# Reactions

Reactions involve transformations of chemical species or biological entities. The discussion the follows will initially focus on chemical reactions, but then it will be broadened to include biological reactions.

## Conservation of Mass

We assume that the mass of a chemical species is conserved within a control volume.

  (1)

In this case s, the mass of a chemical species, and it follows that , the mass concentration. It is important to recognize that the chemical species likely shares the control volume with other compounds.

Mass transport across the boundaries of the control volume will be ignored so **D=A**=0.

Mass added to the control volume by a chemical reaction will be viewed as a source, so 

 S = R (2)

where R is the rate of mass produced by the source per unit volume. Substituting (2) into (1) gives

  (3)

This is the same as the conservation of mass during flow through a porous medium with the porosity and saturation set equal to unity.

## Reactions

Chemical and biological reactions will be included in processes by characterizing the term R in (3). This is done by writing a reaction describing the process and determining an expression for the rate of the reaction. Chemical reactions written in stoichiometric form take the form

 A+2B🡪3P (4)

Where A and B are reactants and P is a product, and the numbers represent stoichiometry. The rates of change during this reaction are

 (5)

Where the square brackets indicate a molar concentration. The sign convention is for rates involving reactants to be negative and rates for products are positive. The coefficients multiplying the rates are the inverse of the stoichiometric terms in the reaction expression (4).

### Ion Activity Product, Reaction Quotient

The general form of the expression describing the reaction kinetics follows from some basic principles from chemistry. Recall that the reaction in (4) can be written like this

  (6)

Where Q is the *ion activity product* or the *reaction quotient*, and the square brackets indicate molar concentrations, as above. The reactants are in the denominator and the products in the numerator by convention. Another way to write this is using an index notation

  (7)

Where *a*i is a molar concentration and the subscripts are used to identify the species, so *a*1=[P], *a*2=[A] and *a*3=[B]. The superscripts on *a* are the stoichiometric coefficients in the reaction, as in (6). The motivation for writing Q using (7) is that we can write the reaction using even more compact notation.

  (8)

where  is a vector of stoichiometric coefficients, = [3,-1,-2]. The capital pi symbol is the product symbol. Eq (8) is written for the example in (4), but the form is general and can be used to represent any standard reaction. The sign convention in (8) is that the products of the reaction have a positive exponent, and the exponent of the reactants is negative because the reactants appear in the denominator in (6) and (7).

Reaction Products >0

Reactants <0

Based on those definitions, it appears that Eq (8) can be rewritten as

  (9)

### Equilibrium Constant

Chemical reactions equilibrate when the concentrations of products and reactants are present in a particular proportion defined when the Q=K, where K is the equilibrium constant. So, from (9) we get the equilibrium constant as

  (10)

where the subscripts indicate equilibrium conditions.

Equilibrium constants can be calculated or measured for different chemical reactions, and they are known for many reactions under many conditions. Equilibrium constants vary with temperature and other conditions, so they are a good measure of how a reaction is affected by environmental conditions.

Here is a summary of important points. Q can be calculated for any assemblage of constituents in a reaction. When the concentration of reactants is large relative to products, then Q will be small, according to (8). As the reactants are consumed, Q increases and the system equilibrates when Q=K. For reversible reactions, it is also possible that the concentration of products is initially large. In this case, Q could initially be larger than K. The reaction would proceed in reverse and Q would decrease until Q=K and the system reached equilibrium.

### Reaction Rate

The forward reaction rate is assumed to be proportional to the product of the reactants, which for the example is

  (11)

where k+ is the forward reaction rate constant. Conceptually, this means that the rate of the forward reaction depends on the concentrations of all of the reactants, which seems reasonable. In general, the forward reaction rate can be generalized using the product symbol as

  (12)

where i,i<0 means that you should take the product of all the terms with a stoichiometric exponent less than 0, which is all the reactants. The negative sign ensures that the exponents in the resulting rate equation are positive, as they are in (11).

Many reactions are reversible, so there will be a backward reaction that proceeds at a rate that depends on the concentrations of the products. The backward reaction would cause reactants to be produced from products when the concentration of the products is large. In this case, the rate for backward reaction in the example is

  (12)

which using the general notation is

  (13)

The overall rate of the reaction is the difference between the forward and backward rates

  (14)

Factoring out the first term

  (15)

Equilibrium occurs when the reaction rate goes to zero, which according to (14) occurs when

  (16)

And then rearranging

  (17)

But the right hand side of (17) is equivalent to the equilibrium constant, according to (11). So

  (18)

According to (18) and (9), we can rewrite (15) to get a general expression for the reaction kinetics of a simple, homogeneous reaction

  (19)

The exponents i are commonly the stoichiometric constants in the reaction equation, but this is not always the case and in general they are determined experimentally, according to Houston [2001].

### Implementation

Implementing the reaction rate is done by relating R to the rate of change of particular species, as in (3). Using the notation developed above

  (20)

 Keep in mind that  for reactants is negative, so the rates for the example in (6) through (8) is

  (21)

which is consistent with (5). We could use (21) in our model, but it will be useful to take a slower start and look at some simple examples that occur in many applications.

### First and second-order reactions

Consider a simple reaction

 [A]🡪Products (22)

Radioactive decay is one example of this type of reaction. According to (20),

 (23)

And then from (19)

  (24)

Now, we will assume the reaction is far from equilibrium. This would happen, for example, when *A* is abundant relative to the products. In this case, *Q*<<*K* and the term in parentheses is equal to unity. Substituting into (23) gives

 (25)

where the square brackets are dropped for convenience. Eq (25) is a called a *first-order* reaction in *A* because *A* on the right side is raised to a power 1. *k*f1 is the first-order forward reaction rate constant.

 We also get from (20)

 

but *P*=*A*0-*A,* so *A=A*0-*P* where the initial concentration of *A* is A0, *A*(0)=0. We also assumed *P*0 = 0. Substituting into (25)

 (26)

(25) and (26) can be solved to give

  (27a)

  (27b)

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|  |
| Fig. 1. First-order decay of A analyzed numerically (dark blue) and the exact solution from (27a) (light blue dashed). Products calculated numerically (green) and the exact result from (27b) as red dashed line. |

#### The right hand side of equations (25) and (26) are R in eq. 3. These are the forms that will be used when the reactions are analyzed numerically.

#### Example

 An analysis of a first order reaction was conducted numerically using the rate expressions in (25) and (26). Initial values of *A*0=1.0 mol/m3 and *P*0=0 mol/m3, and *kf*1=0.1 s-1. were used.

The reactants decay and the products are created within approximately 80 s. The numerical results are within 1 percent of the exact results using (27), as shown in Figure 1.

#### Second-order reaction

Another simple reaction is

2A=🡪Products (28)

In this case, =-2, so we again assume the system is far from equilibrium so (19) becomes

  (29)

and

 (30)

This reaction is *second-order* in *A* because *A* is raised to the power 2. In these two examples, the exponent *v*i, in (19) is the same as the stoichiometric coefficient. It follows that this will be the case in most circumstances by extending the logic above, however, there are some reactions that do not behave this way, so it is not a general rule (see *Houston* [2001, pg 36] for an exception).

#### Pseudo-First Order Reaction

Here is a reaction of mixed third order

 2A+B🡪P (31)

Following (19) and the example shown above, the kinetics are inferred to be

  (32)

This form can used in the analysis, but it is cumbersome to solve analytically and can be simplified. According to (5)

  (33)

where *A*0 and *P*0 are the initial concentrations of *A* and *P*. (*A*0 - *A*) is the amount of *A* consumed by the reaction. Now, assume that the initial concentration of the product is zero, *P*0=0, so from (33)

  (34)

and similarly with *B*

  (35)

Now assume that *A* is abundant and the reaction is limited by the concentration of *B*. As a result, *P* is much smaller than *A*, so (34) becomes

  (36)

Substituting (35) and (36) into (324) gives

  (37)

This first term in parenthesis is constant, so the reaction is first-order in *P*. You can tell this by comparing (37) to (25). Integrating (37) will give equations with the same form as (27).

This example shows how a reaction with potentially complicated kinetics may behave with kinetics that behave similarly to a first-order reaction. This behavior is common because there are many cases where one of the reactants is limiting the reaction rate, as *B* limits it above.

All of the reactants in the reactions outlined above will be consumed completely and the products will form in concentrations directly in proportion to the reactants.

### Reversible Reactions

Some reactions proceed until the products and reactants change from some initial values to a new equilibrium concentration. This occurs because the reactions occur both in the forward direction, as outlined above, and in the reverse direction, such as

  (38)

There are two reaction rates, one forward and the other backward, so

  (39)

and combining

  (40)

The rate of production of *B* is

  (41)

so

  (42)

This gives two kinetic equations for the two unknowns, *A* and *B*. Using

 

gives

  (43)

Integrating (43) and taking the limit as t-->∞ gives the equilibrium concentration for *A* as

  (44)

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|  |
| Figure 2. Concentration of A (blue) and B(green) as a function of time during a reversible reaction. Red line is the equilibrium concentration predicted by (45).  |

The equilibrium constant is related to the reaction rates using (18) so

  (45)

and it is apparent from (40) that the system goes to steady state when

  (46)

####  Example

An example of the analysis was conducted where the initial concentration of *A*(0)=*A*o=1.0 and *B*o=0.

Both A and B were used as unknowns with the right hand sides of (40) and (42) used as R. Values of the rate constants were selected so the analysis goes to steady conditions during an analysis of 100s.

The results indicate the system going to equilibration in approximately 40s (Fig 2). The concentration of *A* at equilibrium is 0.1, which is confirmed by (45).

### Decay Chain

Some chemical systems decay from one compound to another, forming a chain. This type of reaction is important because all the intermediate reactions must occur to get to an endpoint. The kinetics of required to reach an endpoint is based on all the intermediate reactions.

Conceptually, a decay chain starts with a mass of parent material that decays to a daughter product by some type of kinetic process. The daughter both decays into a grand-daughter product and it is produced by continued decay of the parent. The granddaughter product decays into a greatgranddaughter and is produced by decay of the daughter. Ultimately, the decay process ends in a product that is stable.

Considering a decay chain of A🡪B🡪C🡪D as an example and assume each reaction is first order. The first reaction describes the decay rate of A

  (47)

The first term on the right side of the kinetics for *B* is the first order decay of *B* and the second term is the production of *B* from *A*

  (48)

The kinetics for C include the production from B, which is given by substitution

  49)

The kinetics for D only contains production terms. There is no degradation of D.

  (50)

Each of the reactions in (47-50), and indeed, all of the reactions given in the previous pages will have different reaction rates constants.

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| Figure 3. Example of a decay chain of four compounds undergoing first-order reactions using eq. (47-50) |

####  Example

An example was conducted to illustrate the behavior of a decay chain A🡪B🡪C🡪D. Four unknowns were used, one for each species, and the reaction kinetics were defined using (47-50). Initial conditions were *A*(0) = A0 = 1.0, *B*(0) = *C*(0) = *D*(0) = 0. In other words, we start with 1 unit of species A, but no other compounds. Kinetic constants were adjusted so the reactions occur over 100 s (Fig. 3).

The response is for *A* to decay while *B* is produced, and then *B* decays as *C* is produced. This results in a set of concentrations that increase, reach a peak, and decrease (Fig. 3). The rates of increase and decrease are controlled by the individual rate constants.

### Microbial Reactions

Microbes control important chemical reactions that can degrade problem compounds much more rapidly than they would otherwise degrade. A general reaction for microbial growth includes the following components [Grady and others, 2010]

**Carbon+energy+electron acceptor+nitrogen+other nutrients🡪**

 **biomass+reduced acceptor + products** (51)

A thorough analysis of the process would include the kinetics for each species involved in the reaction. A simplified approach is to lump all of the terms on the right side into “substrate” and the products are biomass, so

 **Substrate (Ss)🡪Biomass (C)** (52)

Many experiments show that kinetics of growth of microbes can be first order, following

  (53)

where *k*1 is the growth rate coefficient. This expression is not valid for an extended period, however, because it predicts an ever increasing rate of growth. As the population of microbes increases, the substrate concentration decreases and at some point this will diminish the rate of growth.

A kinetic expression that includes the effects of substrate concentration was developed by Monod as

  (54)

where *C* is the concentration of microbes, *S*s is the concentration of critical component of the substrate that is limiting growth, and *k*1 and *k*2 are constants. This expression gives a rate that is first order in *C* when the concentration of the substrate is large relative to *k*2.

  (55)

And it is first-order in *S*s and *C* when *S*s is small

  (56)

However, the small value of *S*s will limit the overall rate. The interpretation is that microbes grow at a first order rate when nutrients are plentiful, but their growth is in proportion to the concentration of a critical substrate when the concentration of the substrate is low.

It seems clear that we also need to analyze the kinetics of the substrate in order to evaluate growth of microbes. The rate of change of the biomass concentration is proportional to the rate of depletion of the substrate, so

  (57)

where the yield coefficient, *Y*, is defined as

  (58)

The interpretation is that the yield coefficient is the unit of microbes produced per unit of substrate consumed. Substituting (54) into (57) gives

  (59)

We now have an expression for the kinetics of both the biomass concentration, *C* (54), and the substrate concentration, *S*s (59). These two equations can be solved to determine *C* and *S*s as functions of time, providing the constants are known. The constants, *k*1, *k*2, and *Y* would be determined experimentally.

### Inhibition

Microbial reactions can be inhibited by processes that interfere with the metabolism of the microbes, or otherwise cause difficulties. There are several ways that these inhibition processes are characterized, and one of them includes effects related to large concentrations of a substrate. This is called Haldane inhibition. Another one is related to concentrations of other compounds and it is called competitive inhibition. These effects are included by modifying (59) as

  (60a)

where

  (60b)

The inhibition functions (60b) increase the magnitude of the denominator in (60a) and reduce the rate at which the substrate changes. The magnitude of the effect is controlled by *K*h and *K*c, the Haldane and competitive inhibition constants, respectively.

### Death

Microbes die in response to environmental conditions, age and other factors. This reduces active biomass and the effect is generally represented as first-order, so

  (61)

where *k*d is the death rate coefficient.

### A Microbial System

The factors outlined above can be combined to represent a system where a microbial population grows on a substrate, reaches a stable population that ultimately depletes the available substrate and then the populate declines.

The kinetics of the population contains a Monod equation for growth and a first-order rate equation for death, which we get by adding (54) and (61)

  (62a)

The substrate kinetics will ignore inhibition (that could be added later), so we use (59) and

  (62b)

This system is quite simple because we only have two unknowns, *C* and *S*s, characterizing the behavior of the system and in real system there would be many possible influencing factors. We rationalize this approach by recognizing that in many complicated systems there is commonly one factor that limits the rates much more than the others, and we will assume this is *S*s.

There are four coefficients characterizing this system. *k*c1, *k*c2, control the rate of utilization of substrate, *Y* is the ratio of biomass to substrate, and *k*d is the decay rate due to death of the organisms.

#### Example

The analysis outlined above was applied to an idealized case describing the life cycle of a microbial population. The figure below is from a textbook and several variations of this figure are available showing the same conceptual model of four phases.

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| figure_06_15_labeled.jpg |
| Figure 4. Biomass as a function of time during 4 characteristic phases. Processes during the phases are described below. From <http://www2.raritanval.edu/departments/Science/full-time/Weber/Microbiology%20Majors/Chapter6sub/Chapter6sub_print.html>1.) In the **lag phase**, the organisms are adjusting to their environment. The proteins (enzymes) necessary for energy production and binary fission are being produced and the ribosomes necessary for their production are also being synthesized. Notice the population numbers are stagnant at this phase. 2.) In the **log phase**, the population is most actively growing. This is a linear line when plotted on a semi-log scale. This represents the exponential growth described above. 3.) In the **stationary phase**, new organisms are being produced at the same rate at which they are dying. This represents a sort of equilibrium between cell birth and cell death. The availability of nutrients and oxygen are becoming limiting and the cell are scrambling to survive by making adjustments within the cell. 4.) In the **death phase**, the organisms are dying more quickly than they can be replaced by new organisms. This is a shift away from the equilibrium described in stationary phase. Despite their best efforts, the cells cannot adapt to the harsh conditions descibed above and begin to lyse, deceasing the cell number. Notice, when the population starts to thin out it doesn't die off arithmetically (one-by-one), the population decreases **exponentially** similar to the linear nature of cell birth seen in log phage. It is the exponential death that prevents the earth from being overtaken by bacteria. <http://www2.raritanval.edu/departments/Science/full-time/Weber/Microbiology%20Majors/Chapter6sub/Chapter6sub_print.html> |

The analysis given by equations (62) was set up and parameters were adjusted manually to give responses similar to Figure 4. A *Y* value of 0.7 was used. The first set of analyses used *k*d = 0 and *k*d = 0.0002 s-1 (Fig. 5). The initial substrate concentration was set equal to 1, and the biomass was set to 0.01 initially. The units on substrate and biomass concentration were not given in the figure above, so they are arbitrary.

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| Figure 5. Substrate concentration (black) and biomass concentration with *k*d=0 (blue). *k*d=0.0002 s-1 (green).  |

 The biomass increases sharply initially and levels out at 0.7, a value controlled by *Y*, when kd=0 (Fig. 5). When *k*d=0.0002 s-1, the biomass concentration rises to a peak value of 0.4 and then decreases as the population dies off. In both cases, the substrate concentration decreases and is negligible in roughly 10,000s.

The observations of microbial systems (Fig. 4) generally resembles the green line in Figure 5, but there are some key differences. A lag period is observed in real situations, but the biomass starts to increase immediately in the analysis. The lag period occurs as the microbes figure out what to do with the substrate (the caption in the figure above states this in microbiological terms). As a result, it seems reasonable to expect that the growth mechanisms take some time to mature, so *k*c1 likely increases with time as the microbes mature during the lag phase. This process is represented in the analysis by making *k*c1 step from 0 to a constant value at *t* = 2000s.

The stationary phase is assumed to occur when the organisms are low on substrate and are living on energy reserves. They lack sufficient resources to grow during this time. The mortality rate increases when the energy reserves dwindle. This effect is included in the analysis by using a step function to increase *k*d at 20,000s in the analysis.

Allowing *k*c1 and *k*d to change with time gives a result that is remarkably similar to the result from the textbook. All four stages are evident (Fig. 6).

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| Lag | Log | Stationary | Death |
| Figure 6. Concentration of biomass (blue) and substrate (black) calculated using (43). Biomass growth includes lag, log, stationary and death phases.  |