EXERCISES IN THE GEOCHEMICAL KINETICS OF MINERAL-WATER REACTIONS: THE RATE LAW AND RATE-DETERMINING STEP IN THE DISSOLUTION OF HALITE

Michael A. Velbel
Department of Geological Sciences
Michigan State University
206 Natural Science Building
East Lansing, MI 48824-1115
velbel@pilot.msu.edu

KINETICS LAB EXERCISE: DISSOLUTION OF HALITE

This lab exercise involves measuring several simple properties of halite crystals undergoing dissolution, at room temperature, and at infinite dilution. The data you generate in this lab will be used in homework exercises.

You will work in pairs, teams of two generating the data together. Divide up the labor as you see fit; what usually works best is that one team member does the experiment, the other times the runs and records the data. Make sure both team members get to perform both parts of the exercise.

LAB: For the lab, you will need: A microscope with an eyepiece scale; a wristwatch with a second hand, or equivalent; a thermometer; a micrometer to calibrate the eyepiece scale; and commercial halite (table salt).

PROCEDURE: **Room temperature.** Allow 2 hours.

A. Place halite crystal on glass slide.
B. Measure "diameter" of the grain (length of side of cubic grain). Your instructor will provide you information on the distance between graduations on the crosshairs in your microscope's eyepiece. For greater accuracy, measure at higher magnification (e.g., 100X).
Select only grains with cross-sections as close to a perfect square as possible. Do *not* use irregularly shaped single grains, or clumps of grains.
C. Reduce magnification (e.g., to 40X). This makes it easier to relocate the grain once it starts dissolving. Also, make sure the cover slip is on the specimen before you add water: this makes it easier to focus.
D. Record the temperature of the water you are using (in $^{\circ}C$).
E. Place a drop of water on the specimen. Begin timing the experiment the instant the water hits the grain. Be sure the grain is *completely* surrounded by water as quickly as possible. Having the grain located under the *center* of the cover slip will help.
F. Time the complete destruction of the grain, to the nearest second. Simultaneously, observe and record the changing gross morphology and surface morphology of the halite crystal.
G. Rinse all glassware that came into contact with the salt water (i.e., the slide, cover slip, etc.).
H. REPEAT AT LEAST 9-10 TIMES, USING AS WIDE RANGE OF GRAIN SIZES AS THE SAMPLE CONTAINS. Try to have at least ten trials run by the end of the lab period.
You may want to try it a few times without timing, just to get used to (a) sample handling, (b) what the grain you're measuring looks like as it dissolves, and (c) approximately how long it takes.

PLEASE WIPE UP ALL SPILLS IMMEDIATELY!
When you are done, you should have at least ten sets of measurements of grain size, dissolution time, and temperature, for the room-temperature experiments.
PLEASE TURN OFF ALL EQUIPMENT WHEN YOU ARE FINISHED.

KINETICS PROBLEM SET:
RATE LAWS FROM EXPERIMENTAL DATA I

LIST OF SYMBOLS:

C_{inf}	concentration of Na (or Cl) in the solution at infinite distance
C_{eq}	concentration of Na (or Cl) at equilibrium.
D	diffusion coefficient
D_i	tracer diffusion coefficient for species i at infinite dilution
k	rate coefficient (or decay constant)
L	characteristic length for system
N	number of parent atoms of decaying radioisotope
r	radius of the crystal at any specified t time after the start of the experiment.
r_o	radius of the crystal at the start of the experiment ($t = 0$)
t	time
t_d	time it took to dissolve the crystal with starting radius of r_o
U	advective (flow) velocity of water in system
v	molar volume of halite

1. Plot your data for r_o vs. t (time on the horizontal [x-] axis and grain size on the vertical [y-] axis) for your room-temperature trials (use a spreadsheet or graphing program for this). (You will later plot "theoretical" curves on the same graph). Determine the slope of the "best-fit" straight line that passes closest to all the points, by either (i) using any computer program (e.g., Excel, Lotus 1-2-3, Cricket Graph, etc.) to calculate the linear least squares regression line; the program should give you the coefficients for the equation for the best-fit straight line ($y = mx + b$) to your data; or (ii) doing the same thing on your calculator (yours may even have this as a function; if not, there are formulas in some math books). Most software and calculators also provide the regression coefficient, which describes how well the regression equation fits the actual data. A "perfect" fit yields a regression coefficient of 1.0; lower values mean more deviation of the actual data from the predicted relationship.

By using a straight line to describe the kinetics, we are assuming that the reaction is zero order - that is, that the shrinkage of the grain "diameter" is constant with time - and that the rate does not depend on the composition of the solution. This is almost certainly not true, for a variety of geometric and chemical reasons. However, we did at least start with pure water (which should have no dissolved ions in it), and the geometric assumptions we made will have to do for now. If we used a much larger range of grain sizes, we might be able to observe that the best fit to the data would be some sort of curve. However, there's enough scatter in our data, and the range of values is small enough, that perhaps either a straight line or a curve could be made to fit the data. We will eventually test this idea, but for now we begin by assuming a linear relationship.

With these assumptions,

$$dr/dt = -k$$

which can be integrated between the limits $r = r_o$ @ $t = 0$ and $r = r$ @ $t = t$ (this integration is easy), giving

$$r(t) = r_o - kt.$$

This expression is suitable for describing the radius of an individual grain at different times during its dissolution (if dissolution is actually zeroth order). Alternatively, letting the final condition be

$$r = 0 \ @ \ t = t_d,$$

where t_d is the time it took to dissolve the crystal with starting radius of r_o, gives

$$r_o = kt_d,$$

which relates the total time to dissolution for a grain of initial radius r_o. Thus, the slope of the line passing through the data on a plot of r_o vs. t is the zeroth-order rate coefficient for the reaction (in other words, the slope of the line on the graph = k). If we measured grain size in mm and time in seconds, the slopes on our graphs have units of mm/sec. (Notice that, for tracking the size of an individual grain dissolving with time, the slope would be negative - the grain gets smaller with time. However, on our plot, we have plotted initial grain size *versus* time to complete dissolution. The slope on this plot is positive, which gives us a positive value of k, which is fine.)

You now have retrieved a zeroth-order/linear rate coefficient, and the regression coefficient, for the halite dissolution reaction from the lab data.

2. As Berner (1980) notes, one way to test whether the reaction is transport controlled is to calculate a theoretical rate for a transport process, and compare it to the actual rate. We now examine a simple equation for the spherically symmetrical diffusion-controlled dissolution of a single crystal.

The equation for diffusion-controlled growth of a small crystal completely surrounded by fluid (spherically symmetric case) is (Berner, 1980, Eq. 5-22):

$$\frac{dr}{dt} = \frac{Dv(C_{inf} - C_{eq})}{r}$$

where r = crystal radius, t = time, D = the diffusion coefficient, v = the molar volume of halite, C_{inf} = the concentration of Na (or Cl) in the solution at infinite distance from the crystal surface, and C_{eq} is the concentration of Na (or Cl) at equilibrium.

Integrate the equation between the limits

$$r = r_o \ @ \ t = 0$$

and

$$r = 0 \ @ \ t = t_d.$$

Solve for t_d as a function of r_o, rearrange for r_o as a function of t_d. Be sure to keep your dimensions consistent. How does the particle size scale as a function of time (linearly with time, as the square root of time, exponentially with time, etc.)? Diffusion-limited reactions

should exhibit a square-root of time dependence. Does your solution to the diffusion equation show this? Does the equation, and your solution, preserve appropriate signs? Why?

3. On a separate graph, plot your data for r_o vs. $t^{1/2}$ for your room-temperature trials.

4. On which plot do the experimental data more closely fit a straight line, r_o vs. t (problem 1) or r_o vs. $t^{1/2}$ (problem 3)?

5. Using your measurements of r_o for each individual run, assuming that the ambient concentration of Na^+ (or Cl^-) in the solution is zero, and rearranging your solutions to the diffusion equation as necessary, CALCULATE (theoretical) t_d for each run from your data. This is how long a grain of size r_o would take to dissolve in pure water, if the dissolution were controlled by spherically symmetrical diffusion (that is, if halite dissolution is transport controlled). Plot r_o vs. t as calculated, and plot your actual data (the same data you plotted in problem 1) on the same graph.

When applying the "best fit" line to your theoretical data, make sure you use the same model as you predicted in the previous question; that is, if you think the theoretical equation shows an exponential relationship between grain size and time of dissolution, apply that same concept to your data "fit." The model you choose should be obvious, that is, the mathematical equation tells you which model you must choose. Use the value of the tracer diffusion coefficient for sodium ion, D_{Na}, at infinite dilution (in water; Li and Gregory, 1974; Lerman, 1979);

$$D_{Na} = 1.33 \times 10^{-5} cm^2 sec^{-1}.$$

HINTS:

- What do you suppose would be the dimensions - units - of molar volume? Volume/mole, perhaps? There are at least three ways of getting this number, but everything you need to know about halite to do this is in most mineralogy textbooks.

- You must also know the equilibrium concentration of Na^+ or Cl^-, which you can get from the solubility of NaCl. There are a number of ways of getting this (for example, you covered solubility equilibria in your intro chemistry class!), including looking it up (a number you can use more or less directly is actually in one of the assigned readings for this part of the course; there are others, too.). Whatever way you get it, justify the value you actually use, cite the sources of any numbers you use, and show all necessary work.

6. Repeat the previous step, using the value of the tracer diffusion coefficient for chloride, D_{Cl}, at infinite dilution (in water; Li and Gregory, 1974; Lerman, 1979);

$$D_{Cl} = 2.03 \times 10^{-5} cm^2 sec^{-1}.$$

7. Write approximately one page comparing the actual measured value of t_d from your experiments with the values calculated theoretically from the diffusion equation. Also, summarize your observations regarding the morphology of the halite crystals as they dissolve.

KINETICS PROBLEM SET:
RATE LAWS FROM EXPERIMENTAL DATA II

1. Using a simplified dimensional analysis analogous to the Einstein-Bose equation,

$$L^2 = Dt$$

the characteristic length scale, L, for diffusion of Na and/or Cl ions away from the grain over the relevant time-scale (in this case, the duration of the experiment, t_d) can be calculated. Determine a characteristic length scale for diffusion of ions in the present experiment.

2. Diffusion is the slowest form of transport. However, advection (flow) is another, faster form of transport. Thus, a reaction could be transport controlled, but be faster than the diffusion-controlled rate, if flow rates are sufficiently high. Could advection be rate-determining in our experiments? Explain.

Estimate the velocity of water flow (cm/sec) past the dissolving halite grain in our experiment. Estimate how long it took for the water to penetrate as far as it did beneath the cover slip (seconds? tens of seconds?). Cover slip dimensions are 24 x 40 mm for the larger rectangular ones, or 22 x 22 mm for the small square ones.

The Peclet number, N_{Pe} (Domenico, 1977; see also Lerman, 1979; Berner, 1980, p. 117; Richardson and McSween, 1989) is

$$N_{Pe} = LU/D_i$$

where D_i is the diffusion coefficient, L is a characteristic length scale for the system of interest, and U is the flow velocity. The Peclet number is a dimensionless number (or dimensionless group) that permits us to evaluate whether advection/flow or diffusion is the dominant transport process in any specific case. If it is very small ($LU/D_i \ll 1$; $D_i \gg LU$), then diffusion is the dominant transport process; if it is very large ($LU/D_i \gg 1$; $LU \gg D_i$), then flow is the dominant transport process.

What is the Peclet number for our experimental system? Which transport process dominates in our experiments, advection (flow) or diffusion? Is movement of water - flow - the rate-determining factor in our experiment (in other words, what variable can you change that can give you larger or smaller Peclet numbers)?

3. Perhaps we need to be less restrictive in our assumptions than we were in using the equation for spherically symmetrical diffusion controlled growth and dissolution (problem 2 in the previous homework set); maybe the data show a non-linear time dependence different from the one predicted in that case.

Hodder (1990) reminds us that any equation for diffusion-limited, square-root-of-time kinetics can also be logarithmically transformed, allowing us to test whether the exponent is really 1/2. For our case, a simplified form of the solution for the spherically symmetric diffusion controlled dissolution equation from the previous homework set is,

$$r(t) = r_o - kt^{1/2} \qquad \text{giving} \qquad r_o = kt^{1/2}$$

for time to complete dissolution of a grain of initial radius r_o. The base 10 logarithmic transformation of this equation is

$$\log_{10} r_o = 0.5 \log_{10} t + \log_{10} k.$$

Once again, this is the equation for a straight line ($y = mx + b$) on a plot of $\log_{10} t$ on the x-axis and $\log_{10} r_o$ on the vertical axis. Create this log-log plot of your data, and determine the slope of the best-fit line. If the slope is 1.0 (within experimental error), the data obey a linear relationship between of size and time (that predicted from a zeroth-order rate law). If the slope is 0.5 (within experimental error), the data obey a parabolic (square root of time) dependence of size with time (like that predicted from diffusion equations). If the slope is not 0.5, the dependence of rate on time is not the parabolic one predicted by diffusion equations, and perhaps some process other than diffusion is rate-determining.

4. Do the experimental data plot as a straight line on any of the plots you've made so far? You can probably force a straight line through each of the data plots. Is any one of them a "better" fit to the data? (The scatter of the data is probably too great to tell.) Recall that a square-root-of-time relationship has often been interpreted as a basis for concluding that the reaction is diffusion-limited. Can you draw any preliminary inferences from the various data plots & theoretical & regression lines/curves?

5. Nielsen (1964; see reference in Berner, 1980) derives a relationship for surface-controlled precipitation, where a layer of material grows as soon as a single surface nucleus forms (mononuclear layer mechanism). If we assume a similar mechanism can operate during dissolution (that is, that an entire layer of the dissolving mineral dissolves as soon as the first successful dissolution site forms, and before the next successful dissolution site forms), changing the sign in Nielsen's equation gives

$$dr/dt = -kr^2$$

Because surface area scales with r^2, this is roughly equivalent to saying that the dissolution rate is proportional to surface area; the number of active sites for nucleation of dissolution centers (etch pits) is proportional to surface area - which is a good first approximation for an interface-controlled reaction.

Integrate the equation between the limits

$$r = r_o \; @ \; t = 0 \qquad \text{and} \qquad r = r \; @ \; t = t.$$

Solve for t as a function of r, rearrange for r as a function of t. According to this equation, what happens to the dissolution rate as the radius of the crystal becomes small? Is this a physically reasonable result? If necessary, ignore the range over which r is small. Make an appropriate plot of the data, and retrieve the "mononuclear interface-limited" rate coefficient. The data appear to be too "messy" to determine a single best-fit relationship; however, if you were working for an environmental consulting firm or petroleum exploration firm, you wouldn't have time to wait for more research to give you the "right" answer. Quite often in cases such as this, if selecting among different equations is difficult to justify, it is sometimes the custom to just choose the simplest rate law. Up to and including this homework, you have now examined several cases; (i) a (highly oversimplified) zeroth-order rate law; (ii) a simple (empirical) parabolic rate law; (iii) a theoretically derived rate law explicitly involving diffusion as the rate-determining process; and (iv) a rate law for one possible simple interface-limited case. Which relationship, if any, best describes the data set? Choose your rate equation carefully. Choosing the most useful rate law, even if based on limited data, is required for remediation or exploration. On the basis of your attempts at modeling, what process(es) is(are) rate-determining in the dissolution of halite? What other observations have you made that are relevant to the question of the rate-determining step in halite dissolution? What conclusion do those observations support? Emphasize possible sources of error in the experimental design, and in applying the various equations to the actual experiment.

IMPORTANT NOTES ON THE KINETICS PROBLEM SETS

These homework exercises use the measurements you made in the room-temperature halite-dissolution lab to explore the rate law and the rate-determining mechanism for the dissolution of halite in pure water.

- We actually measured the length of one side of a cube. For many of the equations, it would be simpler to deal with a sphere; a sphere with the same diameter as the length of our cube (d) would have a radius $r = d/2$.

- To do many of the following problems, you must determine the slope of the best-fit straight line that passes closest to all the points. Remember, the equation for a straight line is $y = mx + b$. There are several ways you might do this: (i) use any computer program you might have access to (e.g., Excel, Lotus 1-2-3, Cricket Graph, etc.) to calculate the linear least squares regression line; or (ii) do the same thing on your calculator (yours may even have this as a function; if not, there are formulas in some math books).

- In some problems, you are not given all the information required to solve the problem. However, if you think about the dimensions (units) of the number you are trying to calculate, and of the numbers you are given in the problem, you can determine the units of the missing information. Usually (in all cases in these homework sets), once you know what you are looking for, it is pretty easy to put together information you have access to (e.g., in your textbooks or other assigned class readings) to get the information you need to complete the problem.

- You are almost all science majors, so you shouldn't have to be warned about this, but be *extremely* careful when converting units. Also, beware of dimensions in any numbers you need to look up. You may find the number you are looking for, but its dimensions may not be exactly the units you're looking for. Incorrect conversions of mm to cm, diameter to radius, liters to cm^3, grams to moles, and so on, are the biggest mistakes students make in these homework exercises.

- If you look up a number, and it's wrong, *you* are responsible. (Similarly, if you look up the right numbers, but your calculations are wrong, *you* are responsible.) Your consulting firm is liable for erroneous recommendations made to a client, regardless of why the error was made, so your calculations MUST be correct. Bad recommendations are bad business for your company. That's why you MUST double check any numbers used in your calculations, AND the calculations themselves.

The limits of integration for all parts of this exercise are (unless otherwise stated)

$$r = r_o \ @ \ t = 0 \qquad \text{and} \qquad r = r \ @ \ t = t,$$

where r_o is the radius of the crystal at the start of the experiment ($t = 0$), and r is the radius at any specified t time after the start of the experiment. In some cases, we will specify the final condition

$$r = 0 \ @ \ t = t_d,$$

where t_d is the time it took to dissolve a crystal of starting radius r_o.

Berner (1978, 1980, 1981) states that dissolution reactions are either transport-controlled (that is, some transport process governs the rate of dissolution) or interface-controlled (a reaction process at the mineral-solution interface is rate-determining). There are at least 4 possible "tests" for identifying the rate-determining mechanism (in no particular order of importance): (1) Stirring (advection/flow-rate/flushing-rate) dependence (for transport-controlled) or lack thereof (for interface-controlled) of the reaction rate (Berner, 1978); (2) Comparison and "goodness of fit" of theoretical equations to the experimental data; (3) Grain morphology; (4) The Arrhenius activation energy of the process (Berner, 1978; Lasaga, various). We will investigate the first three here.

REFERENCES

Berner, R.A. (1978) Rate control of mineral dissolution under earth surface conditions. American Journal of Science, 278, 1235-1252.

Berner, R.A. (1980) Early Diagenesis: A Theoretical Approach. 241 p. Princeton University Press, Princeton, N.J

Berner, R.A. (1981) Kinetics of weathering and diagenesis. In Mineralogical Society of America Reviews in Mineralogy, 8, 111-134.

Brownlow, A.H. (1996) Geochemistry, second edition. 580 p. Prentice Hall, Upper Saddle River, N.J.

Cussler, E.L. (1984) Diffusion: Mass transfer in fluid systems. 525 p. Cambridge University Press, Cambridge, U.K.

Domenico, P.A. (1977) Transport phenomena in chemical rate processes in sediments. Annual Reviews of Earth and Planetary Science, 5, 287-317.

Drever, J.I. (1988) The Geochemistry of Natural Waters, second edition. 437 p. Prentice Hall, Englewood Cliffs, N.J.

Drever, J.I. (1997) The Geochemistry of Natural Waters, third edition. 436 p. Prentice Hall, Upper Saddle River, N.J.

Faure, G. (1991) Principles and Applications of Inorganic Geochemistry. 626 p.Macmillan, New York.

Gill, R. (1995) Chemical Fundamentals of Geology, second edition. 289 p. Chapman & Hall, London, U.K. (1st ed., 1989, Unwin Hyman).

Henderson, P. (1982) Inorganic Geochemistry, 353 p. Pergamon Press, Oxford, U.K.

Hodder, A.P. (1990) Practical weathering for geology students. Journal of Geological Education, 38, 306-310.

Krauskopf, K.B., and Bird, D.K. (1995) Introduction to Geochemistry, third edition. 647 p. McGraw-Hill, New York.

Langmuir, D. (1997) Aqueous Environmental Geochemistry. 600 p. Prentice Hall, Upper Saddle River, N.J.

Lasaga, A.C. (1981). Rate laws of chemical reactions. In Mineralogical Society of America Reviews in Mineralogy, 8, 1-68.

Lasaga, A.C. (1984) Chemical kinetics of water-rock interactions. Journal of Geophysical Research, 89B, 4009-4025.

Lerman, A. (1979) Geochemical Processes: Water and Sediment Environments. 481 p. John Wiley & Sons, New York.

Li, Y.-H., and Gregory, S. (1974) Diffusion of ions in sea water and in deep-sea sediments. Geochimica et Cosmochimica Acta, 38, 703-714.

Nahon, D.B. (1991) Introduction to the Petrology of Soils and Chemical Weathering. 313 p. John Wiley & Sons, New York, N.Y.

Nielsen, A.E. (1964) Kinetics of Precipitation, 151 p. Pergamon Press, Oxford, U.K.

Richardson, S.M., and McSween, H.Y., Jr. (1989) Geochemistry: Pathways and Processes. 488 p. Prentice Hall, Englewood Cliffs, N.J.

Robinson, R.A., and Stokes, R.H. (1959) Electrolyte Solutions. 559 p. Butterworths, London.

Sposito, G. (1994) Chemical Equilibria and Kinetics in Soils. 268 p. Oxford University Press, Oxford, U.K.

Stumm, W. (1992) Chemistry of the Solid-Water Interface: Processes at the Mineral-Water and Particle-Water Interface in Natural Systems. 428 p. John Wiley & Sons, New York.

Stumm, W., and Morgan, J.J. (1996) Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. 1022 p. John Wiley & Sons, New York.

NOTES TO THE INSTRUCTOR

OBJECTIVES

This module consists of a laboratory exercise and related homework problems on geochemical kinetics of mineral-solution reactions for undergraduate mineralogy. Students measure the grain sizes of equant halite crystals, and the time for complete dissolution of each grain. From these data, students retrieve a rate law, from several possible. Additional homework problems allow various chemical and physical transport processes in mineral-fluid systems to be evaluated.

The lab and homework illustrate several basic principles of chemical kinetics directly relevant to geology, including rate laws of reactions, diffusion, advective transport, and the relationship between rate-limiting mechanisms and crystal-surface morphology.

REQUIRED BACKGROUND

A treatment of chemical kinetics (rate laws, diffusion) equivalent to that of chapter 3 in Gill (1995) is assumed. I also require the students to read Berner (1978), for its emphasis on low-temperature aqueous reactions. Treatments comparable to either or both of these references are found in Brownlow (1996, p. 210-213 and p. 355-365), Krauskopf and Bird (1995, ch. 11), Drever (1988, ch. 7; 1997, ch. 11), Langmuir (1997, ch. 2), Faure (1991, ch. 19), and Henderson (1982, ch. 8). The treatments in Berner (1980, p. 78-79; 1981, ch. 3), Sposito (1994, secs. 1.3-1.5, 3.1 & 4.5), Lasaga (1981, ch. 1), Richardson and McSween (1989, chs. 5 & 10), Stumm (1992, chs. 5 & 6), Stumm and Morgan (1996, ch. 2 p. 58-87 & ch. 13), Nahon (1991, ch. 1) and Lerman (1979, chs. 3 & 5) are more advanced. Cussler (1984) is a superb treatment of diffusion.

The treatment of kinetics in Gill (1995), Krauskopf and Bird (1995), Henderson (1982), and Richardson and McSween (1989) emphasize applications to igneous and metamorphic rocks; the other references emphasize weathering, diagenesis, and aqueous geochemical applications. These textbooks and journal articles, and other resources useful for or cited in the homework exercises, are included in the reference list.

EQUIPMENT & LAB MANAGEMENT

The exercise requires microscope stations each consisting of equipment readily available in most science departments: a petrographic microscope with a graduated reticle; beakers, medicine droppers, glass slides, cover slips, water (preferably distilled); a thermometer; a timepiece good to the nearest second (a wristwatch will suffice); and table salt. Students work in pairs in the laboratory, alternating tasks. One member manipulates the experimental materials, the other times the runs and records the data. Students can generate a dozen or more trials during one two-hour lab period. There must be half as many stations as students in the largest lab section.

The most critical material factor noted to date in the success of the exercise is the morphology of the initial halite crystals. Much individually packaged salt from "fast-food" restaurants has skeletal morphology, which makes measurement of a useful grain size impossible. Bulk grocery store table salt is generally perfect cubes. Data scatter decreased noticeably when equant crystals

were introduced. Select only grains with cross-sections as close to a perfect square as possible. Do *not* use irregularly shaped single grains, or clumps of grains.

As wide a range of grain sizes should be used as the sample permits.

Stabilize the temperatures of the beakers of water and other items before the lab; allow as much as one full day. Temperature drift during the lab period can be an important source of error.

HOMEWORK MANAGEMENT

I usually give a preparatory homework assignment, to familiarize students with some of the quantitative aspects of kinetics prior to actual data reduction, and to allow them to make their "dumb" mistakes (unit conversion errors, &c.) early. Most of these problems come directly, or are adapted, from the geochemistry textbooks listed above. I also ask the students to perform a few simple indefinite and definite integrations (to review their elementary calculus skills). Homework problems involving first-order kinetics can be adapted from any treatment of radioactive decay. Basing the "rate law" review and the "calculus review" on the students' presumed familiarity with radioactive decay works well; if they understand any rate law at all from their previous geologic background, it's exponential decay.

The subsequent homework exercises included here use the student-generated data to retrieve a simple rate law for the dissolution of halite in pure water, and to investigate the possible influence of several transport processes.

For truly mathophobic students, the instructor can supply any or all integrated forms of rate laws.
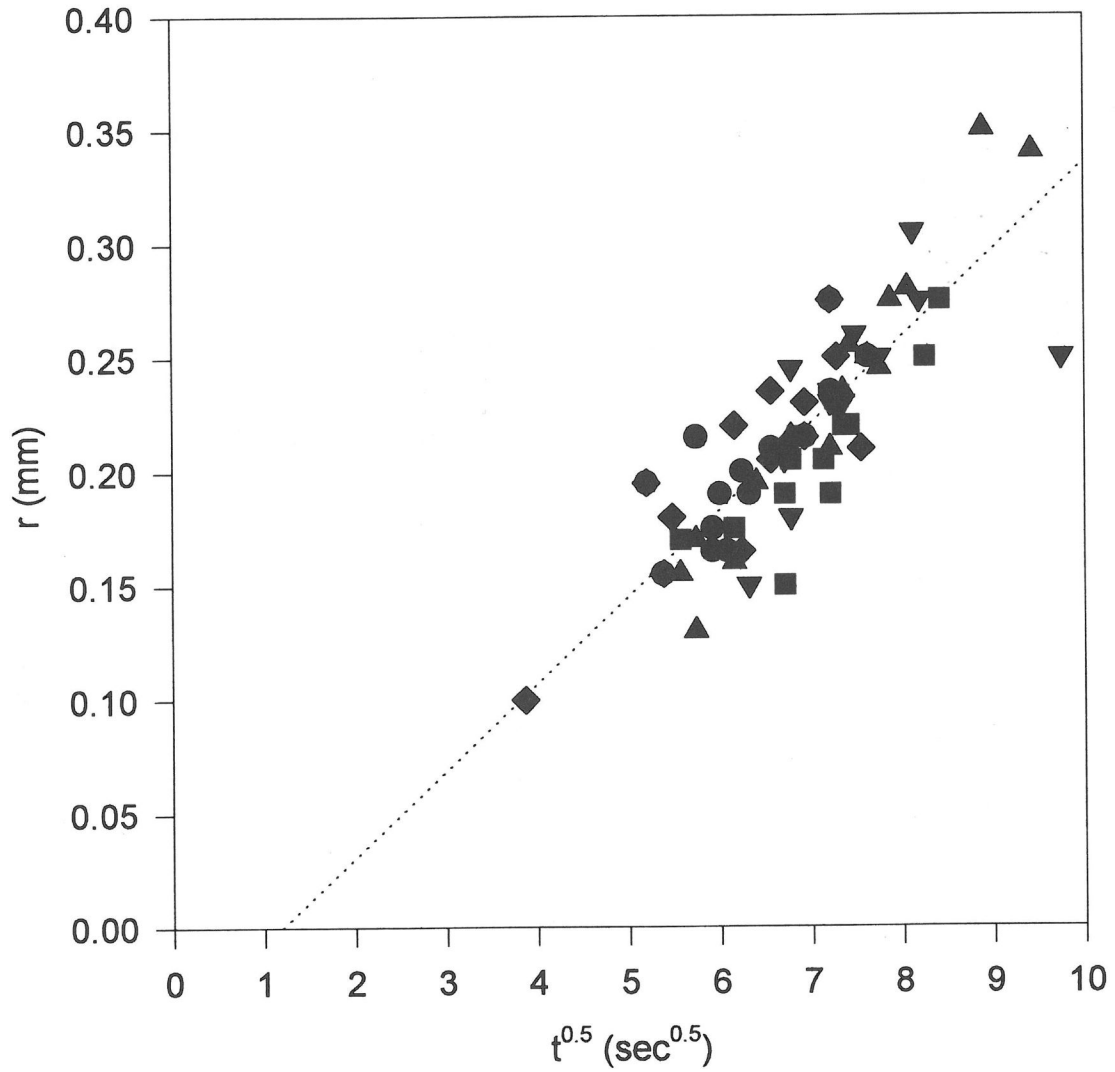
Diffusion is well treated in most available geochemistry textbooks. Advective transport properties are usually not covered until the fluid-flow part of sedimentology, or possibly in really process-oriented petrology texts and courses, but all that one needs to know for the present purpose is the dimensions of velocity. The last homework set is pushing the envelope for a one semester class; I last used it only for extra credit.

The instructor can supply the solubility of halite. Alternatively, if the students have already had some equilibrium thermodynamics, they can calculate the solubility from Gibbs free energies. Finally, the instructor can turn this into a resource-search exercise, and have the students find the solubility of halite in some reference.

ACKNOWLEDGEMENTS

Halite dissolution, 20-22°C (5 datasets)
Square-root-of-time (parabolic) plot

Halite dissolution, 20-22°C (5 datasets)
Linear plot

$k(\text{ave.}) = 2.76 \times 10^{-3}$ mm/s