast in the form of a quadratic

\[
K[\text{Mg}^{2+}]C_{\text{SO}_4} - K[\text{Mg}^{2+}]C_{\text{Mg}} + K[\text{Mg}^{2+}]^2 = C_{\text{Mg}} - [\text{Mg}^{2+}]
\]

Set equal to zero and solve with the quadratic formula
Equation from previous slide

\[ K[Mg^{2+}]C_{SO_4} - K[Mg^{2+}]C_{Mg} + K[Mg^{2+}]^2 = C_{Mg} - [Mg^{2+}] \]

Set equal to 0 & rearrange in form for quadratic formula

\[ K[Mg^{2+}]^2 + K[Mg^{2+}]C_{SO_4} - K[Mg^{2+}]C_{Mg} + [Mg^{2+}] - C_{Mg} = 0 \]

Gather terms

\[ K[Mg^{2+}]^2 + (KC_{SO_4} - KC_{Mg} + 1)[Mg^{2+}] - C_{Mg} = 0 \]

Remember the quadratic formula?
Equation from previous slide

$$K[Mg^{2+}]^2 + (KC_{SO_4} - KC_{Mg} + 1)[Mg^{2+}] - C_{Mg} = 0$$

Quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Solve for $x$ which for us is $[Mg^{2+}]$ where

$$a = K \quad b = (KC_{SO_4} - KC_{Mg} + 1) \quad c = -C_{Mg}$$
Solving this problem with the quadratic formula
And substituting in the known values for:

K_f' which equals K_f \gamma^2

Where K_f = K_{MgSO_4} = 2.29 \times 10^2 \text{ and } \gamma = 0.23

C_{Mg} = 5.28 \times 10^{-2} \text{ mol/kg}

C_{SO_4} = 2.82 \times 10^{-2} \text{ mol/kg}

The answer is: \ x = [Mg^{2+}] = 4.35 \times 10^{-2} \text{ mol/kg}

Since C_{Mg} = 5.28 \times 10^{-2} \text{ mol/kg} then [Mg^{2+}] = 82 \%
Activity Coefficient

At typical ionic strengths for SW \( I = 0.5 \) to 0.7

From Davies Equation \( \text{Mg}^{2+} \) activity coefficient

\[
\ln \gamma = - A \ Z^2 \ \left[ \frac{I^{0.5}}{(1 + I^{0.5})} - 0.2 \ I \right]
\]

If \( Z = 2 \) & \( A = 1.17 \) then \( \ln \gamma = - 1.47 \) & \( \gamma = 0.23 \)
Calculate All Species

Given \( C_{\text{Mg}} = 5.28 \times 10^{-2} \text{ mol/kg} \)
and \( C_{\text{SO}_4} = 2.82 \times 10^{-2} \text{ mol/kg} \)

We calculated \( [\text{Mg}^{2+}] = 4.35 \times 10^{-2} \text{ mol/kg} \) or 82 %

By difference \( [\text{MgSO}_4] = 9.30 \times 10^{-3} \text{ mol/kg} \) or 18 %

We can likewise calculate \( [\text{SO}_4^{2-}] \) concentration & %

\( C_{\text{SO}_4} - [\text{MgSO}_4] = [\text{SO}_4^{2-}] = 1.89 \times 10^{-2} \text{ mol/kg} \)
Problems

- Went through a moderately difficult calculation & only calculated species for 1 reaction in SW
- If considered more complicated equilibria where several reactions were going on, the math would quickly get out of hand
- Didn’t consider any other reactions involving Mg or SO$_4$ that might influence our results
Other Problems

- Equilibrium constants can vary as much as 5% depending on the source.
- Concentration data vary as well.
- Activity corrections can also vary depending on the method used.
- We only considered activity corrections for charged species, while neutral species may also have \( \gamma \)'s that are non unity (e.g., \( \text{MgSO}_4 \)).
Problems Mentioned

- Only 1 reaction, 1 set of species, simple equilibrium
- Didn’t consider any other reactions involving Mg or SO$_4^-$ that might influence our results

Other reactions influence amount of MgSO$_4$ produced
Must Consider Other Reactions

Beside $\text{Mg}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} \rightleftharpoons \text{MgSO}_4_{(aq)}$

There are also

$\text{Ca}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)} \rightleftharpoons \text{CaSO}_4_{(aq)}$

$\text{Na}^+_{(aq)} + \text{SO}_4^{2-}_{(aq)} \rightleftharpoons \text{NaSO}_4^-_{(aq)}$

$\text{K}^+_{(aq)} + \text{SO}_4^{2-}_{(aq)} \rightleftharpoons \text{KSO}_4^-_{(aq)}$

and

$\text{Mg}^{2+}_{(aq)} + \text{CO}_3^{2-}_{(aq)} \rightleftharpoons \text{MgCO}_3_{(aq)}$

as well as others
Several Questions to Ponder

1) Based on the knowledge that there are other competing reactions in SW, is our calculation accurate? (82 % free Mg$^{2+}$?)

2) How do we know what other reactions are going on in SW that we should consider?

3) How do we include all the other equilibrium reactions that we might consider important?

4) How do we deal with the increased complexity of the mathematics?

5) Why did I take this course?
Answers to Question #1

Based on the knowledge that there are other competing reactions in SW, is our calculation accurate? (82 % free Mg$^{2+}$?)

The calculation is only an estimate because we did not consider the formation of other species

\[
\text{CO}_3^{2-} \quad \text{Ca}^{2+} \quad \text{Na}^+ \\
\text{Mg}^{2+} \quad \text{SO}_4^{2-} \quad \text{MgSO}_4^{(aq)} \\
\text{F}^- \quad \text{K}^+ \quad \text{Zn}^{2+}
\]

their influence on the amount of MgSO$_4$ produced
Answers to Question #2

How do we know what other reactions are going on in SW that we should consider?

We will largely rely on the literature for known reactions in SW (e.g., books & papers such as the handout provided this week). Chemical Intuition also helps.
Answers to Question #3

How do we include all the other equilibrium reactions that we might consider important?

Using our manual approach to solving equilibrium problems, we would have to expand our mass balance equations as well as add additional equilibrium constant expressions. The number of species for which the concentration is unknown & the number of equations grows rapidly as we add equilibria.
Answers to Question #4

How do we deal with the increased complexity of the mathematics?

Solving 5 or more equations simultaneously can only be handled in two ways:

1) Assumptions or approximations can be made to simplify the equations to something more manageable

2) Computer programs designed to solve ionic equilibrium problems can be used
Computer programs

MINEQL+ – we will use this exclusively
http://www.mineql.com/

MINTEQA2 – EPA DOS version of MINEQL
http://www.epa.gov/ceampubl/mmedia/minteq/index.htm

GEOCHEM – geochemical modeling software
http://envisci.ucr.edu/downloads/parker/geochem.zip

Visual MINTEQ – user friendly MINTEQA2
www.lwr.kth.se/english/OurSoftware/vminteq/index.htm

PHREEQC – USGS modeling software
wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/
Computer programs (continued)

HYDRA/MEDUSA

http://w1.156.telia.com/%7Eu15651596/

PHRQPITZ – USGS, for high ionic strength

http://water.usgs.gov/software/phrqpitz.html

WinHumicV – Includes humic binding model

http://www.lwr.kth.se/english/OurSoftware/WinHumicV

CHEAQS

http://home.tiscali.nl/cheaqs/
Speciation of Metals in the Oceans. I. Inorganic Complexes in Seawater, and Influence of Added Chelating Agents

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Department of Chemistry, Texas A&M University, College Station, TX 77843 (U.S.A.)
(Received April 3, 1986; revision accepted January 29, 1987)
Motekaitis & Martell (1987) Table I

Note molar concentration units (M) & multiplier

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration, M × 10³</th>
<th>Trace Element</th>
<th>Concentration, M × 10⁹</th>
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<tbody>
<tr>
<td>Na⁺</td>
<td>479</td>
<td>Mn</td>
<td>4</td>
</tr>
<tr>
<td>Mg²⁺</td>
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<td>Fe</td>
<td>8</td>
</tr>
<tr>
<td>Ca²⁺</td>
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<td>Ni</td>
<td>5</td>
</tr>
<tr>
<td>K⁺</td>
<td>10.4</td>
<td>Cu</td>
<td>4</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>559</td>
<td>Zn</td>
<td>5</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>28.9</td>
<td>Cd</td>
<td>0.1</td>
</tr>
<tr>
<td>HCO₃⁻, CO₃⁻</td>
<td>2.35</td>
<td>Hg</td>
<td>0.02</td>
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<tr>
<td>Br⁻</td>
<td>0.86</td>
<td>Pb</td>
<td>0.05</td>
</tr>
<tr>
<td>F⁻</td>
<td>0.075</td>
<td>U</td>
<td>14</td>
</tr>
</tbody>
</table>
Motekaitis & Martell (1987) Table I, Major Ions

Major and some minor constituents of seawater

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration, M × 10³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>479</td>
</tr>
<tr>
<td>Mg²⁺</td>
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<tr>
<td>Br⁻</td>
<td>0.86</td>
</tr>
<tr>
<td>F⁻</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Note: These numbers have been multiplied by 10³ or 1000 so they are millimolar (mM) or 479 is really 0.479 M or 4.79 x 10⁻² M
<table>
<thead>
<tr>
<th>Trace Element</th>
<th>Concentration, $M \times 10^9$</th>
</tr>
</thead>
<tbody>
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<tr>
<td>Fe</td>
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<td>Ni</td>
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<tr>
<td>Cu</td>
<td>4</td>
</tr>
<tr>
<td>Zn</td>
<td>5</td>
</tr>
<tr>
<td>Cd</td>
<td>0.1</td>
</tr>
<tr>
<td>Hg</td>
<td>0.02</td>
</tr>
<tr>
<td>Pb</td>
<td>0.05</td>
</tr>
<tr>
<td>U</td>
<td>14</td>
</tr>
</tbody>
</table>

Note: These numbers have been multiplied by $10^9$ and are nanomolar (nM) or 4 is really 4 nM or $4 \times 10^{-9}$ M
Motekaitis & Martell give a long list of species with equilibrium constants

Note: Values are Log $\beta$ not K, also I (\(\mu\)) = 0.70

**TABLE II**

Log overall stability constants for soluble components of seawater

<table>
<thead>
<tr>
<th>Species</th>
<th>Log $\beta$</th>
<th>Species</th>
<th>Log $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$</td>
<td>2.21</td>
<td>FeH$_{+2}$</td>
<td>-5.88</td>
</tr>
<tr>
<td>CaHCO$_3^+$</td>
<td>9.90</td>
<td>FeH$_{-4}$</td>
<td>-20.76</td>
</tr>
<tr>
<td>CaSO$_4$</td>
<td>1.03</td>
<td>Fe$<em>2$H$</em>{-2}^{+}$</td>
<td>-3.08</td>
</tr>
<tr>
<td>CaF$_+$</td>
<td>0.60</td>
<td>MnHCO$_3^+$</td>
<td>10.00</td>
</tr>
<tr>
<td>CaH$_{+1}$</td>
<td>-12.20</td>
<td>MnSO$_4$</td>
<td>0.80</td>
</tr>
<tr>
<td>MgCO$_3$</td>
<td>2.05</td>
<td>MnCl$_+$</td>
<td>-0.20</td>
</tr>
<tr>
<td>MgHCO$_2^+$</td>
<td>9.80</td>
<td>MnCl$_2$</td>
<td>-0.3</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>0.90</td>
<td>MnCl$_3^-$</td>
<td>-0.50</td>
</tr>
<tr>
<td>MgF$_+$</td>
<td>1.30</td>
<td>MnH$_{+1}$</td>
<td>-10.80</td>
</tr>
</tbody>
</table>
The difference between $\beta$ & $K$

$K$ is a stepwise formation constant

$$\text{Cd}^{2+} + \text{Cl}^- \rightleftharpoons \text{CdCl}^+ \quad K_1 = \frac{[\text{CdCl}^+]}{[\text{Cd}^{2+}][\text{Cl}^-]} = 1.0 \times 10^2$$

$$\text{CdCl}^+ + \text{Cl}^- \rightleftharpoons \text{CdCl}_2 \quad K_2 = \frac{[\text{CdCl}_2]}{[\text{CdCl}^+][\text{Cl}^-]} = 4.0 \times 10^0$$

$\beta$ is an overall formation constant

$$\text{Cd}^{2+} + \text{Cl}^- \rightleftharpoons \text{CdCl}^+ \quad \beta_1 = \frac{[\text{CdCl}^+]}{[\text{Cd}^{2+}][\text{Cl}^-]} = 1.0 \times 10^2$$

$$\text{Cd}^{2+} + 2 \text{Cl}^- \rightleftharpoons \text{CdCl}_2 \quad \beta_2 = \frac{[\text{CdCl}_2]}{[\text{Cd}^{2+}][\text{Cl}^-]^2} = 4.0 \times 10^2$$
Notes on $\beta$ & $K$

- $K_1 = \beta_1$ (from previous slide)
- $K_2$ is not equal to $\beta_2$ (note denominators of each expression)
- $\beta_2 = K_1 \times K_2$
  
  $$\beta_2 = \frac{[\text{CdCl}_2]}{[\text{Cd}^{2+}] [\text{Cl}^-]^2} = \frac{[\text{CdCl}^+]}{[\text{Cd}^{2+}] [\text{Cl}^-]} \times \frac{[\text{CdCl}_2]}{[\text{CdCl}^+][\text{Cl}^-]}$$

- $\beta_3 = K_1 \times K_2 \times K_3$ (etc.)
Seawater speciation in the absence of added ligands at pH 8.1.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Cl&lt;sup&gt;-&lt;/sup&gt;</th>
<th>Br&lt;sup&gt;-&lt;/sup&gt;</th>
<th>F&lt;sup&gt;-&lt;/sup&gt;</th>
<th>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;</th>
<th>(H)CO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</th>
<th>OH&lt;sup&gt;-&lt;/sup&gt;</th>
<th>Uncomplexed</th>
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</thead>
<tbody>
<tr>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.01</td>
<td>9.8</td>
<td>0.54</td>
<td></td>
<td></td>
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<td>79.0</td>
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<tr>
<td>Mg&lt;sup&gt;2+&lt;/sup&gt;</td>
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<tr>
<td>K&lt;sup+&lt;/sup&gt;</td>
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<td>2.2</td>
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<td>97.8</td>
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<tr>
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<td>0.3</td>
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<td>0.05</td>
<td>2.9</td>
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<tr>
<td>Hg&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>99.9</td>
<td>0.05</td>
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<td></td>
<td></td>
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<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
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<td>1.71</td>
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<tr>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>1.9</td>
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<td>0.2</td>
<td>22.4</td>
<td>73.6</td>
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<tr>
<td>Zn&lt;sup&gt;2+&lt;/sup&gt;</td>
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<td>0.02</td>
<td>4.86</td>
<td>0.40</td>
<td>0.47</td>
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<tr>
<td>Pb&lt;sup&gt;2+&lt;/sup&gt;</td>
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<td>0.02</td>
<td>0.3</td>
<td>71.9</td>
<td>3.9</td>
<td></td>
<td>1.5</td>
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<tr>
<td>Ni&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>29.6</td>
<td>0.01</td>
<td>3.1</td>
<td></td>
<td>0.67</td>
<td></td>
<td>66.6</td>
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<tr>
<td>UO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;2+&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.0</td>
<td></td>
</tr>
</tbody>
</table>
Computer programs

MINEQL+ – we will use this exclusively

http://www.mineql.com/

Program still requires setting up the Equilibrium Problem
- Must list species of interest
- Must have total concentration data for each constituent

Other needed information may include
- Ionic strength
- pH
- $\text{CO}_2$/Carbonate
Steps in the MINEQL+ Solution of Simple Equilibrium Problems

1) Start with a recipe:
   \[ C_{\text{Mg}} = 5.28 \times 10^{-2} \text{ mol/kg} \]
   \[ C_{\text{SO}_4} = 2.82 \times 10^{-2} \text{ mol/kg} \]

2) List the species: \( \text{Mg}^{2+}, \text{SO}_4^{2-}, \text{MgSO}_4 \)

3) Run the program

4) Interpret the results