

**Example 1:**  $[\text{Na}_2\text{CO}_3]_{\text{T}} = 10^{-3} \text{ M}$ ,  $[\text{HCl}]_{\text{T}} = 10^{-3} \text{ M}$

1. Open up MINEQL+. The first screen that you will see is for selecting components.
2. Select the necessary components (note that you do not have only one possible set).
3. Click “Scan Thermo”, which has MINEQL search its database for reactions involving those components. It will then bring up a screen of aqueous complexes. If the aqueous complexes screen does not appear (it won't if autopilot is off), you can access this menu from Model -> Tableau.

Types of Species in MINEQL+

- Components (Type I) (not shown in the tableaus in MINEQL+)
- Aqueous Complexes (Type II)
- Fixed Entities (Type III)
- Dissolved Solids (Type V)
- Species not Considered (Type VI)

4. Select the “Wizard” option to begin specifying values for the problem.
5. Enter totals for  $\text{Na}^+$  and  $\text{Cl}^-$ . Why don't  $\text{H}^+$  and  $\text{CO}_3^{2-}$  appear here.
6. Select the “pH” tab. Choose pH calculated by MINEQL using electroneutrality.

Methods for Handling pH in MINEQL+

- pH supplied by user: particularly useful for creating LogC-pH plots
- pH calculated by MINEQL
  - using TOTH (use if recipe not given in terms of components)
  - using electroneutrality (use if recipe given in terms of components)

7. Select “CO2” tab. Choose closed to the atmosphere and enter the TOTCO3.
8. Select the “Solids Mover” tab. Turn all solids off. We will do this until we begin looking at dissolution-precipitation reactions.
9. Close the wizard by clicking “OK” and then close the tableau view.
10. You will be brought to the calculation window (again, if autopilot is not on, you will need to select “Calculate” from the Model menu.
11. Give the output data the name “example1” and leave ionic strength and temperature corrections off.
12. Select run, which will then bring up the Output Manager (this too is available from the Model menu).

13. The two types of output that we will usually view are “components” and “special reports.” Choose special reports by checking it, clicking view, and then selecting Summary of All Species for a Single Run.
14. This menu provides the concentrations of all of the species in the system, including some dummy values for the species not considered. Note that at the very bottom of the screen, there is an entry for Activity of H<sup>+</sup>. The reason for this is that for Type I species, MINEQL will report the concentration of H<sup>+</sup>, but the activity of H<sup>+</sup> is the value that determines the pH. Without activity coefficient corrections, the concentration and activity will be identical.
15. Close the special report and now check components, then highlight CO<sub>3</sub><sup>2-</sup> as the component, choose how to display CO<sub>3</sub><sup>2-</sup> data as Obs x Species, and then choose LogC. Note that you can display the concentrations in many different ways. The right-most column is a Type VII species called TOTAL CO<sub>3</sub>, which is the total dissolved concentration of inorganic carbon. This Type VII species will be particularly useful in solubility problems.
16. Close the windows and repeat the problem at a fixed ionic strength of 0.1M. How are the concentration and activity of H<sup>+</sup> different?

### **Example 1**

**Conc and activity of H<sup>+</sup> is 5.120E-9, tot C=10<sup>-3</sup>**

**Conc of H<sup>+</sup> = 1.050E-8, activity of H<sup>+</sup> = 8.130E-9**

**Example 2: LogC-pH diagram of a generic diprotic acid ( $H_2AGen$ ) with  $pK_{a1} = 3$  and  $pK_{a2} = 6$ .  $[H_2AGen]_T = 10^{-4} M$ ,  $[HAc]_T = 10^{-2} M$**

1. Return to select components uncheck previous components and select acetate, which will serve as a reference monoprotic acid for this problem.
2. Then check "Edit Mode" and select one of the NULL species near the bottom. Give the species the name "AGen" with a charge of -2. This will be the fully unprotonated form. Then return to "Select Mode" and select this new component.
3. Click Scan Thermo. The acidity reaction for acetic acid shows up with its  $pK_a$  of 4.76. We now need to add the reactions for  $H_2AGen$ . Insert two reactions, which will provide new lines. Enter the correct coefficients in the tableau and the reaction constants of 6.00 and 9.00 (Note: MINEQL+ takes acids as cumulative reactions involving  $2H^+$  and not as stepwise reactions and reactions are written for the formation of the species listed in the far left column).
4. Use the wizard to select the desired totals. Under pH select specified by the user. Now go look at the tableau for species of fixed entities and see the new line for pH.
5. Go to the calculate menu. Give the file the name example2. Choose Multirun, titration for type of calculation, select variable, choose LogK of pH, set limits of 0 to 14 with 57 datapoints (note this will give pH increments of 0.25 units).
6. In the output manager, first take a look at the graph as created by MINEQL by choosing Graph It. Select the AGen species as the one to graph and then select the 3 species containing AGen. Click Plot to view the results.
7. Now we will use the output manager to get the data in a format that we can export and later open up in Excel. Choose component groups,  $H^+$ , Obs x Species, LogC, and then click View. This will open up a window with columns for each species and 57 rows, one for each pH calculation. By looking at the  $H^+$  components group window, we can verify that each row is a calculation at a new pH, done in increments of 0.25.
8. Close this window, and open up a similar one for the AGen component. Click on save. You can either save the file as a .wks (format of a spreadsheet program that at one time was a legitimate rival to Excel) or as a text (.txt) file. Either of these formats can be opened up easily within Excel and other spreadsheet programs. Be sure to note the name and location of the file that you are saving so that you can easily open it up from another program. (Note: sometimes opening the file in Excel will turn off Excel's automatic calculation feature, which means that any calculations (i.e., formulae) that you input in the Excel worksheet might not update automatically. Typing the key F9 will recalculate the formulae if this happens.)

You can also cut the table in MINEQL and paste it into Excel. To do this, click Clip Board in MINEQL. Then go to Excel, select a cell for the upper-right cell of the table, and then select paste. The numbers will be pasted in but they will include commas between them. **Click on the small clipboard icon in Excel and select the Text Import Wizard. Follow the instructions for Delimited data with commas as the delimiters.**

**Example 3: LogC-pH diagram of an open system.  $P_{\text{CO}_2} = 10^{-3.5}$  atm,  $[\text{Na}_2\text{HPO}_4]_{\text{T}} = 10^{-4}$  M.**

1. Reselect components and click Scan Thermo.
2. Select the wizard.
3. Enter totals for Na(+) and PO4(3-).
4. In the pH tab, click pH calculated by MINEQL. Because the phosphate-containing species was not added as the component ( $\text{PO}_4^{3-}$ ), we need to use the TOTH input box. Enter into this box 1E-04, which is the value of the TOTH equation that would result if the problem were set up using as components  $\text{PO}_4^{3-}$ ,  $\text{Na}^+$ ,  $\text{CO}_2$ , and  $\text{H}^+$ .
5. In the CO2 tap, select open to the atmosphere and enter -3.5 in the logPCO2 box.
6. Turn off the solids in the solids mover tab.
7. Close the wizard by selecting OK, and then take a look at the tableau for fixed entities. Note how  $\text{CO}_2(\text{g})$  is included as a fixed entity.
8. Calculate the equilibrium speciation as a single run. Check out the pH by going to the output manager.
9. Go back to the Wizard and adjust the pH calculations so that you can prepare a LogC-pH plot (pH supplied by user).
10. In the calculate menu, set up the calculation as multirun to look at the speciation over a range of pH. Graph your result to make sure that you get the answer you were expecting.

### Example A (Problem 2 from Problem Set 2):

For an aqueous system with  $\text{TOTPb} = 10^{-6}$  M,  $\text{TOTPO}_4 = 10^{-4}$  M, and  $\text{TOTCl} = 10^{-4}$  M, consider the precipitation of the following three solids: pyromorphite (CPY:  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}_{(s)}$ ), hydroxypyromorphite (HPY:  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}_{(s)}$ ), and lead hydroxide ( $\text{Pb}(\text{OH})_{2(s)}$ ).

1. Select as components Pb(2+), PO4(3-) and Cl(-), then click “Scan Thermo.”
2. Click “Scan Thermo”, which has MINEQL search its database for reactions involving those components. This will then bring up a screen of aqueous complexes. If the aqueous complexes screen does not appear (it won't if autopilot is off), you can access this menu from Model -> Tableau.
3. Select the “Wizard” option to begin specifying values for the problem.
4. Enter totals for the three components.
5. Select the “pH” tab. Choose pH calculated by MINEQL using electroneutrality.
6. Select the “Solids Mover” tab. Turn all solids off and then click the boxes for the three solids of interest.
7. Close the wizard by clicking “OK” and then close the tableau view.
8. You will be brought to the calculation window (again, if autopilot is not on, you will need to select “Calculate” from the Model menu.
9. Give the output data the name “exampleA” and leave ionic strength and temperature corrections off.
10. Choose Multirun, titration for type of calculation, select variable, choose LogK of pH, set limits of 0 to 14 with 57 datapoints (note this will give pH increments of 0.25 units).
11. Select run, which will then bring up the Output Manager (this too is available from the Model menu).
12. The two types of output that we will usually view are “components” and “special reports.” To view components, check components, then highlight Pb(2+) as the component, choose how to display data as Obs x Species, choose “LogC” in the drop down menu, and then click the “View” button. Note that you can display the concentrations in many different ways. The right-most column is a Type VII species called TOTAL Pb, which is the total dissolved concentration of lead. This Type VII species is particularly useful in solubility problems.
13. Note the values given for the solids and that there are two different types of numbers or letters in front of the solid names. “S” means that the solid was included in the calculations, and “6” means that the solid was not considered. If the data are shown for “LogC” for solids, MINEQL actually returns the value of the saturation index (SI) for that solid. Recall that the **SI is  $\log(Q/K_{sp})$  and that when SI is negative the system is undersaturated**, when SI is positive the system is supersaturated, and when SI is zero the system is in equilibrium with that solid. Which solids are predicted to form in this system? Do they coexist at any pH or are they strictly competitive?
14. Return to the Output Manager and now select “Conc (M)” to see lead concentrations. Now note that for the “S” species the value is given as moles/L of solid present. For type “6” species, which were not considered, the value listed is  $10^{\text{SI}}$ .
15. Return to the Output Manager screen click the “Graph IT” button to prepare a graph of the results. Choose Pb(2+) as the component and LogC for the units. Keep the X-axis as pH. Click the species that you want to view on the Y-Axis; note that you can only select 10 species. Be sure to include Total Pb(2+).
16. Repeat this problem for different total amounts of lead, phosphate, and chloride. An interesting system is one with 1 g/L pyromorphite ( $\text{TOTPb} = 3.69$  mM;  $\text{TOTP} = 2.21$  mM;  $\text{TotCl} = 0.737$  mM).

**Example B (Problem 4 from Problem Set 2):**

Precipitation reactions are often used to remove cadmium from water. Two potential precipitates are  $\text{Cd}(\text{OH})_{2(s)}$  and  $\text{CdS}_{(s)}$ .

1. Return to the “Select Components” screen. Click “New” to clear all existing components, and then select the components that you will need for this problem.
2. For a solution with  $8.9 \cdot 10^{-6}$  M Cd, plot the logarithm of the dissolved cadmium concentration as a function of pH for (i)  $\text{Cd}(\text{OH})_{2(s)}$  in pure water and (ii)  $\text{CdS}_{(s)}$  in a solution with  $10^{-4}$  M TOTS(-II) ( $\text{TOTS}(-\text{II}) = [\text{H}_2\text{S}_{(\text{aq})}] + [\text{HS}^-] + [\text{S}^{2-}]$ ).
3. For an acidic solution containing 1 mg/L dissolved cadmium ( $8.9 \cdot 10^{-6}$  M Cd) and no sulfide, base will be added to increase the pH. At what pH will  $\text{Cd}(\text{OH})_{2(s)}$  first precipitate? Can the minimum pH at which the drinking water standard of 0.005 mg/L ( $4.4 \cdot 10^{-6}$  M) dissolved cadmium be met?
4. 9.5
5. For the solution with  $10^{-4}$  M TOTS(-II), what is the minimum pH at which the drinking water standard for cadmium will be met? Yes. 5.05

**Example C (Example with Oxidation-Reduction Chemistry):**

1. Return to the “Select Components” screen. Click “New” to clear all existing components, and then select the components that you will need for this problem: Fe(2+), Fe(3+),  $\text{CrO}_4(2-)$ ,  $\text{Cr}(\text{OH})_2(+)$ , and e(-). Click “Scan Thermo.”
2. Go to the “Wizard.” In the totals tab, enter  $10^{-4}$  for  $\text{CrO}_4(2-)$  and  $10^{-4}$  for Fe(2+). In the select pH tab, choose pH specified by user and enter pH 8.0. In the solids tab, first turn off all solids, and then check the boxes for  $\text{Cr}(\text{OH})_3(\text{am})$  and Ferrihydrite. In the redox tab, select “fixed pe.” Note the other options available.
3. Go to the calculation menu and give the file name examplec. Leave temperature and ionic strength corrections off. Choose Multirun, titration for type of calculation, select variable, choose LogK of pe, set limits of -10 to 10 with 21 datapoints (note this will give pe increments of 0.5 units).
4. Go to the Output Manager and view the results of the calculation. For which pe values are Fe(II) species dominant and for which are Fe(III) species dominant? How does pe affect Cr(VI) and Cr(III) concentrations? Note a disadvantage of viewing these results with the interface available in MINEQL is that you can not simultaneously view results for two different oxidation states. However, the data can be easily exported to another program (such as Excel) and then plotted there.

### Example D:

Preparing a Langmuir Isotherm Using MINEQL. The Langmuir isotherm assumes (a) a finite number of sorption sites and (b) one type of sorption site.

1. In the select components screen, scroll to the bottom to find components labeled “Null.” Click the boxes for two of these components.
2. At the top of the components screen click the “Edit Mode” button. Then scroll down to find the two Null species. Click one of them and give it the name “A” and then click the other and give it the name “S.” Do not enter anything for the ionic charge.
3. Go back to the top of the screen and click the “Select Mode” button. You have now added two new components.
4. Click the “Scan Thermo” button. Only the reaction for the dissociation of water should appear, because you have not yet added the adsorption reaction.
5. Click the “Insert” button to add a new reaction. Enter a value of 1 in the column for A and also a 1 in the column for B. Give the reaction a logK value of 5.0.
6. Enter the “Wizard” and enter a total concentration of  $10^{-4}$  M for S. This is setting a fixed concentration of reactive surface sites. Leave A as zero for now. You can skip the screens for pH, solids, carbonate, and redox.
7. Go to the calculate menu and select “Multirun” and then “Titration.” Select “Total Concentration of A” and choose to titrate from 0 to  $5 \cdot 10^{-4}$  M with 51 points. Click “OK” until you get back to the calculate screen.
8. Give the problem the name exempld and then click “Run.”
9. Go to the “Output Manager” and select “Graph IT.” Choose the component A, units of “Conc. (M)”, and check the box for SA. When you graph this, it will plot the adsorbed concentration of A vs. the total concentration of A. Ultimately, you would also like to be able to plot the adsorbed concentration of A vs. the dissolved concentration of A. You can export the data to do plot it with those units.
10. Try different values of TOTS, logK, and the range of data to see what effects those parameters have on the simulation.
11. Try to modify the problem so that you can simulate the competitive adsorption of two adsorbates “A” and “B” that have different total concentrations and equilibrium adsorption constants.

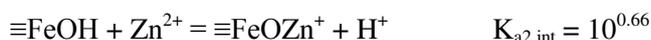
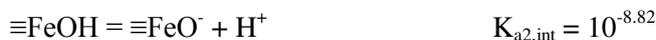
MINEQL and Surface Complexation: MINEQL has three methods of accounting for electrostatic contributions in SCM.

- Double Layer Model: select as components “Coul.”, “S(st)OH”, and/or “S(wk)OH”
- Double Layer Model Specific to Ferric Hydroxide (uses the database of Dzombak and Morel): select as components “Coul.”, “Fe(st)OH”, and “Fe(wk)OH”
- Triple Layer Model: select as components “PSIO”, “PSIB”, and “SOH”
- Constant Capacitance Model: select as components “Coul.”, “SC(st)OH”, and/or “SC(wk)OH”

Although the DLM specific to ferric hydroxide already has constants in the database and is therefore convenient to use, it has an **unrealistically high site density and specific surface area**. Consequently, it is preferable to use the generic DLM when working problems.

### Example E:

Examine the adsorption of Zn to Fe(OH)<sub>3</sub>(s) using the double layer model (DLM). This is the same as example 9.5 of Aquatic Chemistry by Stumm and Morgan. The goals are (a) to find the pH<sub>pzc</sub> with and without Zn, (b) to examine the effect of ionic strength on the pH<sub>pzc</sub>, (c) to plot the adsorption edge of Zn with and without EDTA.



TOT≡FeOH = 10<sup>-3.7</sup> = 2 · 10<sup>-4</sup>, TOTZn = 10<sup>-7</sup>, A = 600 m<sup>2</sup>/g, [solids] = 0.021 g/L, I = 0.1 M

Note: this specific surface area is also unreasonably high (it is that used by Dzombak and Morel)

1. In the select components screen, select H(+), H<sub>2</sub>O, S(st)OH, Coul, Zn(2+), and EDTA-4. Click “Scan Thermo.”
2. In the screen for Aqueous Complexes, add the three reactions shown above. Write the reactions as formation reactions (i.e., for the first reaction, you should enter the reverse of what is written above). For the column “Coul.” enter the value of Δz for that reaction.
3. Enter the “Wizard” and enter the total concentration of total concentration of S(st)OH, but for now leave the totals for zinc and EDTA as zero. Also leave the total value for Coul. as zero (as the calculations are run, this value will actually change and TOTCoul will represent the total surface charge. For the pH screen, make sure that the option “pH is supplied by user” is selected.
4. For the solids tab of the Wizard, turn off all solids.
5. Go to the calculate menu and select “Multirun” and then “Titration.” Select “logK” and then “logK of pH” and choose to titrate from 2 to 12 M with 51 points. Click “OK” until you get back to the calculate screen.
6. Back at the calculate window, enter I = 0.1 M (fixed).
7. For “Adsorption Model” select “2-layer” and then click “Options.” Enter the values as defined in the problem statement.
8. Give the problem the name examplee and then click “Run.”
9. Go to the “Output Manager” and select “Graph IT.” Choose the component S(st)OH, units of LogC, and check the boxes for the three surface species that don’t include Zn. Note the pH at which the concentrations of S(st)O<sup>-</sup> and S(st)OH<sub>2</sub><sup>+</sup> are equal. This will be the point of zero charge. [(8.82+7.18)/2=8] Note the intersections of S(st)OH<sub>2</sub><sup>+</sup> with the neutral S(st)OH. You

can also plot the component "Coul." with "TOTCoul" selected and plotted as "Conc." To see the change in total surface charge with pH.

10. Run this same calculation at a lower ionic strength of 0.001 M. Examine the ways in which the graph of the surface species is different and is similar to the calculations run at 0.1 M ionic strength.
11. Add the desired concentration of Zn and re-run the calculation. Now examine, all four surface species of S(st)OH) and also the Tot Coul. species to see how the adsorption has affected the point of zero charge.
12. Next in the "GRAPH IT" screen, select Zn(2+) as the component, select "percent species", and select "7: TOT Ads Zn(2+)." This "Type 7" species is very useful because it includes all of the Zn present in adsorbed forms. This is particularly valuable if the model included more than one Zn surface complex. Try rerunning the problem at higher Zn concentrations.
13. Now add a concentration of EDTA comparable to that of the Zn and examine how this affects the adsorption edge.