

Chapter 18 Problems

1. The decomposition of nitrogen pentoxide is $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$. Given the following data, calculate the order of reaction and the rate constant. (NB: 1 Torr is 1 mm Hg pressure; 760 mm Hg = 1 atm.)

| Time, t s | $P_{\text{N}_2\text{O}_5}$ Torr | Time, t s | $P_{\text{N}_2\text{O}_5}$ Torr |
|------------------|------------------------------------|------------------|------------------------------------|
| 0 | 348.4 | 4200 | 44 |
| 600 | 247 | 4800 | 33 |
| 1200 | 185 | 5400 | 24 |
| 1800 | 140 | 6000 | 18 |
| 2400 | 105 | 7200 | 10 |
| 3000 | 78 | 8400 | 5 |
| 3600 | 58 | 9600 | 3 |

2. It is next to impossible to do reaction path calculations for any significant system by hand, or with a calculator, and of course no one does. Two excellent implementations of the computer code required are PHREEQC and program REACT in The Geochemist's Workbench™. In the following I assume the use of PHREEQC, but you can use either program. As mentioned in Chapter 16, PHREEQC can be downloaded from the USGS web site.

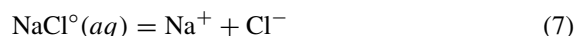
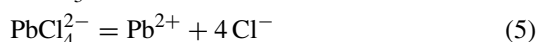
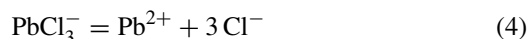
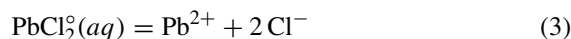
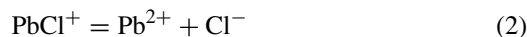
Calculation of sulfide mineral solubilities is fundamental to all modeling of ore deposit problems. It has also been a highly controversial topic, because the solubilities are generally quite low in the presence of reduced sulfur, which severely limits the transport of metals in reducing environments. Thus a still controversial problem is whether metal transport takes place under oxidizing or reducing conditions. At low temperatures (say up to 150°C or so), the answer seems to be both, or neither. In other words, the solutions are not at equilibrium, and some components can be reduced (organics) and some oxidized (sulfur, carbon).

Geochemical modeling cannot directly answer controversial questions, but it can make the calculations easier. Suppose we need to know the solubility of galena (PbS) in water at these conditions:

- 300°C
- 0.001 molal H_2S
- 1.0 molal NaCl
- pH 4.0
- $\log f_{\text{O}_2} = -35$ (chosen so that the stable phase is galena, not anglesite).

No experiments have been done at exactly these conditions. In fact, no experiments have been done at most of the conditions you might be interested in. We must have a model which fits the experiments which have been done, and which predict solubilities under other conditions.

In this case, the model is provided by equilibrium thermodynamics. However, there is still the choice of data and the choice of calculation methods to be made. The minimum data required are the equilibrium constants for the following reactions:



Recall that these K values are for activities. That is, reaction (1) has

$$\frac{a_{\text{Pb}^{2+}} a_{\text{HS}^-}}{a_{\text{H}^+}} = K_1$$

- Get the relevant equilibrium constants from SUPCRT92 and from LLNL.DAT for 300°C, vapor saturated conditions.
- With your calculator, calculate $a_{\text{Pb}^{2+}}$ at a pH of 4.0. Assume $a_{\text{H}_2\text{S}(aq)} = 0.001$. Check this assumption and your $a_{\text{Pb}^{2+}}$ later against the PHREEQC results.
- Calculate the solubility using PHREEQC with database LLNL.DAT.
- Calculate galena solubility for the same conditions, but pH 3, 4, and 5 instead of just 4. Plot log total Pb and log $a_{\text{Pb}^{2+}}$ vs. pH.
- Use PHREEQC to calculate the solubility of sphalerite and chalcocite under the same conditions. Plot the results as before.
- Calculate the solubilities of each of the three sulfides at 150°C, pH values of 3, 4, and 5. To remain in the stability field of the sulfides you must reduce log f_{O_2} to -50.
- So far, you have calculated each sulfide separately in a 1 molal NaCl solution. Now calculate their solubilities at both 300 and 150°C when all three minerals are in the same solution. Remember to change log f_{O_2} as well as T . Plot the results.
- Of course, Chalcopyrite is much more common than Chalcocite, because iron is ubiquitous. See if the presence of Chalcopyrite and Pyrite instead of Chalcocite makes much difference at 150°C.
- It is naturally of interest to compare calculated and experimental results. Barrett and Anderson (1982)¹ report regression lines through 37 data points

¹Econ. Geol. (1982), v. 77, p. 1923–1933.

at 80°C, 1 molal NaCl, H₂S saturation (0.02 molal), for sphalerite:

$$\log m_{\text{totalZn}} = -2.101 \text{pH} - 0.303$$

and for galena:

$$\log m_{\text{totalPb}} = -2.051 \text{pH} - 2.098$$

These solubilities were measured in very acid solutions, between about pH 1 and pH 2. Calculate the solubilities under these conditions, and check against these regression curves. You should change $\log f_{\text{O}_2}$ to -65 to remain in the sulfide solubility fields at this temperature.

Note the experimental slopes are close to -2 (-2.101 and -2.051). Why? The agreement with experimental results is satisfying, and lends some confidence to the calculated results under other conditions.

Once you have an input file for PHREEQC that works, all these calculations take only a few minutes, making minor changes to the input file. Most of the time is spent transferring data to a spreadsheet and plotting. Even so, it does not take long, as long as you make use of the `SELECTED_OUTPUT` statement, which collects just the data you want for plotting.

The things to note from these results are the very different relative solubilities at low and high temperatures, and the differences created by having all three minerals in the same solution as opposed to doing them separately. You should understand the reasons for these differences. Note that in spite of understanding all this, it is still not possible to tell by theoretical means which mineral will precipitate first from solution. It depends a great deal on the concentrations of the metals in solution, before precipitation starts.²

It is a simple matter to demonstrate this using titration. Also, because the results are simple, it is a good example to show the usefulness of the graphics capabilities of PHREEQC for Windows. Use the input file below, which titrates H₂S into a chloride solution containing Cu, Pb and Zn ions, precipitating sulfides. (To get familiar with PHREEQCW enter these statements yourself. To save time, use file `tit_sulf.in`). You should play with this for a while, changing (at first) the concentrations of Cu, Pb, and Zn, showing that you can cause them to precipitate in any order. Later, you can change any of the other parameters (pH , T , NaCl, steps) if you wish, to see the effect. Remove the comment symbols (#) to get more output. The BASIC terms used in the `USER_GRAPH` statement are explained under `RATES` (pp. 127–129) in the PHREEQC documentation.

```
TITLE Titration of metal ions with sulfide
PHASES
Fix_H+
```

²Taylor, H.P. (1963) Importance of chalcophile element abundances in determining the sequence of sulfide mineral deposition from monoascendant ore-forming solutions. Symposium – Problems of Postmagmatic ore Deposition, Vol. 1, Prague pp. 267–272.

```

H+ = H+
log_k 0.0
SOLUTION      1
  units      moles/kgw
  temp       150
  pe         4          O2 (g)          -50
  pH         5
  Na         1
  Cl         1
  Pb         1e-7
  Zn         1e-5
  Cu         1e-6
EQUILIBRIUM_PHASES      1
  Chalcocite      0.0      0.0
  Galena          0.0      0.0
  Sphalerite      0.0      0.0
  Fix_H+         -5.0      NaOH          10.0
REACTION
  H2S
  1.0025e-4 moles in 50 steps
SELECTED_OUTPUT
  -file          tit_sulf
  -reset         false
  -step          true
  -equilibrium_phases  Chalcocite Galena Sphalerite
  -totals        Cu      Pb      Zn
USER_GRAPH
  -headings Steps Chalcocite Galena Sphalerite #Cu Pb Zn
  -axis_titles "steps" "moles"
  -start
  10 GRAPH_X STEP_NO
  20 GRAPH_Y EQUI("Chalcocite") EQUI("Galena") EQUI("Sphalerite")
  #30 GRAPH_SY TOT("Cu") TOT("Pb") TOT("Zn")
  -end
END

```

Here are some results for galena at 300°C, pH 4:

| Program | Total molal Pb |
|---------------------|----------------|
| using SUPCRT92 data | 0.0125 |
| using SOLVEQ data | 0.0607 |
| SOLVEQ | 0.0444 |
| SOLMIN88 | 0.00611 |
| LLNL.DAT | 0.009541 |

You can spend a *lot* of time tacking down the reasons for these discrepancies.

So you see the answer to this simple question is, perhaps not a matter of opinion, but certainly a matter of some debate. And the debate never ends.

3. Differentiate equation (18.65) with respect to ξ . Equate this to zero, and solve for ξ at temperatures of 25, 100, 200, and 300°C. The result for 200°C is in the text. Don't even try this without a program that does symbolic algebra, such as Maple or Mathematica.
4. Solve for ξ at the same temperatures using equation (18.66) and the equilibrium constants in Table 18.4. This is also easily done in programs such as Matlab, Maple or Mathematica, but can also be done in a spreadsheet. Compare the answers with the results from the previous question.