

Tutorial No 2: Kinetics

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Background

Where to Find the Information

- Zhu C, Anderson G. Kinetics Modeling. Cambridge University Press; 2002:230-252. [1] (available in library - online). A copy of the chapter is also on the GitHub repository.
- Input files are on GitHub

Our goal in this tutorial is to assess PHREEQC capabilities to study chemical kinetics relevant to contaminant transport.

Some Basic Theory

We need a mathematical expression relating the concentrations of reactants and products in a given chemical reaction to how far the reaction has proceeded over time. First, we introduce a variable that indicates how far the reaction has progressed.

The Reaction Rate

Having defined reaction increments $d\xi$, we can now define the rate of reaction as

$$\frac{d\xi}{dt} = \frac{1}{\nu_A} \frac{dn_A}{dt} = \frac{1}{\nu_B} \frac{dn_B}{dt} = \dots = \frac{1}{\nu_i} \frac{dn_i}{dt} \quad (1)$$

where dt is an increment of time, and $d\xi/dt$ is the derivative of ξ with respect to t , an expression of the amount of progress of the reaction as a function of time, or simply the rate of reaction. This expression (1) is written in terms of the absolute number of moles of A, B, and so on, (n_A , n_B , . . .), but by considering a fixed volume we could change these to concentration terms. Thus,

$$\frac{d\xi}{dt} = \frac{1}{\nu_A} \frac{dC_A}{dt} = \frac{1}{\nu_B} \frac{dC_B}{dt} = \dots = \frac{1}{\nu_i} \frac{dC_i}{dt} \quad (2)$$

where C is in some unit of concentration such as moles per cubic centimeter. So, evidently, the rate of reaction can be determined by measuring the concentration of any of the reactants or products as a function of time. With one important stipulation: the reaction we have written must be what is actually happening.

Elementary and Overall Reactions If we measure the rate of change of concentration of products and reactants in many ordinary chemical reactions, we find that the relationship in (2) is often not obeyed.

This is because the reaction does not actually proceed as written, at the molecular level. The reaction may well represent the overall result of a series of elementary reactions. Thus A and B may in fact react to form a number of intermediate species such as X and Y, which then react with each other or with A or B to form C and D. In thermodynamics, the existence of intermediate species is not important to the overall reaction study, as long as equilibrium is attained. However, in kinetics, these species contribute to the overall reaction rate and may be rate controlling, even if their concentrations are small.

The reaction mechanism describes an overall reaction in terms of the separate involved elementary reactions.

The Steady State Of course, it is also possible that intermediate species do form, but they achieve a steady-state concentration; that is, they break up just as rapidly as they form.

In this case, Equation (2) would be obeyed, even though it does not represent what actually occurs at the molecular level. Steady-state conditions are common in experimental and natural settings.

For example, the CO₂ concentration in the atmosphere is not controlled by any equilibrium reaction; it is the net result of a balance between various inputs and outputs from different processes. The “steady-state” concentration may gradually change, but so slowly compared to other rates in the system that considering it a constant in kinetic models is correct.

Rate Laws

A rate law is a statement about how the rate of a reaction depends on the concentrations of the participating species. If one thinks about chemical reactions as something that happens at the molecular level when molecules collide with one another, it makes sense that the number of collisions, and hence the rate of reaction, should depend on how many molecules of each type there are; that is, their concentrations

In most cases, a simple power function of concentrations is found to apply. For reaction (11.1)



it is

$$\text{rate of reaction} = R = \frac{d\xi}{dt} = k \cdot C_A^{n_A} C_B^{n_B} C_C^{n_C} C_D^{n_D} \quad (4)$$

The constant of proportionality, k , is called the rate constant. The exponents $n_A \dots n_D$ are often integers, but can be fractional or decimal numbers, especially in heterogeneous reactions where adsorption and other surface-related effects can influence reaction rates.

They define the order of the reaction. If n_A is 2, the reaction is said to be second order in A. The sum of the exponents gives the overall order of the reaction.

If the reaction is heterogeneous (more than one phase is involved), one or more of the “concentrations” in (4) must refer to the specific area (surface area per unit volume of solution) or the reactive surface area of the solids involved, because obviously the rate of reaction will depend on how much of the solid is available to react.

This is one of the most difficult parameters to quantify, especially in field situations.

Simple Rate Equations

Rate equations or rate laws are determined by analyzing one or more reactant or product species as a function of time as a reaction proceeds, and then inspecting the results to see what theoretical form best fits the data.

The simplest examples are those for elementary reactions, but the kinetics of more complex (multi-step) reactions can often be expressed by the same equations in certain cases, such as by using suitable constraints.

Zereth Order A zereth-order reaction obeys the relation

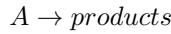
$$-\frac{dC}{dt} = k \quad (5)$$

or

$$C = C^\circ - kt \quad (6)$$

where C° is the initial concentration. A plot of concentration vs. time will thus give a straight line. Bacterial reduction of sulfate in marine environments (where variables other than SO₄²⁻ are constant) appears to be zeroth order.

First Order Rate laws for elementary reactions are for the most part what one would expect. For example, a simple molecular (or nuclear) decomposition,



proceeds at a rate that depends only on the concentration of A; the more A, the more decomposition per unit time. If all exponents in Equation (4) are zero except for $n_A = 1$, the rate law becomes

$$\frac{d\xi}{dt} = -\frac{dC_A}{dt} = k \cdot C_A \quad (7)$$

and the reaction is first order. The decay of radioactive elements is an example of such reactions. If we simplify C_A to C and let $C = C^\circ$ at time $t = 0$, integration of (7) gives

$$\int_{C_0}^C \frac{1}{C} dC = -k \int_0^t dt \quad (8)$$

$$\ln \frac{C^\circ}{C} = kt \quad (9)$$

$$\ln C = \ln C^\circ - kt \quad (10)$$

(11.17)

$$C = C_0 \circ e^{-kt} \quad (11)$$

(11.18) These equations suggest various ways of plotting data to see if they fit a first-order rate law. For example, a plot of $\ln(C^\circ/C)$ vs. t will give a straight line with a slope equal to the rate constant for concentration data from a first-order reaction.

Second Order The most common type of elementary reaction resulting from bimolecular collisions is



Here we expect the frequency of reaction to be proportional to the concentrations of the reactants and the concentration of products to have no effect, and so the rate law is

$$\frac{d\xi}{dt} = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = k \cdot C_A^1 C_B^1 \quad (13)$$

and the reaction is second order. If the initial concentrations of A and B are C_A^0 and C_B^0 , the stoichiometry of (12) requires that

$$C_A^0 - C_A = C_B^0 - C_B \quad (14)$$

Solving this for C_B and substituting this result in (13) yields

$$-\frac{dC_A}{dt} = k \cdot C_A (C_A - C_A^0 + C_B^0) \quad (15)$$

Integration of (15) then gives

$$\ln \frac{C_A^0 C_B}{C_B^0 C_A} = (C_B^0 - C_A^0) kt \quad (16)$$

(11.22) Therefore, a plot of

$$\ln \frac{C_{ACB}^\circ}{C_{BCA}^\circ} \quad (17)$$

vs. time t will result in a straight line with a slope equal to the rate constant for concentrations taken from a second-order reaction. Similar equations can be derived for reactions with different stoichiometric coefficients.

There are a number of other rate laws, but this will suffice to give an idea of the procedures involved. However, it should be emphasized that most chemical reactions are “overall” reactions, and that understanding them in terms of their fundamental elementary reactions is a goal not often and not easily achieved.

Pseudo-Order Reactions As mentioned above, complex reactions can often be expressed by the simple equations of zeroth-, first-, or second-order elementary reactions under certain conditions.

For example, the dissolution of many minerals at conditions close to equilibrium is a strong function of the free energy of the reaction, but far from equilibrium the rate becomes nearly independent of the free energy of reaction.

In other words, the rate of dissolution will be virtually constant under these conditions, or pseudo-first-order.

In a reaction involving A and B which is truly second order, choosing conditions such that the concentration of B is held essentially constant (which might be done in several ways) reduces Equation (13) for second-order reactions to

$$-\frac{dC_A}{dt} = k_C_B C_A = k_{app} C_A \quad (18)$$

(11.23) which is the equation for a first-order reaction, where $k_{app} = k_C_B$, is a pseudo-first order rate constant, or apparent-first-order constant. If all reactant concentrations are held essentially constant, a pseudo-zeroth-order reaction is generated.

Exercise

Kinetic rate expressions can be defined in a completely general way in PHREEQC by using Basic statements in the RATES data block. The rate expressions can be used in batch-reaction and transport calculations with the KINETICS data block.

For transport calculations (ADVECTION or TRANSPORT), kinetic reactions can be defined cell by cell by the number range following the KINETICS keyword (KINETICS m-n).

The rate expressions are integrated with an embedded (up to) 5th-order Runge-Kutta-Fehlberg algorithm, or with a stiff, variable-order, variable-step multistep solver.

The Runge–Kutta–Fehlberg (RKF) algorithm is a numerical method for solving ordinary differential equations (ODEs) that controls the step size to achieve desired accuracy.

Equilibrium is calculated before initiating a kinetic calculation and again when a kinetic reaction increment is added. Equilibrium includes

- solution species equilibrium;
- exchange
- equilibrium-phase
- solid-solution
- surface-assemblage equilibrium
- gas-phase equilibrium

A check ensures that the difference between integrated rate estimates over a time interval is smaller than a user-defined tolerance. If the tolerance is not met, the integration over the time interval is automatically restarted with a smaller interval.

Kinetic reactions between solids and the aqueous phase can be calculated *without modification of the database*. PHREEQC can also calculate kinetic reactions among aqueous species normally assumed to be in equilibrium, but this requires redefining the database with separate SOLUTION_MASTER_SPECIES for the aqueous species that react kinetically.

This exercise here illustrates the procedure for decoupling two valence states of an element (iron) and shows how PHREEQC can be used to calculate the kinetic oxidation of Fe^{2+} to Fe^{3+} in water.

The rate of oxidation of Fe^{2+} by O_2 in water is given by:

$$\frac{dm_{\text{Fe}^{2+}}}{dt} = - [2.91 \times 10^{-9} + 1.33 \times 10^{12} a_{\text{OH}^-}^2 \cdot P_{\text{O}_2}] m_{\text{Fe}^{2+}} \quad (19)$$

where t is time in seconds, a_{OH^-} is the activity of the hydroxyl ion, m_{Fe} is the total molality of ferrous iron in solution, and P_{O_2} is the oxygen partial pressure (atm).

The time for complete oxidation of ferrous iron is a matter of minutes in an aerated solution when pH is above 7.0. (see [2])

However, Fe^{3+} forms solute complexes with OH^- and it may also precipitate as iron oxyhydroxides, so that pH decreases during oxidation. Because the rate has quadratic dependence on the activity of OH^- , the oxidation rate rapidly diminishes as pH decreases.

The rate equation is highly *non-linear* in an unbuffered solution and must be integrated numerically.

This example models a reaction vessel with 10 mmol/kgw NaCl and 0.1 mmol/kgw FeCl_2 at pH = 7.0 through which air is bubbled; the change in solution composition over time is calculated.

The calculation requires the uncoupling of equilibrium among the $\text{Fe}(2)$ and $\text{Fe}(3)$ species. Two new “elements” are defined in **SOLUTION_MASTER_SPECIES** - $\backslash\text{Fe_di}$ ”, which corresponds to $\text{Fe}(2)$, and “*Fe_tri*”, which corresponds to $\text{Fe}(3)$. The master species for these elements are defined to be *Fe_di* + 2 and *Fe_tri* + 3, and all solution species, phases, exchange species, and surface species must be rewritten using these new elements and master species.

```

TITLE Example 9.--Kinetically controlled oxidation of ferrous
      iron. Decoupled valence states of iron.

SOLUTION_MASTER_SPECIES
  Fe_di          Fe_di+2    0.0      Fe_di           55.847
  Fe_tri         Fe_tri+3   0.0      Fe_tri          55.847
SOLUTION_SPECIES
  Fe_di+2 = Fe_di+2
    log_k  0.0
  Fe_tri+3 = Fe_tri+3
    log_k  0.0
#
# Fe+2 species
#
  Fe_di+2 + H2O = Fe_dioH+ + H+

```

Figure 1: Input code - part 1

A few transcriptions are shown in table 2, which provides the partial input file for this example.

The **SOLUTION** data block defines a sodium chloride solution with 0.1 mmol/kgw ferrous iron (*Fe.di*), in equilibrium with atmospheric oxygen.

The **EQUILIBRIUM_PHASES** data block specifies that all batch-reaction solutions will also be in equilibrium with atmospheric oxygen; thus, there is a continuous supply of oxygen for oxidation of ferrous iron.

In the **RATES** data block, the rate expression is designated with the name “*Fe_di_ox*” and defined according to equation 19. Note the use of the special Basic function “TOT” to obtain the total concentration (molality) of ferrous iron (line 10), “SR” to obtain the saturation ratio, or, in the case of a gas, the partial pressure, here of oxygen (line 30), and “ACT” to obtain the activity of OH^- (line 40). Line 40 defines the moles of reaction. Notice also that the variable moles is calculated by multiplying the rate times the current time interval (TIME) and that the rate definition ends with a SAVE statement. The SAVE and TIME statements must be included in a rate definition; they specify the moles that reacted over the time (sub-)interval. The interval given by TIME is an internal PHREEQC variable that is adapted automatically by the code to obtain the required accuracy of the integration.

In the **KINETICS** data block, the rate expression named “*Fe_di_ox*” is invoked and parameters are defined. When the rate name in the **KINETICS** data block is identical to a mineral name that is defined under **PHASES**, the stoichiometry of that mineral will be used in the reaction. However, because no mineral is associated with the rate name of this example, the identifier **-formula** must be used to specify the reaction stoichiometry. The reaction involves loss of *Fe_di* [equivalent to $\text{Fe}(2)$] from solution as indicated by the stoichiometric coefficient of -1.0. The loss is balanced by a gain in solution of *Fe_tri*[equivalent to $\text{Fe}(3)$] with a stoichiometric coefficient of +1.0. Note that the formula contains only the elements for which the mass changes in the system. Thus, the overall kinetic reaction of the example is, but the

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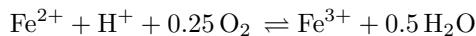
        log_k    -9.5
        delta_h 13.20   kcal
#
#... and also other Fe+2 species
#
#
# Fe+3 species
#
Fe_tri+3 + H2O = Fe_trioH+2 + H+
        log_k    -2.19
        delta_h 10.4    kcal
#
#... and also other Fe+3 species
#
PHASES
Goethite
        Fe_trioOH + 3 H+ = Fe_tri+3 + 2 H2O
        log_k    -1.0
END
SOLUTION 1
        pH    7.0
        pe 10.0  O2(g) -0.67
        Fe_di  0.1
        Na  10.
        Cl  10. charge
EQUILIBRIUM_PHASES 1
        O2(g)           -0.67
RATES
Fe_di_ox
        -start
        10  Fe_di = TOT("Fe_di")
        20  if (Fe_di <= 0) then goto 200
        30  p_o2 = SR("O2(g)")
        40  moles = (2.91e-9 + 1.33e12 * (ACT("OH-"))^2 * p_o2) * Fe_di * TIME
        200 SAVE moles
        -end
KINETICS 1
Fe_di_ox
        -formula Fe_di -1.0 Fe_tri 1.0
        -steps 100 400 3100 10800 21600 5.04e4 8.64e4 1.728e5 1.728e5 1.728e5 1.728e5
        -step_divide 1e-4
INCREMENTALREACTIONS true
SELECTED_OUTPUT
        -file ex9.sel
        -reset false
USER_PUNCH
        -headings Days  Fe(2)  Fe(3)  pH  si_goethite
        10 PUNCH SIM_TIME / 3600 / 24, TOT("Fe_di")*1e6, TOT("Fe_tri")*1e6, -LA("H+"), \
        SI("Goethite")
USER_GRAPH Example 9
        -headings _time_ Fe(2) Fe(3) pH
        -chart_title "Oxidation of Ferrous Iron"

```

Figure 2: Input code - part 2

reaction of protons and oxygen to form water does not change the total mass of hydrogen or oxygen in the system.

Thus, the overall kinetic reaction of the example is



, but the reaction of protons and oxygen to form water does not change the total mass of hydrogen or oxygen in the system.

Hydrogen and oxygen are not included in the formula. The phase O₂(g) in EQUILIBRIUM_PHASES maintains dissolved oxygen in equilibrium with atmospheric oxygen gas. In a system closed to oxygen, the dissolved oxygen would be partly consumed.

The identifier -steps in the KINETICS data block gives the time step(s) over which the kinetic reactions must be integrated. When INCREMENTAL_REACTIONS true is used, each time step increments the total time to be simulated, and the results from the previous time step are used as the starting point for the current time step.

The SELECTED_OUTPUT data block specifies the file name of the selected-output file and eliminates all default printing to that file (-reset false). The only output to the selected-output file in this example is defined with the USER_PUNCH data block.

The Basic program in USER_PUNCH specifies that the following be printed after each kinetic time step (-steps defines 11 kinetic time steps): the cumulative time of the simulation, in days; the total ferrous and ferric iron, in $\mu\text{mol}/\text{kgw}$; the pH; and the saturation index of goethite.

The results also are plotted with USER_GRAPH, and the points can be saved to a file by right-clicking the mouse when the cursor is inside the chart area.

When the input file is run, two warning messages are generated during integration. If the integration time interval is too large, it is possible that the initial estimates of kinetic reaction increments produce negative solution concentrations. In this case, the programme prints a warning message, decreases the time interval size, and restarts integration. The messages are warnings, not errors, and the programme successfully completes the calculation. The warning messages can be eliminated by reducing the initial integration interval. No warning messages are printed if the identifier -step_divide 100 is used (KINETICS), which divides the initial (overall) time step by 100.

Likewise, no warning messages are printed if the identifier -step_divide 1e-7 is used, which causes the reaction increment to be less than 1×10^{-7} mol. The former approach, with -step_divide 100, is usually preferable because, although initial reaction increments are compelled to be small, later in the integration, large reaction increments are possible. Using -step_divide 1e-7 forces reaction increments to remain small throughout the entire integration, and in this example, the run time is about 5 times longer than using -step_divide 100, and about 10 times longer than not using -step_divide at all.

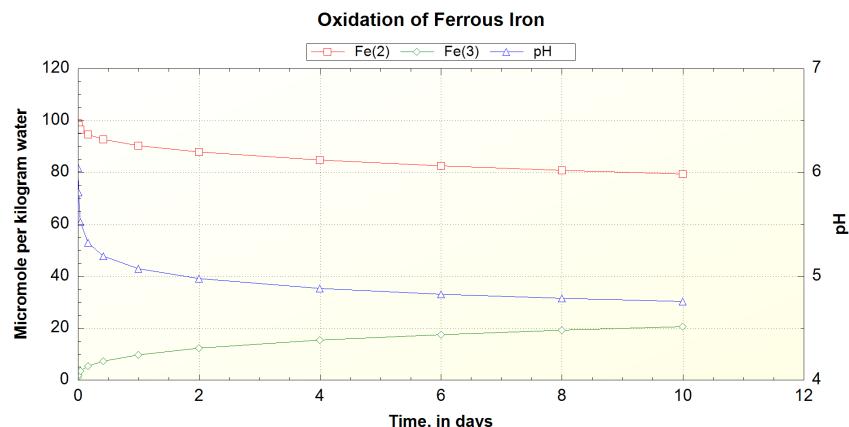


Figure 3: Concentration of total Fe(2), total Fe(3), and pH as dissolved ferrous iron [Fe(2)] is kinetically oxidized to ferric iron [Fe(3)] by oxygen.

Figure 3 shows the concentration of total Fe(2), total Fe(3), and pH in the reaction vessel over the 10 days of the simulation.

It can be seen that the pH rapidly decreases at the beginning of the reaction. The slope of Fe(2) against time is initially steep, but lessens as the reaction progresses, which is consistent with equation 19.

When the experiment is performed in reality in an unbuffered solution, it is noted that the pH initially rises. This rise in pH is consistent with slowly forming hydroxy-complexes of Fe(3). Because the oxidation reaction by itself consumes protons, the pH would initially rise if the hydroxy-complexes that lower the pH form slowly. Such kinetic formation of aqueous complexes also could be included in PHREEQC simulations, but it would require that the hydroxy-complexes of Fe(3) also be defined by using a separate **SOLUTION_MASTER_SPECIES** and that a rate expression be defined for the kinetic formation of the complexes.

Problem Sets

The oxidation of Fe^{2+} by O_2 in water is described by:

$$\frac{dm_{\text{Fe}^{2+}}}{dt} = - [2.91 \times 10^{-9} + 1.33 \times 10^{12} a_{\text{OH}^-}^2 P_{\text{O}_2}] m_{\text{Fe}^{2+}} \quad (20)$$

where:

- $m_{\text{Fe}^{2+}}$ = molality (mol/kgw)
- a_{OH^-} = hydroxyl activity
- P_{O_2} = oxygen partial pressure (atm)
- t = time (s)

Exercise 1

- Determine the overall reaction order.
- Under what conditions does the reaction become pseudo-first order?
- Explain why the rate law is highly non-linear in an unbuffered system.

Exercise 2 Initial Rate Calculation

Given is:

- pH = 7.0
- P_{O_2} = 0.21 atm
- $m_{\text{Fe}^{2+}}$ = 0.1 mmol/kgw

Calculate the initial oxidation rate.

Exercise 3 Numerical Integration

- Why is numerical integration required?
- How does Runge-Kutta-Fehlberg control error?
- Why may PHREEQC restart integration?

Exercise 4 Redox Decoupling

- Why must Fe_di and Fe_tri be defined?
- What happens if they are not separated?
- Write the overall kinetic reaction.

Exercise 5 PHREEQC Coding Problem

Write a minimal PHREEQC input file that:

- Defines a solution with 0.1 mmol/kgw Fe(II) at pH 7
- Is in equilibrium with atmospheric O_2
- Defines a kinetic rate named Fe_di_ox
- Uses `-formula` to convert Fe_di to Fe_tri
- Integrates for 10 days with incremental reactions
- Outputs time, Fe(II), Fe(III), and pH

References

1. Zhu, C. & Anderson, G. *Environmental Applications of Geochemical Modeling* (Cambridge University Press, 2002).
2. Kirby, M. E. *et al.* Determining the effect of pH on iron oxidation kinetics in aquatic environments: exploring a fundamental chemical reaction to grasp the significant ecosystem implications of iron bioavailability. *Journal of Chemical Education* **97**, 215–220 (2019).