Overview of reaction modeling with The Geochemist's Workbench®

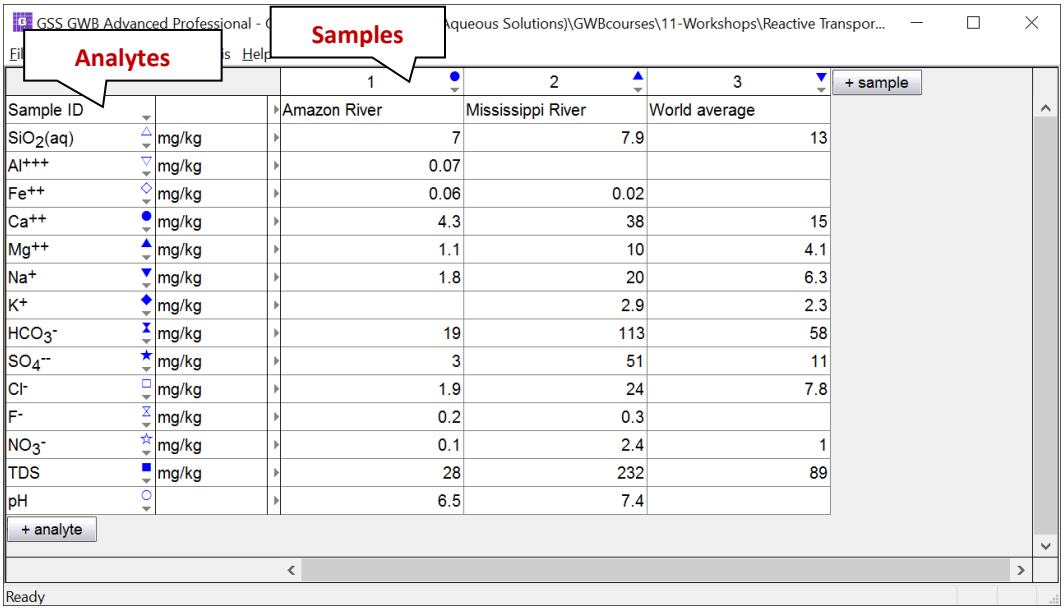
This lab serves to introduce the GWB and the basis swapping technique upon which its programs are founded.

Demo 1 — The Geochemist's Spreadsheet

GSS is a spreadsheet designed for geochemists. The program works with the other software tools in The Geochemist's Workbench. You enter, paste, or drag the analyses for your samples into a **GSS** data sheet.

You can then convert units, create plots and diagrams, mix samples, compare replicate analyses and check standards, calculate speciation and saturation, and more. You can drag samples into the other GWB apps, and drag calculations results from the other apps into **GSS**.

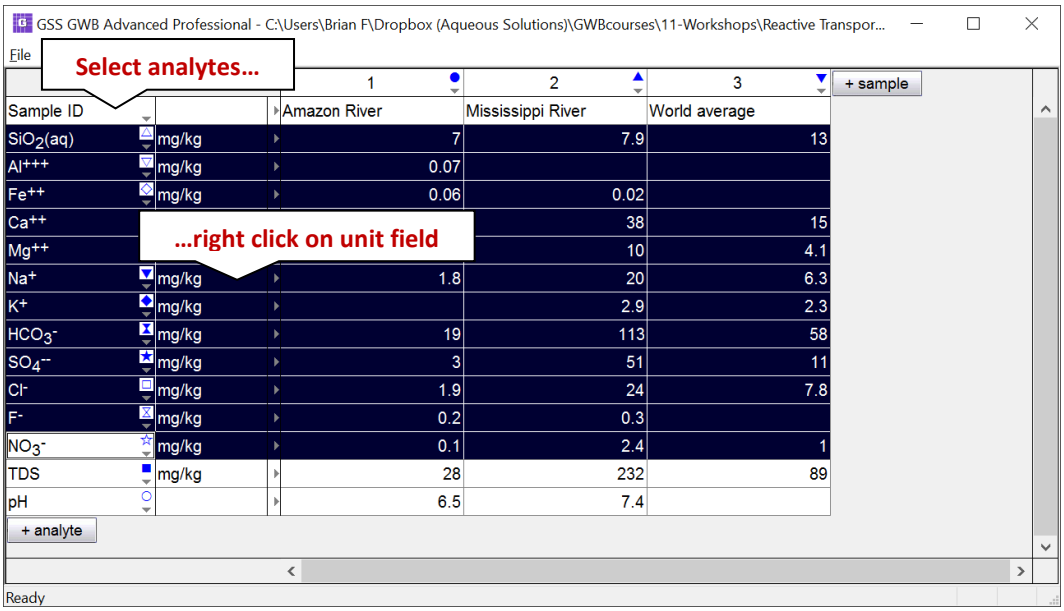
To get started, double click on "RiverWaters.gss":



Sample ID		1 Amazon River	2 Mississippi River	3 World average
$SiO_2(aq)$	mg/kg	7	7.9	13
Al^{+++}	mg/kg	0.07		
Fe^{++}	mg/kg	0.06	0.02	
Ca^{++}	mg/kg	4.3	38	15
Mg^{++}	mg/kg	1.1	10	4.1
Na^{+}	mg/kg	1.8	20	6.3
K^{+}	mg/kg		2.9	2.3
HCO_3^{-}	mg/kg	19	113	58
SO_4^{--}	mg/kg	3	51	11
Cl^{-}	mg/kg	1.9	24	7.8
F^{-}	mg/kg	0.2	0.3	
NO_3^{-}	mg/kg	0.1	2.4	1
TDS	mg/kg	28	232	89
pH		6.5	7.4	

Analytes and their units are listed in the leftmost columns. Columns to the right hold data for the samples. You add analytes to the datasheet by clicking on the + analyte button, and samples with the + sample button. Exchange rows and columns by selecting **Edit → Transpose Data Sheet**.

To convert units, select one or more analytes



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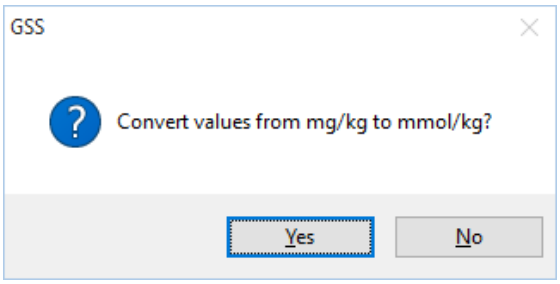
then right-click on the unit field and select a new unit under the **Units** pulldown.

To complete the task, select each of the chemical components listed with units of “mg/kg”, then click on **Units** → **“**mmol” → **“**mmol/kg”. When the program prompts



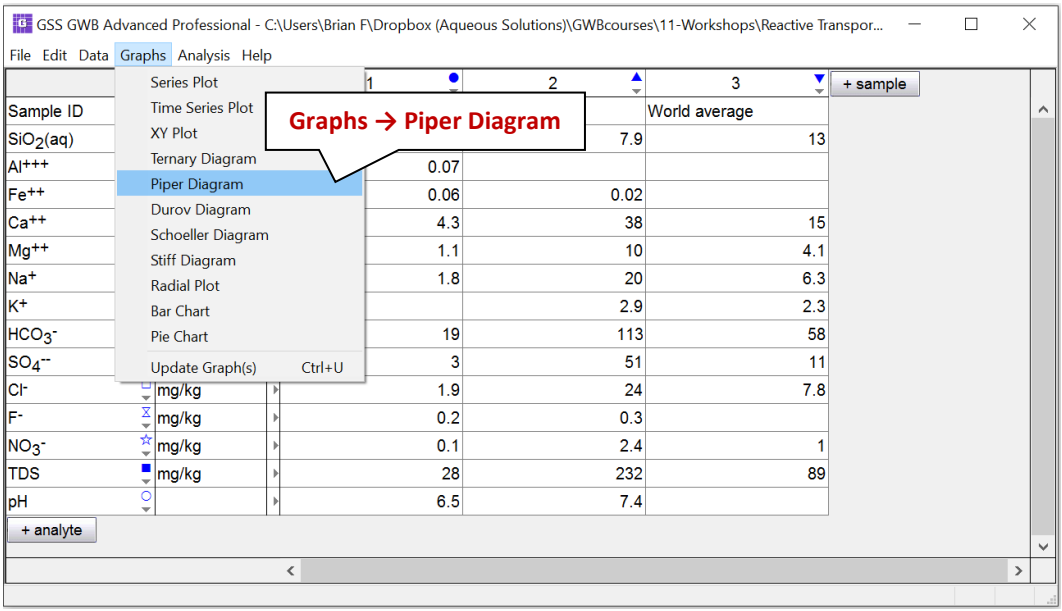
select **Yes**. The analyses for the components you selected should now appear in the new units. If you had selected **No**, the unit designation would have changed, but the numerical values would have remained unaltered.

Why can’t TDS (Total Dissolved Solids) be converted to mmol/kg like the chemical components?

Laboratories commonly report analyses in elemental equivalents, such as sulfate as mg/kg of sulfur, or bicarbonate as mg/kg of carbon. To specify such a unit in a **GSS** spreadsheet, choose the “SO_4^{--}” analyte, for example, right-click the units column, and select **As** → “S” rather than **As** → “SO_4^{--}”.

You can similarly set concentrations in species equivalents, in terms of protonated or deprotonated forms of the species in the spreadsheet, such as bicarbonate as mg/kg of carbon dioxide, or ammonium as mg/kg of ammonia. To specify such a unit, choose the “HCO_3^{-}” analyte, for example, right-click the units column, and select **As** → “CO_2(aq)”.

To plot the data, go to **Graphs** and choose from the list of plots and diagrams



Sample ID		1	2	3
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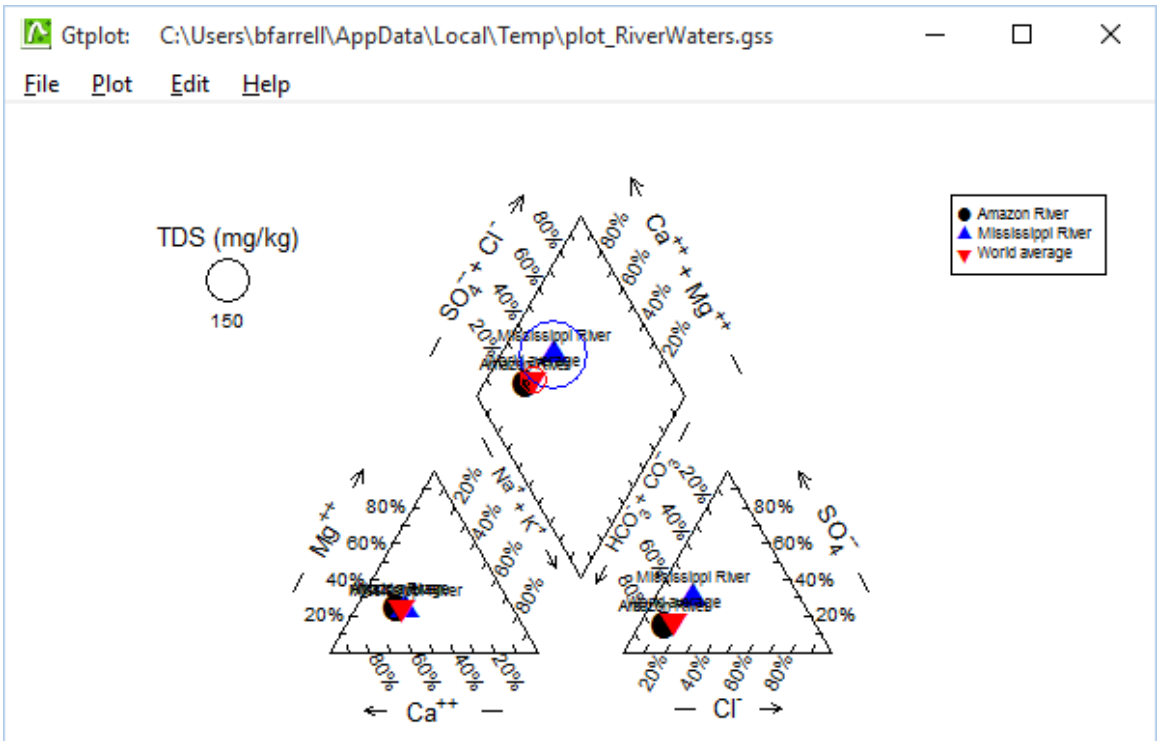
The Piper diagram is useful for portraying the major ion composition of a suite of samples. How does the Mississippi River sample differ from the others?



Right-click in various places on the plot—on the samples, labels, and axes—to explore how you can modify its appearance. You can turn sample legends and labels on or off, for example, and change the size, font, or color of text.

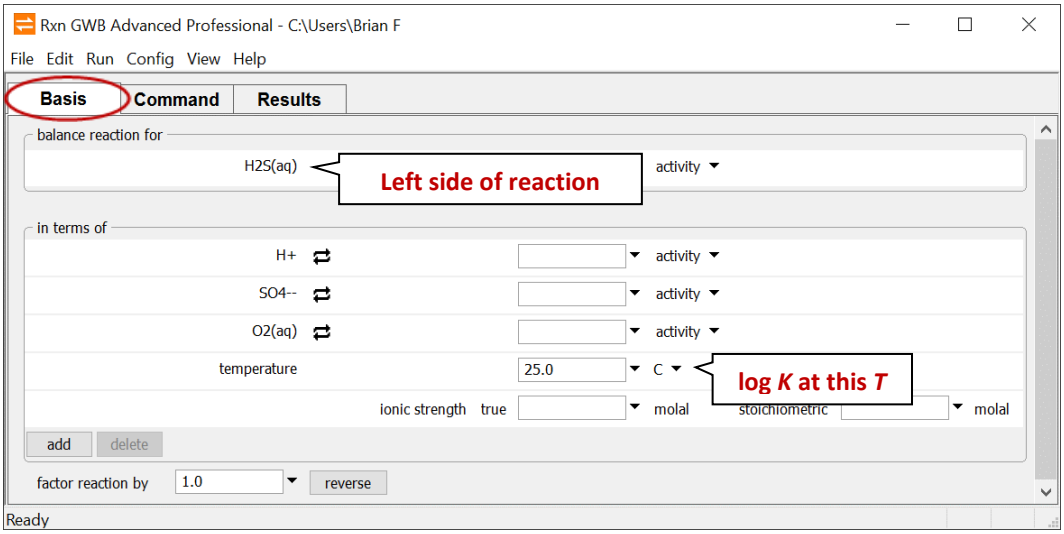
GSS works with **SpecE8** to quickly perform tasks such as computing mineral saturation or gas fugacity. Go to + analyte → **Calculate** and choose from the lists of analytes for the various variable types.

*Demo 2 — Reaction balancing with **Rxn***

To balance a reaction with **Rxn**, first set a species, mineral, etc., to appear on the left side of the reaction. Then, swap the basis to pull in the various species you want to appear in the reaction.

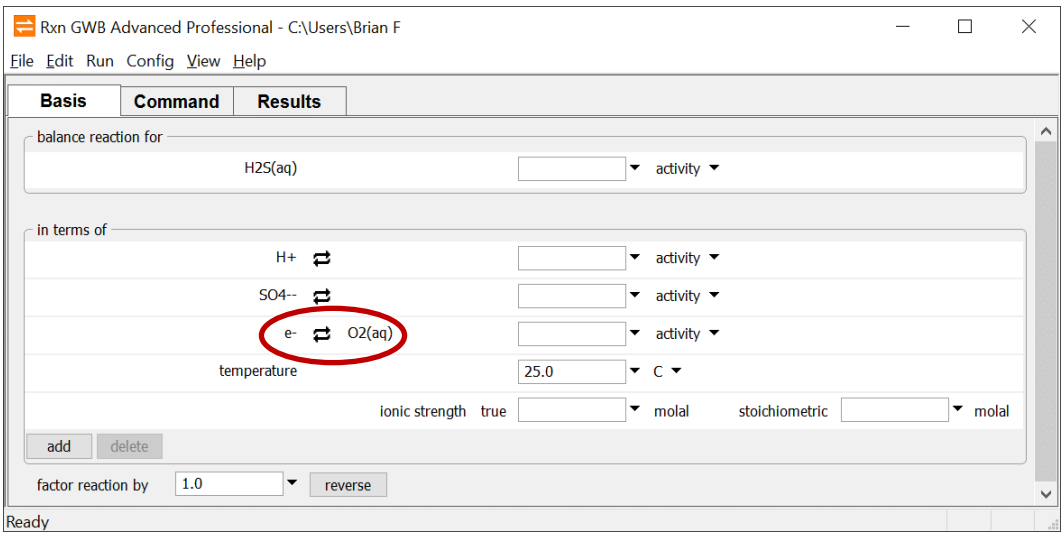
For example, to show the reaction by which H_2S(aq) oxidizes to sulfate, start **Rxn** and move to the **Basis** pane. Under "balance reaction for", select "???"→ **Aqueous…** → H_2S(aq). Set "temperature" to 25 °C.

The pane should look like this



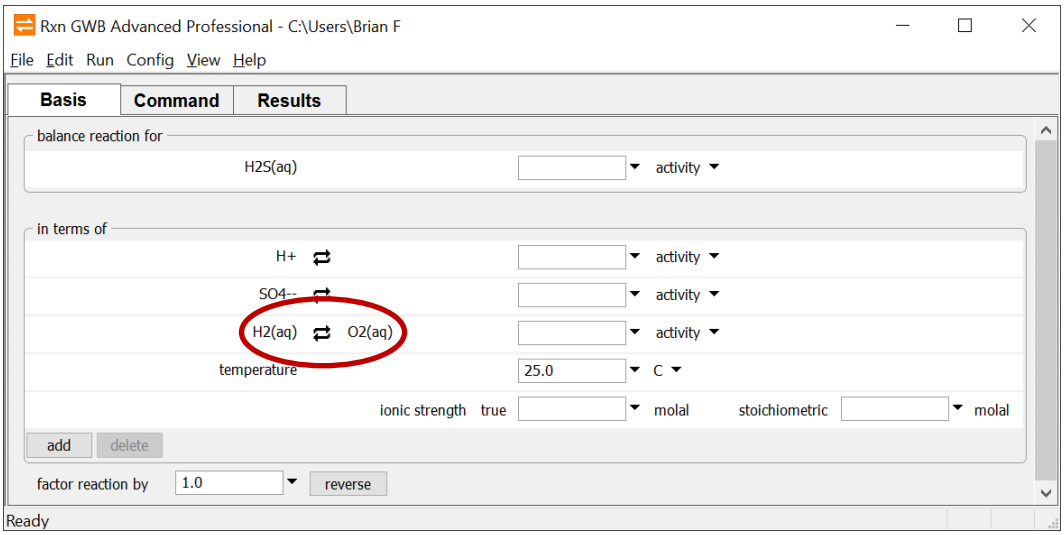
Move to the **Results** pane and click Run. What chemical reaction does the program give? What is its log *K*?

Now let's balance the corresponding half-cell reaction. Click on the swap button ⇄ next to the basis entry for "O2(aq)" and select **Aqueous…** → e−



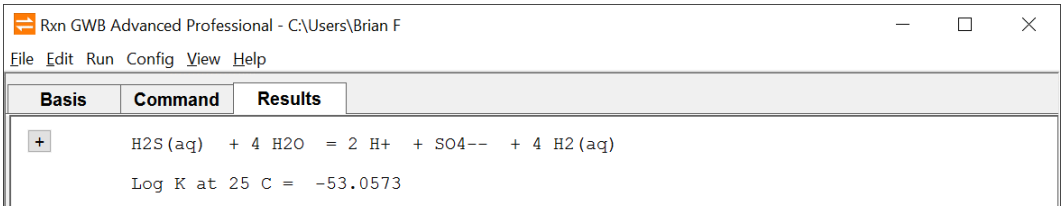
Move to the **Results** pane and click Run. How has the reaction changed?

To recast the reaction to liberate dihydrogen, once again click on the swap button ⇄ next to the basis entry for “O2(aq)” (where e− is currently swapped in) and select **Aqueous…→** H2(aq)



Return to the **Results** pane and click Run. How has the reaction changed?

To see more information about the reaction, including the corresponding equilibrium equation and the equilibrium constant at each of the principal temperatures, click the + button



Demo 3 — Eh-pH diagrams

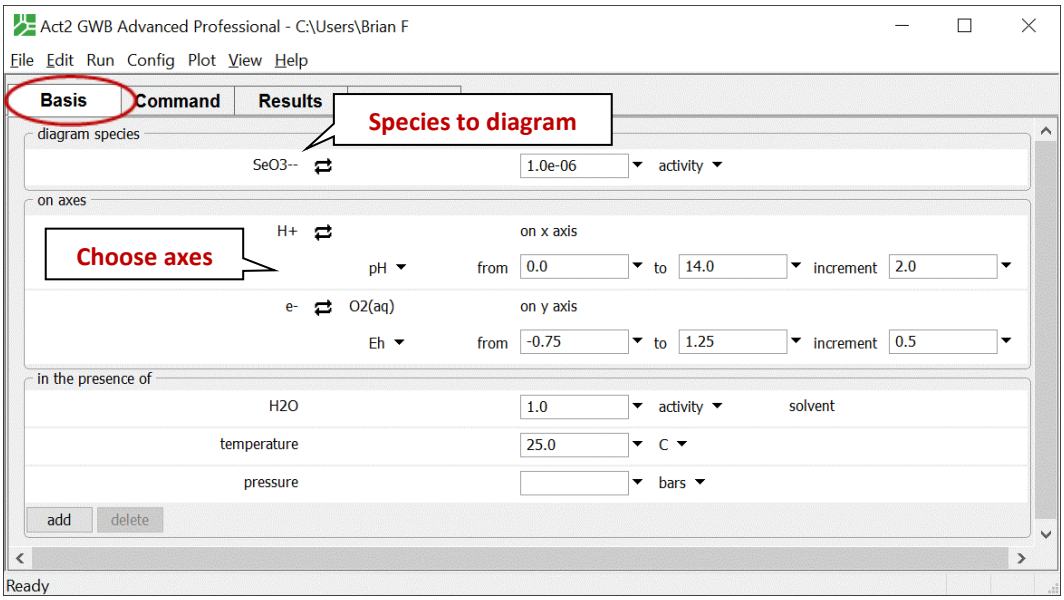
Act2 calculates geochemical stability diagrams on activity or fugacity coordinates. To calculate an Eh-pH diagram for selenium, for example, start the program and move to the **Basis** pane:

1. Under “diagram species”, click on “???” and select “SeO3−−”. Set activity to 10^-6.

2. Under “on axes”, for “on x axis” click on “???” and select “H+”. Change the unit from “log activity” to “pH”. The axis automatically spans from 0 to 14, but you can adjust the range.

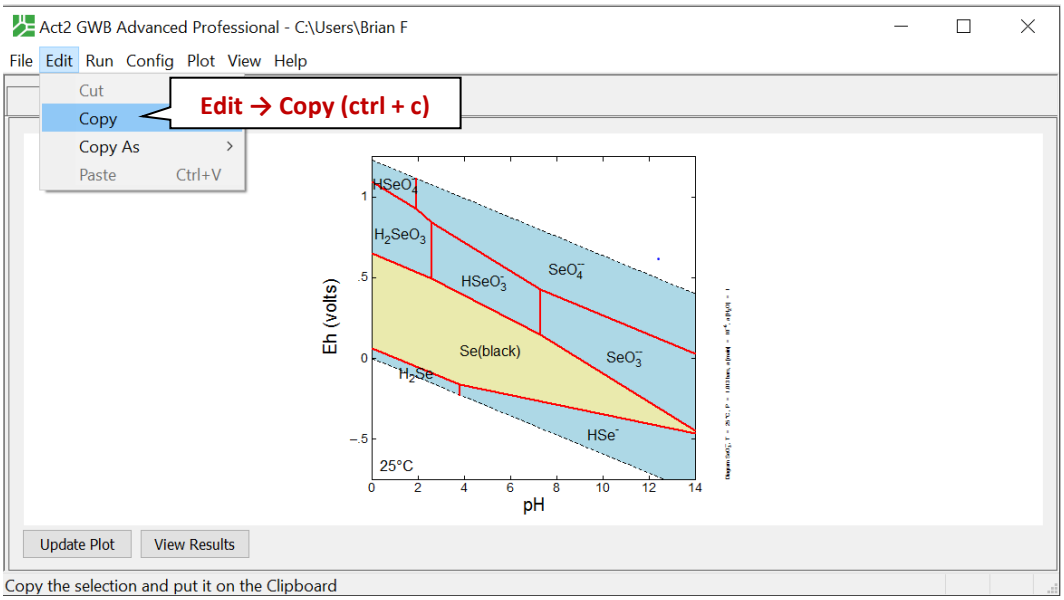
3. For “on y axis” click on “???” and select “O2(aq)”. Click on the swap button ⇄ next to the basis entry for “O2(aq)” and select **Aqueous…→** e−. Change the unit from “log activity” to “Eh”.

The pane should look like this:

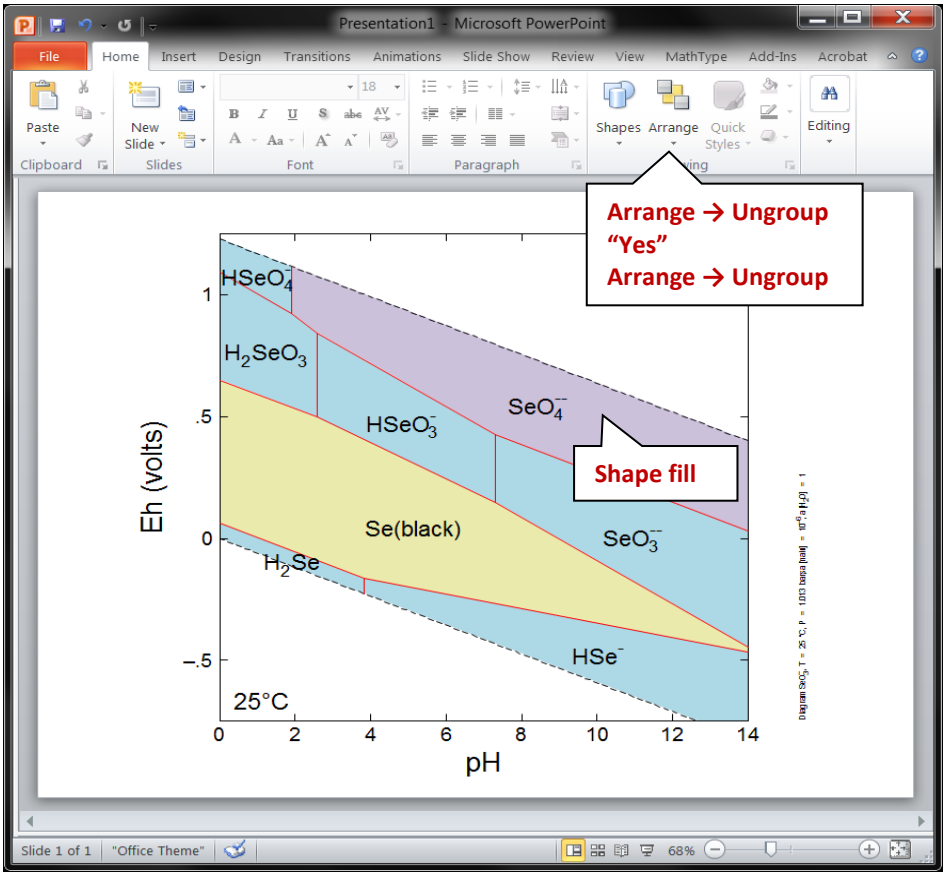


Move to the **Plot** pane to view your diagram.

You can copy your plot and paste it into your documents, including Microsoft Word, Excel, and PowerPoint, or Adobe Illustrator. First, select **Edit → Copy**



then, paste into PowerPoint as an Enhanced Metafile. Ungroup the image to enable editing



Demo 4 — Electrochemistry and Microbial Metabolism

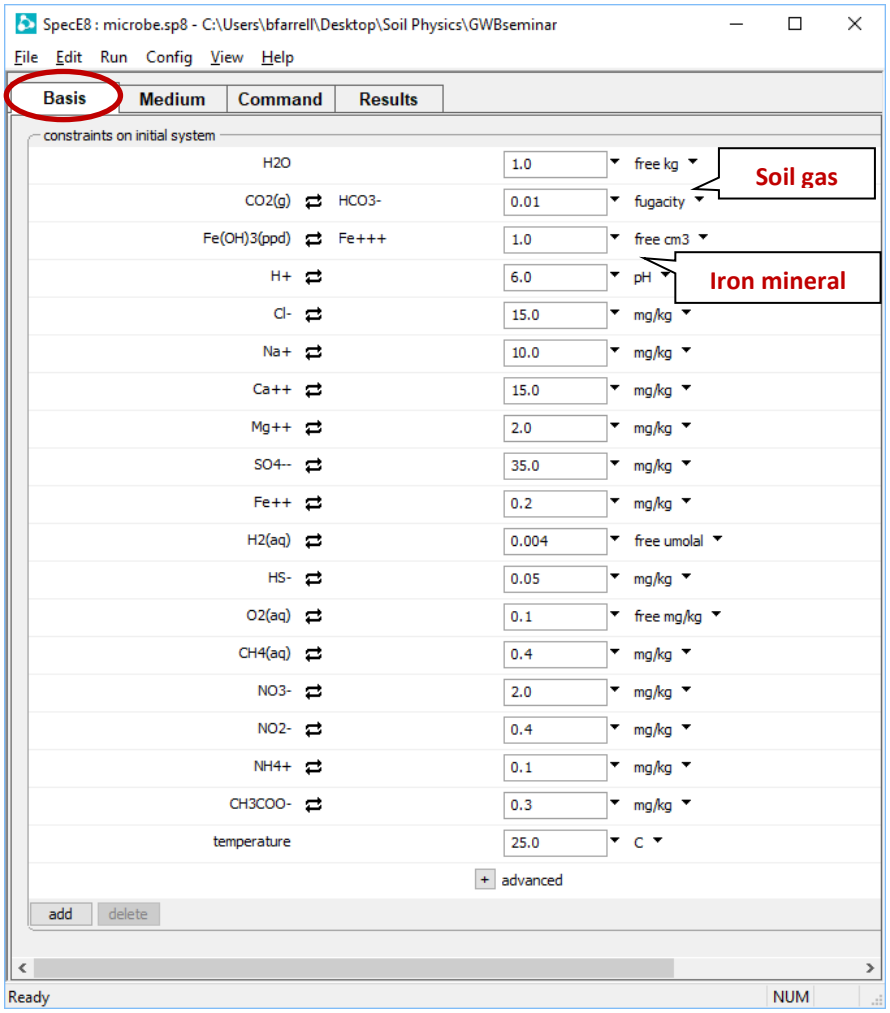
Microbes take advantage of the redox disequilibrium found in the natural environment to derive energy. Respiring microbes trap energy released when electrons liberated by an electron donating reaction are taken up by an electron accepting reaction.

The difference Δ*Eh* between the *Eh* for the accepting and donating reactions is a measure in volts or mV of the energy released. The value is given as

$$\Delta Eh = Eh_{acc} - Eh_{don} = -\frac{\Delta G_r}{nF}$$

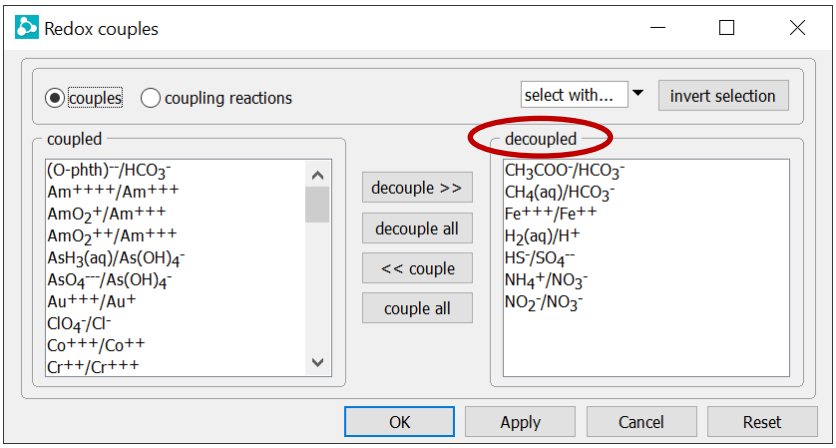
where *n* is the number of electrons transferred and *F* is the Faraday constant. Reactions with positive *Eh* values release energy.

Double click on file "microbe.sp8". When **SpecE8** opens, move to the **Basis** pane



The input describes the analysis of a hypothetical groundwater, assuming equilibrium with ferric hydroxide and a soil gas in which $f\,CO_2 = 10^{-2}$. Note that constraints are provided for the distribution of several elements across differing redox states.

To see why, opening the **Config → Redox Couples…** dialog



Several redox pairs have been disabled.

Move to the **Results** pane and click Run, then View Results. In **SpecE8**'s output file, check the Nernst Eh values for the following redox couples:

Redox couple	*Eh (mV)*
$e^- + ¼\ O2(aq) + H^+ \leftrightarrow ½\ H_2O$	836
$2\ e^- + 2\ H^+ + NO_3^- \leftrightarrow H_2O + NO_2^-$	481
$8\ e^- + 10\ H^+ + NO_3^- \leftrightarrow 3\ H_2O + NH_4^+$	443
$e^- + Fe^{+++} \leftrightarrow Fe^{++}$	322
$8\ e^- + 9\ H^+ + SO_4^{--} \leftrightarrow 4\ H_2O + HS^-$	–126
$8\ e^- + 9\ H^+ + HCO_3^- \leftrightarrow 3\ H_2O + CH_4(aq)$	–187
$2\ e^- + 2\ H^+ \leftrightarrow H_2(aq)$	–199
$8\ e^- + 9\ H^+ + 2\ HCO_3^- \leftrightarrow 4\ H_2O + CH_3COO^-$	–230

Which couple is the most energetically favorable as an electron donating reaction? Which is the best at accepting electrons?

For each of the following metabolisms, determine Δ*Eh*. Which metabolisms are favorable for microbes living in contact with this groundwater?

- Oxidation of acetate by ferric iron.
- Oxidation of methane by molecular O_2.
- Reduction of sulfate by ferrous iron.
- Oxidation of H_2 by nitrate.