
10. Reactions

The concept of a *reaction mechanism* from chemistry serves as a fruitful organizing idea in modeling. In this chapter we wish to develop this idea and explore some of its uses.

10.1 Petri nets

Petri nets are a special class of networks, introduced in 1962 by Carl Adam Petri, that provide a convenient language and graphical representation for many kinds of processes in a variety of areas of science and engineering. Some of the terms used in our discussion will come from chemical kinetics, an area where Petri nets are widely employed, but it will be clear that their applicability extends well beyond chemistry. I will often call them simply *nets*, for short.

The first special feature of a Petri net is that the underlying graph is *bipartite*. We begin by defining this and other basic terms concerning graphs and networks. A *directed graph*, or *digraph*, is a pair $\mathcal{G} = (V, E)$ where V is a set whose elements are called *vertices*, or *nodes*, and E is a subset of the product $V \times V$. Elements of E are called *edges*, or *arcs*. An edge is thus simply an ordered pair of vertices, (u, v) . We sometimes write $u \rightarrow v$ if (u, v) belongs to E , and say that this edge *connects* u to v .

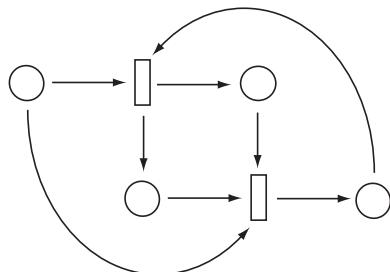


Figure 10.1: An example of a bipartite graph.

A graph is said to be *bipartite* if the set V of vertices decomposes into a disjoint union of two sets, $V = P \cup R$, and each element of E has the form (p, r) or (r, p) , where r belongs to R and p belongs to P . In other words, an edge can only connect vertices of different types. Vertices from P are called (in the Petri nets literature) *places*, and will be represented by circles in the graph diagram. Vertices from R are usually called *transitions*, and will be represented by rectangles. We will also use the terms (*molecular*) *species* and *reactions*, respectively. Figure 10.1 shows an example of a bipartite graph.

The *state* of a net is defined as an assignment of a non-negative integer, $M(p)$, to each place $p \in P$. We call $M(p)$ the *population size* of the species p . We also use, alternatively, the term *number of tokens*, which is more standard in the net literature.

In addition to the above basic structure, the edges of a net are assigned weights, defined by functions Pre and Post. To an edge (p, r) (going from a place to a transition) we associate a non-negative integer $\text{Pre}(p, r)$, and to each edge (r, p) , from a transition to a place, we associate a non-negative integer $\text{Post}(r, p)$.

I wish to think of each place as representing a molecular species and the number of tokens $X(p)$ as the number of molecules of species p at a given time. (Time will be brought into this general set up explicitly once we define a Markov process subordinate to a given Petri net. This will be done shortly when we introduce *stochastic* Petri nets.) In the same spirit, I wish to view a transition r as a reaction. The number $\text{Pre}(p, r)$ indicates how many molecules of type p are consumed in the reaction r , and $\text{Post}(r, p)$ indicates how many molecules of type p are produced by r . For example, consider the graph of figure 10.2.

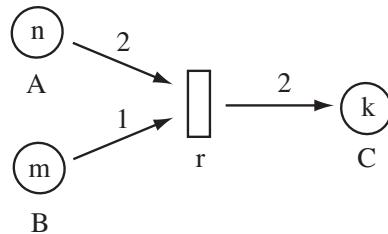


Figure 10.2: The Petri net of the reaction represented in ordinary chemistry notation by $r : 2A + B \rightarrow 2C$.

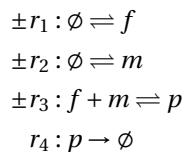
The net with the above diagram and weights $\text{Pre}(A, r) = 2$, $\text{Pre}(B, r) = 1$, and $\text{Post}(r, C) = 2$ (indicated over the arrows), can be viewed as a representation of the reaction $r : 2A + B \rightarrow 2C$ in standard chemical notation. The symbols inside the circles are the number of tokens for each place. They are variables $n = X(A)$, $m = X(B)$ and $k = X(C)$, which we view as the number of molecules of each species at a given time. A reaction event changes the population numbers according to Pre and Post, as follows: n is updated to $n - 2$, m to $m - 1$, and k to $k + 2$ every time the reaction event t “occurs.”

It is useful to consider reactions in which tokens of a given species are created or destroyed. We will indicate such transitions by

$$r : \emptyset \rightarrow A \text{ or } r : A \rightarrow \emptyset.$$

This may represent, for example, migration or transport between separate populations.

In actual chemical processes, reactions usually come together with their reversed form. This is usually the case when the reaction represents an elementary step in an overall complicated reaction mechanism. Given a reaction r , we denote its reversed form by $-r$. This is the reaction in which all the arrows of r are reversed while the weights attached to each arrow are kept. In other words, $\text{Post}(-r, A) = \text{Pre}(A, r)$. (Later we will be regarding reactions as vectors in an appropriate vector space, and the sign will have a more standard mathematical meaning.) It may be convenient to indicate a forward-backward reaction pair by some short-hand convention so as not to crowd the diagram too much. I will do this by drawing a double harpoon such as \rightleftharpoons on top of the reaction box. For example, consider the following set of reactions:



One may think of this system of reactions as a model for a dating service: the reversible pair of reactions $\pm r_1$ represents one woman enrolling in or leaving (still unmatched) the service; the reaction pair $\pm r_2$ represents the same for a man. The reaction r_3 represents the formation of one matched pair, and the reverse reaction $-r_3$ represents the dissociation of the pair and return to the unmatched f and m populations (possibly due to “bad chemistry.”) Reaction r_4 represents a successfully matched pair leaving the service. It is not meaningful to consider the reverse reaction $-r_4$ since a successful pair will not re-enter the service as a pair. (They might subsequently break up and re-enter the system individually through reactions r_1 and r_2 .) We assume the functions Pre and Post take value 1 on all edges.

The diagram of figure 10.3 shows the collection of reactions represented above in standard chemical notation.

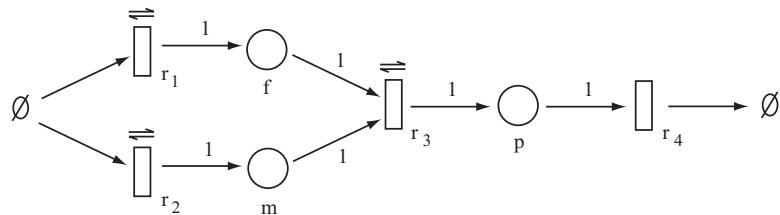


Figure 10.3: A Petri net representation of the reaction mechanism described above in standard notation. The number of tokens are not indicated.

We wish to think of the individual reaction events as taking place along a succession of time steps with each reaction proceeding independently of the other ones. This can be imagined as the work of several agents acting without coordination, following their own individual clocks, each responsible for the execution of one of the reactions in the overall mechanism. An *event* in the process consists of one execution of a given reaction by its agent. Whenever an event occurs, the number count of the populations of species participating in the corresponding reaction changes according to the functions Pre and Post. I.e., the number $X(A)$ is reduced by $\text{Pre}(A, r)$, or increase by $\text{Post}(r, A)$ depending on whether A is a reactant or a product of reaction r . We will translate this picture into a dynamical (stochastic) mechanism in the next section.

Generally, we omit the reaction rectangles if there is no more than one reactant and no more than one product species. Also, for small number of tokens, it is customary to indicate them by dots. The next example can be regarded as a transition diagram for a Markov chain (with transition rates not yet indicated). In this case we assume that the number of tokens at each place is either 0 or 1 and the total number of tokens is 1, the occupied place representing the present state of the Markov chain. State transitions of

Markov chains can be regarded as reactions of type $A \rightarrow B$. In such cases we omit the reaction rectangle.

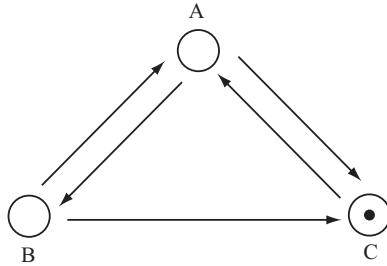


Figure 10.4: The transition diagram for a Markov chain is a special case of a Petri net. Here we omit the reaction rectangles. The token represents the present state.

10.2 State transitions diagram

Recall that the *state* of a net is defined by a function X on the set of places: $X(p)$ indicates the number of tokens occupying a place p . Let S denote the set of all states that a given net can attain. The *state transition graph* is a graph with vertex set S and edges (s, s') where s' is a state that can follow s after the occurrence of one reaction event.

Consider for example the Petri net of figure 10.5.

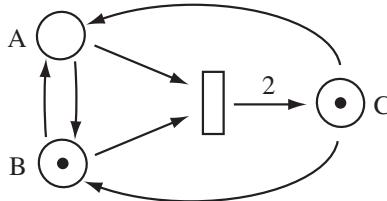


Figure 10.5: A Petri net with a total of two tokens.

Its set of reactions is:

$$\begin{aligned} \pm R_1 : A &\rightleftharpoons B \\ R_2 : A + B &\rightarrow 2C \\ R_3 : C &\rightarrow A \\ R_4 : C &\rightarrow B \end{aligned}$$

To obtain the transition diagram we first enumerate the states. Each state is repre-

sented by a vector (a, b, c) giving the number of tokens in places A, B and C . They are:

$$\begin{aligned}s_1 &= (2 \quad 0 \quad 0) \\ s_2 &= (1 \quad 1 \quad 0) \\ s_3 &= (1 \quad 0 \quad 1) \\ s_4 &= (0 \quad 2 \quad 0) \\ s_5 &= (0 \quad 1 \quad 1) \\ s_6 &= (0 \quad 0 \quad 2)\end{aligned}$$

The transitions diagram for the Petri net of figure 10.5 is given in figure 10.6. Note, for example, that the arrow from s_6 to s_5 is due to reaction $C \rightarrow B$, and the arrow from s_2 to s_6 is due to reaction $A + B \rightarrow 2C$.

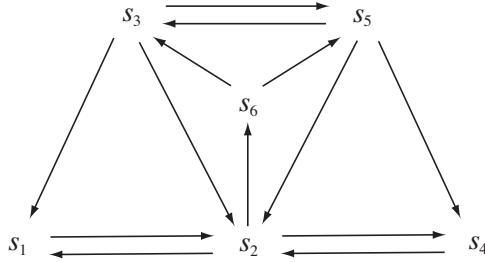


Figure 10.6: State transitions diagram for the Petri net of figure 10.5.

10.3 Stochastic Petri nets

We wish to introduce now a dynamical process that governs the way in which the states of a Petri net change in time. We can define processes that are either deterministic or stochastic. We begin with stochastic evolution model that incorporates the property that the various reactions operate in an uncoordinated, asynchronous way, and the reaction events happen at exponential random times.

The additional data needed to specify the stochastic dynamics are the *reaction rates*, $h(r, X)$. These are functions of the reaction r and of the state X of a Petri net. The reaction rates give the transition probability rates for the state transitions diagram associated to the Petri net, making them transition diagrams for a continuous-time Markov chain.

Note that the way in which the state of the process changes in time has the following general form:

$$X_{t_1}(p) = X_{t_0}(p) + \sum_{r \in R} \#_r([t_0, t_1])(\text{Post}(r, p) - \text{Pre}(p, r)), \quad (10.1)$$

where $\#_r([a, b])$ represents the number of reaction events of type r that occurred during the time interval $[a, b]$. With this in mind, the evolution process of the net can be described as follows:

1. The system is initially (time $t = 0$) in state X_0 . This may be a random variable with probability distribution λ on the set of states.

2. Let t be the time of occurrence of the last reaction and $X = X_t$ the present state.
3. For each reaction $r \in R$ let S_r be an exponential random variable with parameter $h(r, X)$. Let S be the minimum among the S_r and r the random reaction that gives the minimum, i.e., $S = S_r$. Now set the new time $t' = t + S$ and new state

$$X'(p) = X(p) + \text{Post}(r, p) - \text{Pre}(p, r).$$

4. Rename the present time t and present state X and if $t < T_{\max}$, return to step 2. Otherwise, stop.

Using the general properties of exponential distributions, we can restate the third item above as follows: Let X be the present state and t the time of last transition. Define

$$h(X) = \sum_{r \in R} h(r, X)$$

and probabilities

$$p_r = h(r, X)/h(X).$$

Obtain S , an exponential random variable with rate $h(X)$, and new reaction r chosen from R with probabilities p_r . Now set the new time $t + S$ and new state X' as in the above algorithm.

Natural choices of the reaction rates will ensure that the rate for a reaction r will decrease as the population size for a reactant involved in r decreases, so that the states do not take on negative values.

What we have described is, essentially, what is called *Gillespie method* of stochastic simulation. Before implementing this method, we stop to consider a class of rate functions coming from chemical kinetics known as *mass-action law*.

10.3.1 Mass-action kinetics

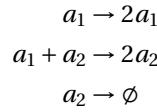
We specialize now to a family of rate functions defining what is called *mass-action kinetics*. First of all, the *order* of a reaction r is defined as the number of reactant species,

$$d = \sum_{p \in P} \text{Pre}(r, p)$$

In situations where a reaction event requires individuals of different species randomly to come together in close proximity at about the same time (a multiple collision), reactions of high order are rare. This is the case in chemistry. In fact, it is often the case in chemistry that reactions of order greater than 2 describe the overall effect of a sequence of elementary reactions of order 2 or less. Because of that, I will only write the precise expression of the mass-action laws up to order 2. This is shown in the next table.

order	reaction r	rate function $h(r, X)$
0	$\emptyset \rightarrow *$	c
1	$p \rightarrow *$	$cX(p)$
2	$p_1 + p_2 \rightarrow *$	$cX(p_1)X(p_2)$
2	$2p \rightarrow *$	$cX(p)(X(p) - 1)/2$

For example, consider the following stochastic version of a classical ecological model of predator-prey interaction known as the Lotka-Volterra system. Here a_1 represents the prey species and a_2 the predator species.



The first reaction represents the reproduction of the prey species. The second indicates the reproduction of predators require consumption and death of preys, and the last reaction represents predator death. The Petri diagram is shown in figure 10.7.

The mass-action rate functions are, respectively:

$$\begin{aligned} h(r_1, X) &= c_1 X(a_1) \\ h(r_2, X) &= c_2 X(a_1)X(a_2) \\ h(r_3, X) &= c_3 X(a_2). \end{aligned}$$

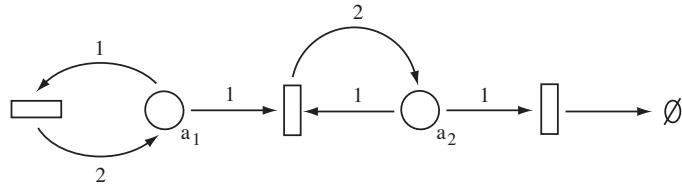


Figure 10.7: A net diagram for the predator-prey reaction model.

For large population sizes, the reaction rate function for the second order equation $2A \rightarrow *$ is approximated by $cX(A)^2$. More generally, the mass-action rate for the reaction

$$r : n_1 p_1 + \cdots + n_k p_k \rightarrow *$$

is taken to be

$$h(r, X) = c X(p_1)^{n_1} X(p_2)^{n_2} \dots X(p_k)^{n_k}$$

if the population sizes are large. Each term of the form x^n in the product can be regarded as an approximation of the binomial coefficient $C(x, n)$ (x -choose- n).

For ordinary chemical mixtures these quantities are typically measured in number of moles, where one mole equals 6.03×10^{23} molecules. This number is known as the Avogadro number. If we are considering reacting substances inside a well-mixed container of fixed volume, these quantities are usually expressed as molar concentrations, i.e., as the number of moles per unit volume.

10.3.2 Simulation of the stochastic Petri net process

The full specification of a stochastic Petri net at any given time involves the data $\mathcal{N} = (P, R, \text{Pre}, \text{Post}, h, X)$, where P is the set of places; R the set of transitions (or reactions);

Pre gives the multiplicities of place-transition edges; Post gives the multiplicities of transition-place edges; h is the probability rates function, which we often choose according to the mass-action law; and X is represents the state of the process at a given time. Recall that X is a function on P that gives the number of tokens, $X(p)$, of each place $p \in P$. We consider the edge-multiplicity functions Pre and Post as defined on all pairs (p, r) and (r, p) respectively, taking the value 0 if a pair is not an element in the edge set E . Thus the set E , which we didn't include in the Petri net data above, is already specified by the edge-multiplicity functions. Also recall that the function $h(r, X)$ is completely specified by the rate constants c_r under the mass-action law.

Before giving a more detailed algorithm for simulating the stochastic Petri net, it is convenient to represent the information in \mathcal{N} in matrix form based on some numbering of the sets P and R . We write $P = \{p_1, p_2, \dots, p_m\}$, $R = \{r_1, r_2, \dots, r_n\}$. (In realistic reaction mechanisms in chemistry, often the number n of reactions is much greater than the number m of molecular species.) Define $h_j(X) = h(r_j, X)$, $j = 1, \dots, n$, and write the state of the system as a column vector with coordinates $X_i = X(p_i)$. Thus we write $X = (X_1, \dots, X_m)^t$, where the upper-script indicates matrix transpose. When we need to write the state vector X as a function of time, we write it X_t or $X(t)$, depending on convenience of notation. We write the individual coordinates of X_t as $X_i(t)$.

Denote by $U = (u_{ij})$ the m -by- n matrix such that

$$u_{ij} = \text{Post}(r_j, p_i) - \text{Pre}(p_i, r_j).$$

This is sometimes called the *stoichiometric matrix* of the net. For example, in the predator-prey reaction model, U has the form

$$U = U^+ - U^- = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \end{pmatrix} - \begin{pmatrix} 1 & 1 & 0 \\ 0 & 1 & 1 \end{pmatrix} = \begin{pmatrix} 1 & -1 & 0 \\ 0 & 1 & -1 \end{pmatrix}.$$

The number of reaction events for each r_j over the interval of time $[a, b]$ will be denoted by $\#_j([a, b])$ and the column vector with these components will be written $\#[[a, b]]$. Formula 10.1 now takes the form

$$X_{t_1} = X_{t_0} + U\#[[t_0, t_1]], \quad (10.2)$$

where $U\#[[t_0, t_1]]$ is the matrix product of U by the column vector $\#[[t_0, t_1]]$. We note that if only one reaction event took place over a given time interval and the reaction was r_j , then

$$X_{t_1} = X_{t_0} + U^{(j)},$$

where $U^{(j)}$ is the j -th colum of U .

A more explicit description of Gillespie's algorithm, in the form of a hold-and-jump process, can now be given in the following way:

1. Initialize the state vector $X = X_0$;
2. for each $i = 1, 2, \dots, n$, calculate $h_i(X)$ based on the current state X ;
3. calculate the combined reaction rate $h(X) = h_1(X) + \dots + h_n(X)$;
4. simulate a sample value of an exponential random variable with rate constant $h(X)$ and call the value s . This is the holding time till the next reaction event;

5. set the current time to $t + s$ and call it t ;
6. simulate a sample value of index k with probabilities $h_k(X)/h(X)$ and call it j ;
7. set the new state of the system as $X + U^{(j)}$, where $U^{(j)}$ denotes the j -th column of the stoichiometric matrix U ;
8. output X and t ;
9. if t is less than a preassigned maximum time (or the number of steps is less than a preassigned value), return to step 2. Otherwise, stop.

10.3.3 A Matlab program for the Gillespie method

We implement here Gillespie method for the special case of reactions satisfying the mass-action law.

```
%%%%%
function [t y]=gillespie(U_pre, U_post, c, x_0, N)
%Simulate a reaction system using the Gillespie
%algorithm.
%Inputs: U_pre is the m-by-n matrix of
%place-to-reaction multiplicities (there are
%m places and n reactions);
%U_post is the m-by-n matrix of reaction-to-place
%multiplicities; c=[c_1 ... c_n] are the reaction
%constants; x_0 is the initial state written as
%a row vector of length m; and N-1 the
%maximum number of reaction steps.
%Outputs: t is a vector of length N of time events;
%y is an m-by-N matrix whose k-th column gives the state
%of the system at time step k. I.e., the system is
%at state y(k) during the interval from times
%t(k) to t(k+1), for each k.
[m n]=size(U_pre); %n=number of reactions; m=number of species
U=U_post-U_pre; %stoichiometric matrix
t=zeros(1,N);
y=zeros(m,N);
y(:,1)=x_0;
for k=1:N-1
    h=c.*prod(repmat(y(:,k),1,n).^U_pre); %reaction rate vector
    h_sum=sum(h);
    pi=h/h_sum; %jump probabilities
    s=-log(rand)/h_sum; %holding time
    t(k+1)=t(k)+s; %time of next reaction event
    %simulate next reaction with probability pi:
    a=rand;
    e=0;
    for i=1:n
        e=e+i*(sum(pi(1:i-1))<=a & a<sum(pi(1:i)));
    end
    y(:,k+1)=y(:,k)+U(:,i);
end
```

```

    end
    y(:,k+1)=y(:,k)+U(:,e);
end
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

```

We apply this program to the predator-prey model. The following commands can be used to obtain the graph of the population sizes as functions of time. Here we have used reaction constants $c_1 = 1$, $c_2 = 0.005$, and $c_3 = 0.6$. The initial population sizes are 50 preys and 100 predators.

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
U_pre =[1 1 0; 0 1 1];
U_post=[2 0 0; 0 2 0];
N=10000;
c=[1 0.005 0.6];
x_0=[50 100];
[t y]=gillespie(U_pre,U_post,c,x_0,N);
plot(t,y(1,:))
hold on
plot(t,y(2,:),'--')
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

```

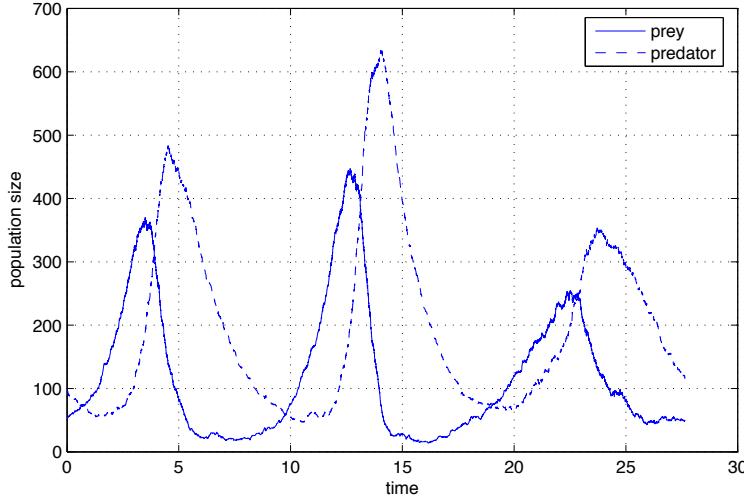


Figure 10.8: Changing populations of predator and prey in the stochastic Lotka-Volterra model.

Exercise 10.3.1. The `gillespie` program, as given, does not take into account the possibility that rate function h may become zero and the reaction network reaches an absorbing state. For example, the species populations may go “extinct.” Modify `gillespie`

so that the program will exit when reaching an absorbing state, returning the sample path of the process up to that moment.

10.3.4 Improvements of gillespie

The above program suffers from a few drawbacks. First, it outputs data of every single event that occurs in the simulation of the reaction network. This is often not desirable for systems with relatively large size and complexity, for which the number of simulated events becomes very large. In this case all that we may want to keep is the state of the system on a sufficiently fine grid of time points rather than the full sequence of states at every event time. Also the program does not take into account the possibility that one species population can go extinct and the reactions cannot continue.

The following modification of the `gillespie` program takes care of these shortcomings.

```
%%%%%%%
function [t y]=gillespied(U_pre, U_post, c, x_0, T, dt)
%Simulate a reaction system using the Gillespie
%algorithm only recording states on a regular grid
%of time points. Adapted from D. Wilkinson, "Stochastic
%Modelling for Systems Biology" (1st edition, page 155).
%Inputs: U_pre is the m-by-n matrix of
%place-to-reaction multiplicities (there are
%m places and n reactions);
%U_post is the m-by-n matrix of reaction-to-place
%multiplicities; c=[c_1 ... c_n] are the reaction
%constants; x_0 is the initial state written as
%a row vector of length m; and T is the
%final time (the initial time being 0).
%Outputs: t is a regular grid of time points with
%step size dt;
%y is an m-by-N matrix whose k-th column gives the state
%of the system at time step k. I.e., the system is
%at state y(k) during the interval from times
%t(k) to t(k+1), for each k.
[m n]=size(U_pre);
U=U_post-U_pre;
N=floor(T/dt);
y=zeros(m,N);
y(:,1)=x_0';
t=0:dt:(N-1)*dt;
ylast=x_0';
tt=0;
target=dt;
k=1;
while k<N
    h=c.*prod(repmat(ylast,1,n).^U_pre);
    h_sum=sum(h);
```

```

if h_sum<10^(-10)
    tt=10^(99);
else
    tt=tt-log(rand)/h_sum;
    pi=h/h_sum;
end
while tt>=target
    y(:,k+1)=ylast;
    k=k+1;
    target=target+dt;
    if k>=N
        return
    end
end
a=rand;
e=0;
for i=1:n
    e=e+i*(sum(pi(1:i-1))<=a & a<sum(pi(1:i)));
end
ylast=ylast+U(:,e);
end
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

```

As an example, we run `gillespied` for the same Lotka-Volterra model and same initial conditions as in the first numerical example, taking $T = 100$ and $dt = 0.05$. The result is shown in figure 10.9.

10.4 Homework 10

We modify the stochastic Lotka-Volterra model to allow migration of both predator and prey between two geographic sites. A diagram is shown in figure 10.10.

Note that the prey population is divided into two Petri net places, a_1 and a_3 . The places corresponding to the two predator populations are a_2 and a_4 . Let us assume that the interactions inside a given site have the same rate constants as in the one-site Lotka-Volterra model we examined before. Somewhat arbitrarily, let us set the migration rate for prey equal to $c_{r_4} = c_{-r_4} = 0.01$ and for predator $c_{r_5} = c_{-r_5} = 0.1$. Thus the full set of reaction rates is:

reaction	r_1	r_2	r_3	r_4	$-r_4$	r_5	$-r_5$	r_6	r_7	r_8
rate constant	1	0.005	0.6	0.01	0.01	0.1	0.1	1	0.005	0.6

1. Write down the matrices U_{pre} , U_{post} and U . (Assume that the reactions are ordered as in the above table of reaction rates and that places are ordered as in the graph a_1, a_2, a_3, a_4 .)
2. Assume that initially the population sizes are 100 at a_1 , 50 at a_2 , and zero at the other places. Do a simulation of the process using `gillespied` for $T = 150$, $dt = 0.05$, and obtain a graph of the predator population at the site that was initially not

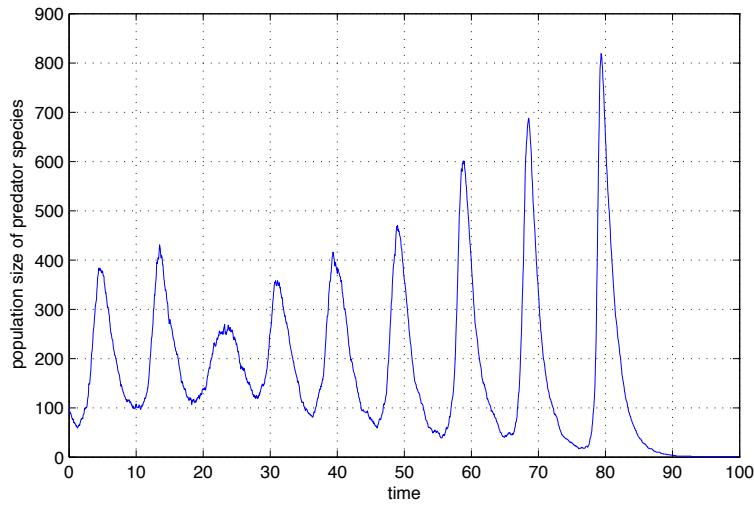


Figure 10.9: Changing predator population in the stochastic Lotka-Volterra model, showing extinction.

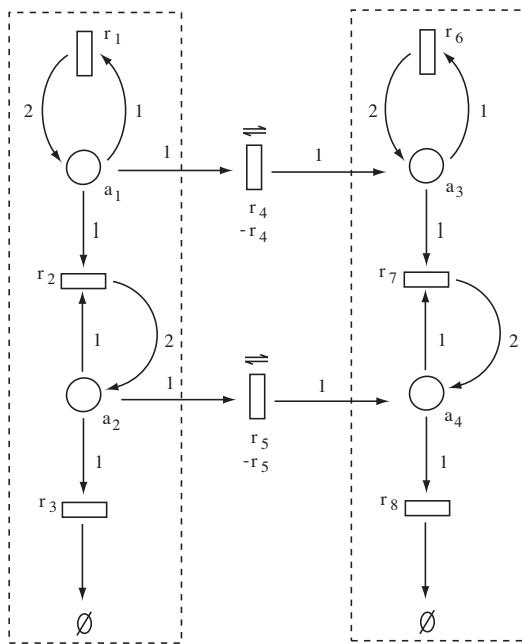


Figure 10.10: Predator-prey model with migration.

populated. I.e., plot the population size of a_4 as a function of time. (This took the `gillespie` program about one minute on my laptop.)

10.5 Homework 10 - Due date: Friday, 4/06/07

1. Read lecture notes on Petri nets, as well as sections 3.5 and 3.6 of textbook.
2. (This is about problem 3.7.1 of textbook. The notions of reaction rate is in the online notes.) Consider a fleet of N buses. Each bus breaks down independently at rate μ and is then sent to the depot for repair. The repair shop can only repair one bus at a time and each bus takes an exponential time of parameter λ to repair.
 - a) Draw a Petri net diagram of this situation. (Note: there are two places: in service buses and out of order buses; and two transitions: bus-breaks-down (in-service \rightarrow out-of-order) and bus-is-repaired (the reverse reaction). Indicate on the diagram the reaction rates. Is the mass-action law applicable to both reactions in this example?)
 - b) Suppose that $N = 4$. Draw the complete state transition diagram (see section 2, page 4, of the notes on Petri nets) indicating the transition rates q_{ij} in terms of μ and λ .
 - c) Obtain analytically the equilibrium distribution of the number of buses in service. (This is the original question in the book.) What is the expected value of the number of buses in service?
 - d) Confirm your answer of the expected number of buses in service by a computer simulation. Assume that $\mu = 1/5$, $\lambda = 1$, and $N = 50$. (Choose any other simulation parameter, such as the number of trials, as you see fit.)
3. (This refers to problem 3.3.1 of textbook.) In our previous homework assignment, you obtained the expected time to hit state 4 starting from 1. Confirm your answer by a computer simulation of the process. Choose any simulation parameter as you see fit.
4. Do the problem of section 4 of the notes. (This is about the stochastic predator-prey model with migration.)

10.6 Solutions

1. Consider a fleet of N buses. Each bus breaks down independently at rate μ and is then sent to the depot for repair. The repair shop can only repair one bus at a time and each bus takes an exponential time of parameter λ to repair.
 - a) The Petri net diagram for this situation is given in figure 10.11.
 - b) Suppose now that $N = 4$. The state transitions diagram with the transition rate constants is shown in figure 10.12.

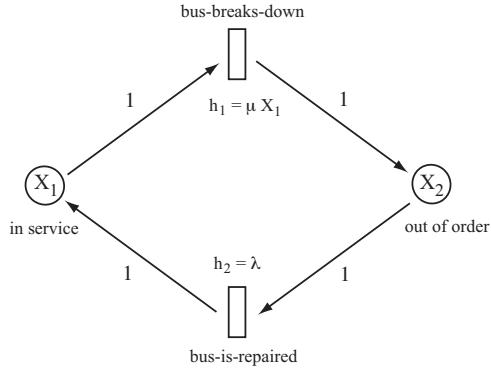


Figure 10.11: The bus-breaks-down reaction satisfies the mass-action law, but the bus-is-repaired reaction does not.

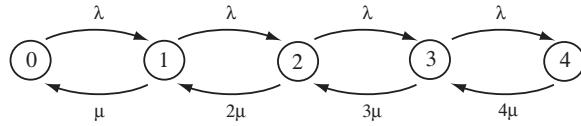


Figure 10.12: States are represented by the number of buses in working order.

c) The transition rates matrix can be written as follows:

$$Q = \begin{pmatrix} -\lambda & \lambda & 0 & 0 & \dots & 0 \\ \mu & -\mu - \lambda & \lambda & 0 & \dots & 0 \\ 0 & 2\mu & -2\mu - \lambda & \lambda & \dots & 0 \\ 0 & 0 & 3\mu & -3\mu - \lambda & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \dots & \vdots \\ 0 & 0 & 0 & 0 & \dots & \lambda \\ 0 & 0 & 0 & 0 & \dots & -(N-1)\mu - \lambda \\ 0 & 0 & 0 & 0 & \dots & N\mu \end{pmatrix}$$

An invariant probability measure p must satisfy $pQ = 0$. This corresponds to the system of equations:

$$\begin{aligned} \lambda p_0 + \mu p_1 &= 0 \\ \lambda p_0 - (\mu + \lambda) p_1 + 2\mu p_2 &= 0 \\ \lambda p_1 - (2\mu + \lambda) p_2 + 3\mu p_3 &= 0 \\ &\dots \\ \lambda p_{N-2} - ((N-1)\mu + \lambda) p_{N-1} + N\mu p_N &= 0. \end{aligned}$$

The solution to this system can be obtained by a simple induction. The result is $p = (p_0, p_1, \dots, p_N)$ where

$$p_k = \frac{(\lambda/\mu)^k / k!}{\sum_{j=0}^N (\lambda/\mu)^j / j!}.$$

The expected value of the number B of in service buses is given by

$$E[B] = \frac{\sum_{j=0}^N j(\lambda/\mu)^j / j!}{\sum_{j=0}^N (\lambda/\mu)^j / j!} = \frac{\lambda}{\mu} \frac{\sum_{j=0}^{N-1} (\lambda/\mu)^j / j!}{\sum_{j=0}^N (\lambda/\mu)^j / j!}.$$

For large values of N , this expected values approaches λ/μ .

- d) We assume that $\mu = 1/5$, $\lambda = 1$, and $N = 50$. By the result of the previous item the expected number of in service buses can be obtained numerically and equals 5.0000.

The following program gives the time average of the number of in service buses over sample paths. The value I obtained is 5.0359 (over 10000 transition events).

Notice that it would give a different result (somewhat higher value) if the average was computed without taking into account the holding times. This is because states corresponding to a higher number of in service buses have shorter holding time.

```
%%%%%%%%%%%%%
tic
rand('seed',157)
N=50; %Total number of buses
lambda=1;
mu=1/5;
M=[5]; %Initial number of in service buses is N
K=10000; %Number of transition events in simulation
q=M(1)*mu+lambda*(M(1)<N);
t=[-log(rand)/q];
for k=1:K-1
    a=length(M);
    m=M(a);
    p=(lambda/(m*mu+lambda))*(m~=N); %Probability of transition
    %m->m+1
    q=m*mu+lambda*(m<N);
    M=[M m-1+2*(rand<=p)];
    t=[t -log(rand)/q];
end
E=sum(M.*t)/sum(t)
toc
%%%%%%%%%%%%%
```

2. In problem 3.3.1 (HW 9), the value for the expected hitting time k_1^4 from state 1 to state 4 was obtained by solving the appropriate linear system and the value obtained was 7. We want to confirm this value now by numerical simulation. The Q matrix of the process is

$$Q = \begin{pmatrix} -1 & 1/2 & 1/2 & 0 \\ 1/4 & -1/2 & 0 & 1/4 \\ 1/6 & 0 & -1/3 & 1/6 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

The following program gave me the approximate value $k_1^4 = 7.0166$.

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
tic
rand('seed',371)
Q=[-1 1/2 1/2 0; 1/4 -1/2 0 1/4; 1/6 0 -1/3 1/6; 0 0 0 0];
pi=[1 0 0 0];
s=0;
for i=1:10000
    [t y]=ctmc(10^7,pi,Q);
    a=length(t);
    s=s+t(a);
end
s=s/10000
toc
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

The above uses the program `ctmc` shown below.

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
function [t y]=ctmc(n,pi,Q)
%Obtain a sample path with n events for a
%continuous-times Markov chain with initial
%distribution pi and generator matrix Q.
%The output consists of two row vectors:
%the event times t and the vector of states y.
%Vectors t and y may be shorter than n if
%an absorbing state is found before event n.
%Uses samplefrommp(pi,n).
t=[0];
y=[samplefrommp(pi,1)]; %initial state
for k=1:n-1
    i=y(k);
    q=-Q(i,i);
    if q==0
        break
    else
        s=-log(rand)/(-Q(i,i)); %exponential holding time
        t=[t t(k)+s];
        p=Q(i,:);
        p(i)=0;
        p=p/sum(p);
        y=[y samplefrommp(p,1)];
    end
end
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

3. Problem from course notes on the predator-prey model with migration.

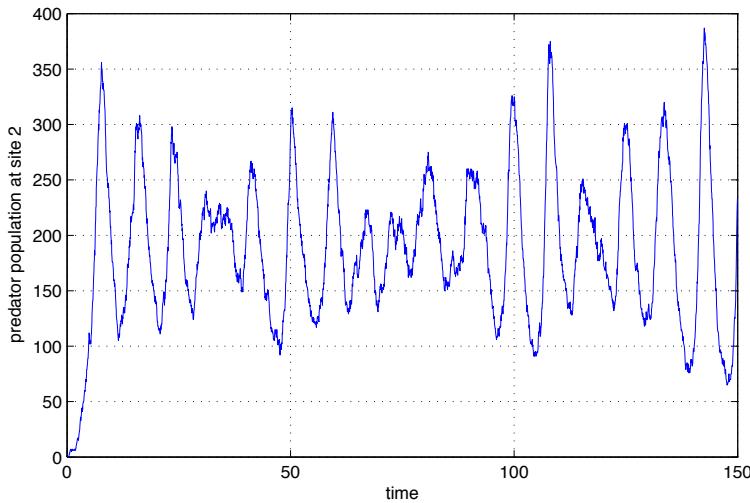


Figure 10.13: Changing population size of predator at the initially unoccupied site.

```
%%%%%%%%%%%%%
U_pre=zeros(4,10);
U_pre(1,1:4)=[1 1 0 1];
U_pre(2,2:3)=[1 1];U_pre(2,6)=1;
U_pre(3,5)=1;U_pre(3,8:9)=[1 1];
U_pre(4,7:10)=[1 0 1 1];
U_post=zeros(4,10);
U_post(1,1)=2;U_post(1,5)=1;
U_post(2,2)=2;U_post(2,7)=1;
U_post(3,4)=1;U_post(3,8)=2;
U_post(4,6)=1;U_post(4,9)=2;
T=150;
dt=0.05;
c=[1 0.005 0.6 0.01 0.01 0.1 0.1 1 0.005 0.6];
x_0=[100 50 0 0];
[t y]=gillespie(U_pre,U_post,c,x_0,T,dt);
plot(t,y(4,:))
%%%%%%%%%%%%%
```

11. Stoichiometry and other chemical ideas

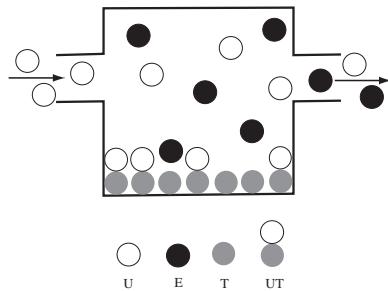
11.1 Examples of Reaction Networks

Very broadly stated, chemistry is the study of processes that involve *transformations* of substances. These transformations are expressed by *reaction* equations and they must satisfy certain physical restrictions, such as conservation of mass and energy. The object of a chemical reaction analysis is to determine how the amounts of the various substances involved in a given process vary in time and space. That analysis is actually very general and applies to situations that are related to chemistry only in a formal way, but for which the idea of transformation is still central.

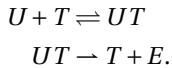
I'd like here to suggest a few examples of reaction mechanisms, some of which unquestionably chemical, others not.

11.1.1 Student-Teacher Interaction

Here the reactor is a “school,” which contains a mixture of four “substances”: (*U*) students without learning, (*E*) educated students, (*T*) teachers, and (*UT*) student-teacher “molecule.”



The school promotes the overall reaction $U \rightarrow E$, in which uneducated students are transformed into educated students. This reaction is mediated by the “catalyst” *T* through the reaction mechanism:

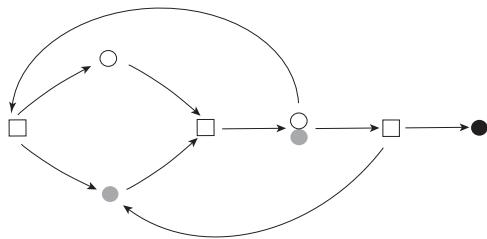


Notice that *T* is not “consumed” in the reaction. Its function is to accelerate the transformation of *U* into *E*.

Exercise 11.1.1. Suppose that the school “reactor” is operating under steady-state condition, that is, there is a constant inflow of students, which is equal to the outflow, so that the total stock of enrolled students is constant. Assume this stock is 8000 students and

that they all graduate after four years. (We say that their residence time is four years.) Calculate the outflow, i.e., the number of graduating students per year.

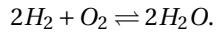
The reaction mechanism can be described graphically as follows:



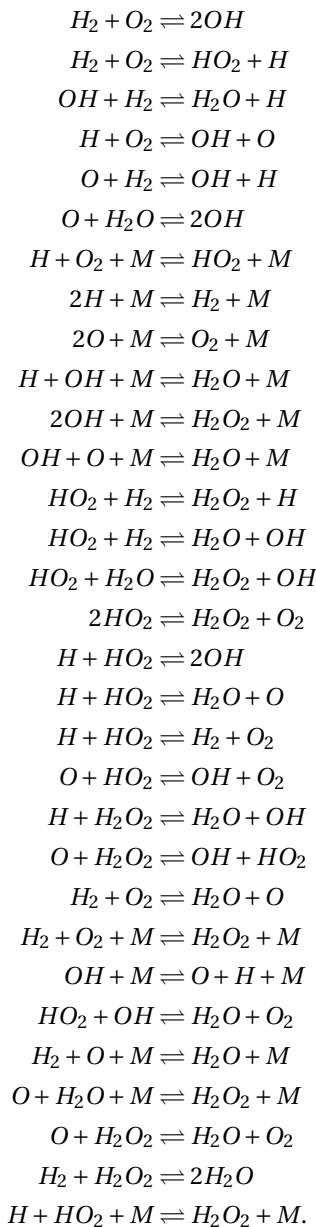
11.1.2 Oxidation of Hydrogen

Most chemical processes involve a large number of elementary reaction steps. The specification of a detailed reaction mechanism for the process requires spelling out those steps, which is usually a difficult experimental problem. Mathematics can help by providing ways to systematically obtain the possible reaction mechanisms and in exploring the consequences of adopting a particular mechanism as a working hypotheses.

As an example, consider the overall reaction



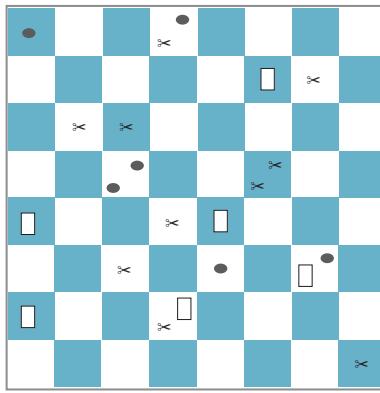
It is perhaps to be expected that three molecules, two of hydrogen and one of oxygen, coming together at nearly the same time with the right amount of energy to produce two molecules of water would be a low probability event. In fact, it is believed that this overall reaction involves a large number of simpler steps. The following mechanism can be found in *Kinetic Models of Catalytic Reactions*, by Bykov et al. M is any substance which can exchange energy with the other molecules.



The difficult task of determining the precise reaction mechanism for a given chemical process, such as the one given above, can be helped if there are ways of systematically enumerating all possible reactions involving a specified set of substances. We will see later how linear algebra can be a useful tool in this respect.

11.1.3 The ‘Rock-Paper-Scissors’ Game

Our next example may seem a bit artificial and is decidedly not chemistry. Consider the following game played by a large number, say N , of players over a checkerboard.



Each player chooses one piece from three kinds: rocks, papers, and scissors, and places it on a square of the checkerboard chosen at random. Let us say that the pieces are initially disposed as shown in the figure. Notice that there are 22 players in this example.

The game now evolves in discrete time, as follows. At time 1 we have the configuration of the game described by the figure. Inductively, suppose that we have obtained the configuration of the game at time n , for some $n = 1, 2, 3, \dots$. Then the configuration at time $n + 1$ is determined by a two-step rule:

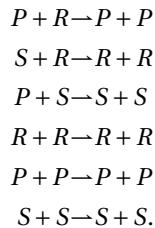
1. Each player chooses according to some random procedure from among the set

$$\{\text{North, South, East, West}\}$$

and moves its piece one square, accordingly. If the piece occupied a boundary square and the move would force it out of the checkerboard, then the player gets to draw again until it is given a move that keeps its piece within the board.

2. Once all players have moved its piece as described in part one, we allow the pieces to ‘interact’ and ‘transform.’ The rules of transformation will apply to each square separately, as follows:
 - a) If a square is empty, or contains a single piece, nothing is done.
 - b) If a square contains more than one piece, we select two pieces in that square at random and transform them by the following rules (‘reactions’) below. We

write S for ‘scissors,’ R for ‘stone’ and P for paper:



For example, if the square contains one paper and one stone, the stone changes into paper and the paper remains unchanged.

Now and later, we reserve the ‘harpoon’ type arrow ‘ \rightarrow ’ to indicate reactions. The ordinary arrow ‘ \rightarrow ’ will be used in the way it is normally used in mathematics, to indicate functions and limit operations.

This is not a win-loose game. The purpose is simply to watch its evolution in time. In other words, we wish to understand how the number of stones, papers and scissors vary as a function of time. Here is a sample of questions we might be interested in answering. Let $\#_S(n)$, $\#_R(n)$, and $\#_P(n)$ represent, respectively, the proportion of scissors, stones, and papers in the population at time n .

1. Do these numbers approach a well defined limit as $n \rightarrow \infty$, or do they oscillate in some unpredictable way? In particular, will one of the pieces go ‘extinct’ after a while?
2. How do these possible asymptotic behaviors depend on the initial configuration of the game?
3. We have defined the game by a number of random procedures. If we modify the probability parameters, how are the possible asymptotic behaviors affected?

Project 11.1.1. *Using your favorite math software (Matlab, Maple, Mathematica, etc.), simulate the stone-paper-scissors game and describe any interesting observation about how $\#_S(n)$, $\#_R(n)$, and $\#_P(n)$ vary with n .*

Here the reactor is the checker-board, which we can view as either an isolated system if no pieces are being added or taken out from the game, or as an open system if we allow “fluxes” in and out, through the sides. Notice that we may be interested not simply with changes in the numbers of S, P, R in time, but with their spatial distribution as well. The random motion described above (without regard to reaction) is a discrete approximation of a diffusion process. Thus in this case we are concerned with a reaction-diffusion system.

We could think of this game as representing a mixture of three interacting gases. More realistic, but similar, models of chemical (isomerization) processes will be shown later.

Exercise 11.1.2. *Give a graphical representation for the reaction mechanism of the SRP-game.*

Although this example is discrete both in space and in time, and the rules of transformation are defined probabilistically, we will for the most part in this course study continuous systems with deterministic rules specified by differential equations. In the continuous version of the problem, the quantities $\#_S(n)$, $\#_R(n)$, and $\#_P(n)$ are replaced with the densities per unit area at time t and the change in time, say $\#_S(n+1) - \#_S(n)$, is replaced with a time derivative.

The continuous version of this game has the following mathematical description. Let C_R, C_P, C_S denote the concentrations of R , P and S over a square with coordinates x, y . Let ∇^2 denote the two-dimensional Laplacian. Then

$$\begin{aligned}\frac{\partial C_P}{\partial t} &= K(C_R - C_S)C_P + D\nabla^2 C_P \\ \frac{\partial C_R}{\partial t} &= K(C_S - C_P)C_R + D\nabla^2 C_R \\ \frac{\partial C_S}{\partial t} &= K(C_P - C_R)C_S + D\nabla^2 C_S.\end{aligned}$$

The constants K and D depend on the precise way in which the passage from discrete to continuous was taken.

11.1.4 Evolutionary Game Theory

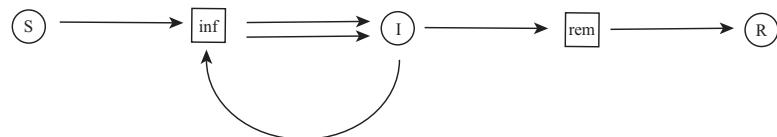
The previous example can be studied from the perspective of *evolutionary game theory*, and is of interest to such areas as evolutionary and population biology, ecology and economics. The SRP-game is treated, for example, in *Evolutionary Games and Population Dynamics*, by J. Hofbauer and K. Sigmund, Cambridge University Press, 1998; *Evolutionary Game Theory*, by J. W. Weibull, The MIT Press, 1995.

11.1.5 Epidemic Models

The following is a simplified form of a mathematical model describing the course of an epidemic. It was proposed and analyzed by Kermack and McKendrick in the 1930's. A population that has been exposed to some contagious disease is divided into three groups: those individuals *susceptible* of contracting the disease, denoted S ; *infective* individuals, I ; and *removed* individuals, R . Individuals of type S may change into type I , through contagion, while those of type I may change into type R , through death, recovery, or isolation from the rest of the population. Thus we have the following reactions:



In the following diagram, reactions are represented by squares. Arrows go from a circle to a square (respectively, from a square to a circle) if the individual type in the circle appears on the left-hand (respectively, right-hand) side of the reaction expression.



Exercise 11.1.3. Devise rules for a checkerboard game that simulates the process of epidemic spread described above.

There are many different ways to give mathematical flesh such set of equations. One way is to construct a probabilistic model along the lines of the rock-paper-scissors game. A deterministic model is obtained as follows. Denote by the same letters, S , R , and I , variables with (continuous) value range between 0 and 1, representing the fractions of the total population in the respective categories.

We interpret the infection reaction by the rule that S decreases in time at a rate proportional to the product of S and I , with proportionality constant σ ; I increases due to the infection reaction at the same rate, and decreases due to removal at a rate proportional to I with constant ρ ; R increases due to removal at the same rate as I decreases. Thus we have the following system of ordinary differential equations, where " $'$ " denotes time derivative:

$$\begin{aligned} S' &= -\sigma SI, \\ I' &= \sigma SI - \rho I, \\ R' &= \rho I. \end{aligned}$$

Exercise 11.1.4. Applying the coordinate changes

$$x = \frac{\sigma}{\rho}S, \quad y = \frac{\sigma}{\rho}I, \quad z = \frac{\sigma}{\rho}R, \quad \tau = \rho t$$

show that the differential equations reduce to

$$\begin{aligned} x' &= -xy \\ y' &= (x-1)y \\ z' &= y. \end{aligned}$$

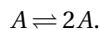
Also show that the quantities $x + y + z$ and $z + \ln x$ do not change in time.

For much more on this subject, see *Mathematics in Population Biology*, by H. R. Thieme. Princeton Series in Theoretical and Computational Biology, Princeton University Press, 2003.

11.1.6 Population Biology

A Primer of Population Biology, by E. O. Wilson and W. H. Bossert. Sinauer, 1971.

The growth of a population of bacteria might be described by a simple minded model defined by the following reactions:



The direct reaction represents the asexual reproduction of the organism whereas the reverse reaction might represent death due to resources competition. (Reactions that involve replication, as indicated by $A \rightarrow 2A$, are characteristic of life.)

Assuming that the reaction rates are given by the mass-action law (this will be explained later) the number density, u , of bacteria (number per unit area) satisfies the differential equation:

$$\frac{du}{dt} = k_1 u - k_2 u^2,$$

where k_1 and k_2 are the rate constants for the direct and reverse reactions, respectively. This (easily solvable) differential equation is called the *logistics equation*.

Suppose now that the population is allowed to disperse over a laboratory dish. If instead of bacteria we were considering small particles of some inert material, dispersion by random motion (brownian motion) would be described the *diffusion equation*:

$$\frac{\partial u}{\partial t} = D \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right).$$

(We will have much more to say about the diffusion equation later in the course.) The right-hand side of the equation is often written $D\nabla^2 u$, where ∇^2 is the Laplace operator in dimension 2.

For the bacteria population subject to reproduction, death, and random dispersal, its number density satisfies the reaction-diffusion equation

$$\frac{\partial u}{\partial t} = k_1 u - k_2 u^2 + D\nabla^2 u.$$

Exercise 11.1.5. Show that by a suitable coordinate change we can write the above equation as

$$\frac{\partial w}{\partial t} = sw(1-w) + k\nabla^2 w,$$

where s and k are positive constants. This is known as the Fisher equation. Find a space-homogeneous solution. (That is, a solution that depends only on t and not on x, y .)

Much more sophisticated models are used in population genetics. This simple equation, however, already exhibits some interesting behavior such as stationary waves. We'll return to this later.

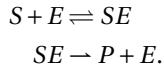
11.1.7 Environmental Science

Consider a Spherical Cow, John Harte. We will discuss a number of processes of interest to environmental sciences very early in the course.

11.1.8 Catalytic and Enzymatic Processes

Introduction to Mathematical Biology, Rubinow.

One of the most basic enzymatic reactions, first proposed by Michaelis and Menten (1913), involves a substrate S reacting with an enzyme E to form a complex SE , which is then converted into a product P and the enzyme. Schematically, this is represented by



(This is the same reaction scheme as for the student-teacher catalytic process suggested earlier.)

11.1.9 Spontaneous Generation of Spatial Patterns - Turing Models

Mathematical Biology, J. D. Murray.

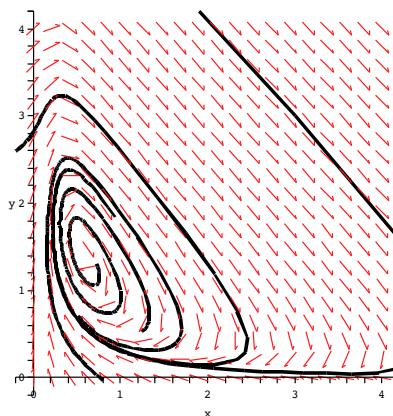
11.1.10 What is a 'Dynamical System'?

The differential equations that arise in chemical kinetics are often non-linear and do not admit the relatively simple and complete description of linear ODEs with which you may be familiar from Math 217. There are many new qualitative features displayed by solutions of non-linear equations that are not present in linear equations, and the systematic exploration of those new features require more sophisticated mathematical ideas. As a simple example, consider the following system of equations. They model a fundamental biochemical process called *glycolysis*, by which living cells obtain energy by breaking down sugar.

$$\begin{aligned}x' &= -x + ay + x^2y \\y' &= b - ay - x^2y.\end{aligned}$$

Here x and y are the concentrations of *ADP* (adenosine diphosphate) and *F6P* (fructose-6-phosphate).

The following picture shows a typically non-linear phenomenon. (For this numerical example $a = 0.08$ and $b = 0.6$.)



Notice that trajectories are attracted to a limit cycle from either inside or outside. (Inside there is an unstable equilibrium point.) This shows that, according to this model, the concentrations of the two substances during glycolysis oscillate. In dimension 3 the structure of the attracting set can be considerably more complicated, and the trajectories can behave in fairly "chaotic" way.

The theory of dynamical systems is concerned with the possible behaviors of trajectories of flows as in this case or discrete systems. Often, as in this example, we are given not a single systems, but a family of systems depending on a number of parameters (a and b in this case). We will be interested in finding out how the systems properties change with the parameters. This consideration will lead us to study so-called *bifurcations*.

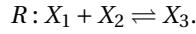
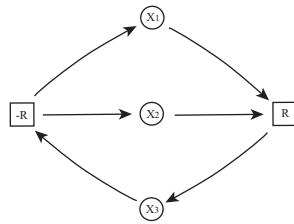
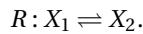
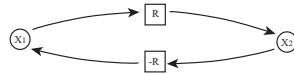
Our main sources for the theory of dynamical systems will be: *Differential Equations and Dynamical Systems*, by L. Perko; and *Nonlinear Dynamics and Chaos*, by S. H. Strogatz.

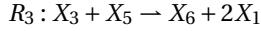
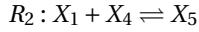
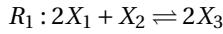
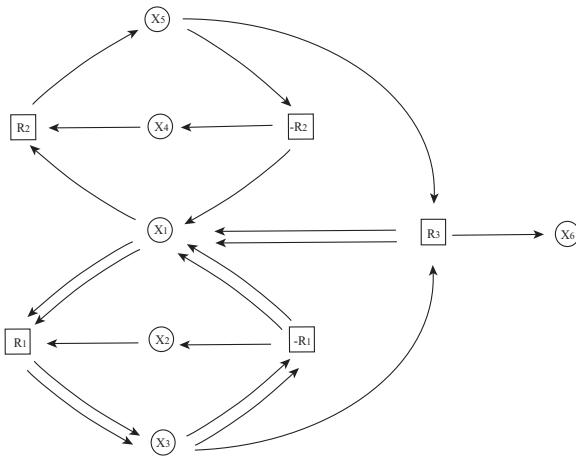
The above picture was produced with MAPLE using the following commands:

```
> with(plots);
> with(DEtools);
> eq1:= diff(x(t),t)=-x(t) + a*y(t) + x(t)^2*y(t);
> eq2:= diff(y(t),t)=b- a*y(t) - x(t)^2*y(t);
> a:=0.08;
> b:=0.6;
> ini1:=x(0)=0.4, y(0)=0.4;
> ini2:=x(0)=3, y(0)=3;
> ini3:=x(0)=0.1, y(0)=3;
> ini4:=x(0)=1,y(0)=1;
> DEplot(eq1, eq2, [x(t),y(t)], -10..10, [[ini1], [ini2], [ini3], [ini4]],
> stepsize=0.1, x=0..4, y=0..4);
```

11.1.11 Graph Representation of Reaction Mechanisms - I

Mechanisms for complex chemical reactions can be represented by graphs in a number of different ways. One way is to draw the reactions and substances as nodes of a graph, with arrows connecting each substance to reactions of which it is a reactant, and arrows from each reaction to its products. The nodes are thus of two different kinds. We represent reactions by square and substances by circles. Here are a few examples. In each case, R represents the direct reaction (\rightarrow). The number of arrows between two nodes indicates how many molecules of a given type are either used or produced in a reaction.





11.2 Steady-State Box Models Without Reactions

This and the next few sections are shamelessly lifted from the excellent *Consider a Spherical Cow*, by John Harte. All data needed can be found in the appendix of that book.

Here is a reminder of some basic chemical terms. *Avogadro's number* (N) is defined as the number of carbon-12 atoms in exactly 12 g of carbon 12. Its value is approximately 0.60229×10^{24} . A *mole* of a substance is defined as Avogadro's number of molecules of the substance. Thus a mole of water is the quantity of water containing N molecules of H_2O . The molecular weight of water is $2 \times 1.01 + 1 \times 16.00 = 18.02$. It follows from the definitions that one mole of H_2O is 18.02 g. One mole of sulfur S weighs 32.06 g.

11.2.1 Sulfur in Coal

This problem is intended for gaining familiarity with the measurement of quantity of matter in units of mass and in moles.

Problem 11.2.1. *How many tonnes (metric tons) and how many moles of sulfur were contained in the coal consumed worldwide in 1980?*

In the appendix Harte's book we find the following information: the consumption of coal worldwide in 1980, in energy (heat) units, was 90×10^{18} joules (the number was 15×10^{18} J for the United States alone); the energy content of coal is 29.3×10^6 J/Kg; sulfur (S) makes up 2.5% of coal composition in weight.

The amount of coal in metric tons consumed in 1980 can be calculated as the quotient

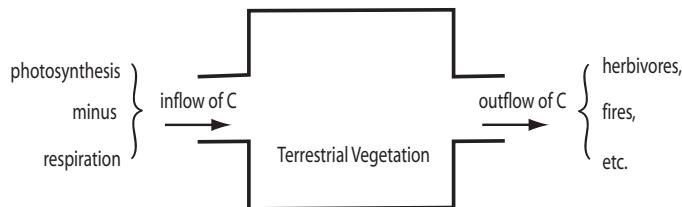
$$\frac{\text{energy derived from coal in 1980 in joules}}{\text{energy content per unit mass of coal in joules per tonne}}.$$

This number is 3.1×10^9 tonnes. Of this amount, sulfur makes up 2.5%, which gives 7.7×10^7 tonnes of S.

If one mole of S weighs 32.06 grams, one metric ton of S contains $10^6 / 32.06$ moles, or 3.1×10^4 moles. Multiplying this number by the amount of sulfur in tonnes gives 2.4×10^{12} moles of S.

11.2.2 Carbon in the Biosphere

Recall from the example of a school, given in class, the following concepts: for a system in steady-state the inflow and outflow of a given substance are equal and constant in time. The total amount of that substance in the system is the substance's total stock, and the residence time of that substance in the system is the total stock divided by the inflow.



Suppose that the system is the living continental (as opposed to marine) vegetation and that we are interested in the flow of carbon through it. The inflow of carbon from the atmosphere is mainly due to photosynthesis, and is called *gross primary productivity*. If we subtract from it the carbon loss due to respiration by the vegetation we obtain the *net primary productivity* of the system. The residence time of carbon in the system, obtained using the net primary productivity as inflow, serves as an estimate of the average life span of plants.

Problem 11.2.2. Calculate the residence time of carbon in continental vegetation.

From the appendix of Harte's book: the net primary productivity of continental vegetation is $(50 \pm 15) \times 10^{12}$ Kg of carbon per year. It also quotes the continental living biomass stock as $500(+300, -100) \times 10^{12}$ Kg of carbon. This number does not seem to distinguish between animal and vegetable biomass, but I'll make the assumption that most of the continental biomass is vegetable. Thus the residence time is

$$\frac{\text{stock of living continental biomass}}{\text{continental net primary productivity}}.$$

This gives a number anywhere between 7 and 23 years.

11.2.3 A Polluted Lake

The main concept here is *steady-state concentration*.

Problem 11.2.3. A stable and highly soluble pollutant is dumped into a lake at the rate of 0.16 tonnes per day. The lake volume is 4×10^7 cubic meters and the average water flow-through rate is 8×10^4 cubic meters per day. Ignore evaporation from the lake surface

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and assume the pollutant is uniformly mixed in the lake. What eventual steady-state concentration will the pollutant reach?

We need first to calculate the stock of pollutant, M_p , in the lake. This is the product $F_p \times T_p$, where F_p is the rate at which the pollutant is being dumped in the lake and T_p is the pollutant residence time. This residence time is equal to the water residence time, T_w , since water and pollutant are uniformly mixed. But

$$T_w = \frac{M_w}{F_w} = \frac{4 \times 10^7 \text{ m}^3}{8 \times 10^4 \text{ m}^3/\text{day}} = 500 \text{ days.}$$

Therefore

$$M_p = F_p \times T_p = 0.16 \text{ tonnes per day} \times 500 \text{ days} = 80 \text{ tonnes.}$$

The amount of water in the lake in weight is the volume times water density (= 1000 kg per cubic meter):

$$4 \times 10^7 \text{ m}^3 \times 1 \text{ metric ton per m}^3 = 4 \times 10^7 \text{ tonnes.}$$

Thus the steady-state concentration of the pollutant is

$$\frac{80 \text{ tonnes}}{4 \times 10^7 \text{ tonnes}} = 2.0 \times 10^{-6}.$$

This is 2 parts per million by weight.

Aqueous concentrations are often specified in units of molarity, or moles per liter. Suppose the pollutant has a molecular weight of 40 (that is, there are a total of 40 protons and neutrons in the atoms of each molecule). Then the number of moles of pollutant is the weight in grams divided by 40 g:

$$\text{number of moles} = \frac{\text{weight in grams}}{\text{molecular weight}} = \frac{80 \times 10^6}{40} = 2.0 \times 10^6 \text{ moles.}$$

The volume of water in liters is 4×10^{10} liters. So the molarity of pollutant is 50×10^{-6} moles per liter, or 50 micromoles per liter. One mole per liter is called a *molar*, and designated M. We can write the solution as $50\mu\text{M}$ (micromolars).

You may have encountered similar problems in Math 217 (differential equations) if you took it before. Let us stop to look at how the same problem is approached in that course. Let x denote the concentration of pollutant (in tonnes per cubic meter). The rate of change of the amount of pollutant, which is the time derivative of $M_w x$, is the difference between the inflow (0.16 tonnes per day) and the outflow of pollutant. The latter is x times the outflow of water measured in volume per time: $8 \times 10^4 x$. Therefore the concentration x satisfies the differential equation:

$$4 \times 10^7 \dot{x} = 0.16 - 8 \times 10^4 x.$$

In steady-state, the concentration is constant in time so $\dot{x} = 0$, and we arrive at

$$x = \frac{0.16}{8 \times 10^4} = 2.0 \times 10^{-6} \text{ tonnes per cubic meter.}$$

If instead of steady-state condition we assume that the lake water is initially clean, then $x(0) = 0$, and we have the initial value problem:

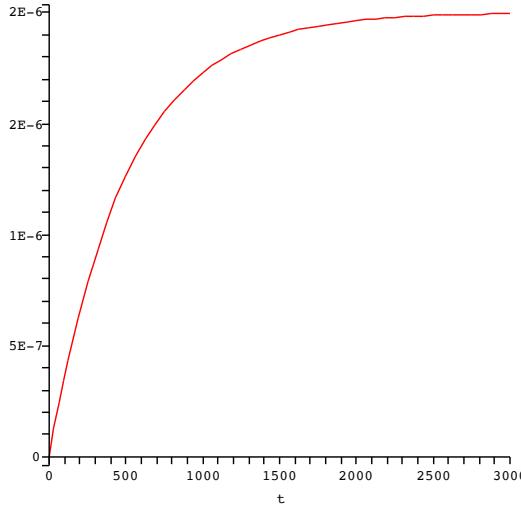
$$\begin{aligned}\dot{x} &= ax + b \\ x(0) &= x_0\end{aligned}$$

where $a = -2 \times 10^{-3}$, $b = 4 \times 10^{-9}$, $x_0 = 0$.

Exercise 11.2.1. Show that the solution to the above initial value problem is:

$$x(t) = \frac{b}{a} (e^{at} - 1) + x_0 e^{at}.$$

What happens to $x(t)$ as $t \rightarrow \infty$?



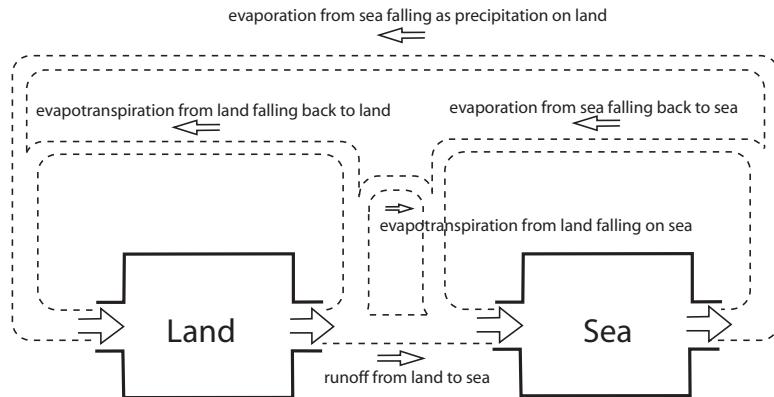
The above graph of the concentration function $x(t)$ was obtained using the MAPLE commands:

```
> f := t -> 2*10^(-6)*(1-exp(-2*10^(-3)*t));
> plot(f(t), t=0..1000);
```

11.2.4 The Global Hydrocycle

Here we are concerned with the flows of water between land and sea. A simplified global water budget is described schematically in the next figure.

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Land water that evaporates from rivers and lakes as well as water from transpiration of the vegetation cover (evapotranspiration) falls as precipitation, partly back to land and partly to sea. Sea water evaporates and falls as precipitation, partly back to sea and partly to land. River water flows from earth to sea (runoff).

Problem 11.2.4. *If evapotranspiration from Earth's land area were to diminish by 20% uniformly over the land area, as might result from widespread removal of vegetation, what changes would occur in the globally averaged precipitation on the land surface and in the globally averaged runoff from the land to the sea?*

It will be helpful to introduce the following rates:

e_{LL} = rate of evapotranspiration from land that falls as precipitation on the land;

e_{LS} = rate of evapotranspiration from land that falls as precipitation on the sea;

e_{SL} = rate of evaporation from sea that falls as precipitation on the land;

e_{SS} = rate of evaporation from sea that falls as precipitation on the sea;

r = rate of runoff from the land to the sea;

p_L = rate of precipitation on the land;

p_S = rate of precipitation on the sea.

Then our problem is to find out how r and p_L will change if e_{LL} and e_{LS} are reduced by 20%.

Here are some numerical values available in the appendix of Harte's book:

world evapotranspiration from land = 62×10^{12} cubic meters per year;

world evaporation from sea = 456×10^{12} cubic meters per year;

world precipitation on sea = 410×10^{12} cubic meters per year;

world precipitation on land = 108×10^{12} cubic meters per year;

world runoff = 46×10^{12} cubic meters per year.

This means that, in units of 10^{12} cubic meters per year:

$$e_{LL} + e_{LS} = 62 \quad (\text{eq. 1})$$

$$e_{SL} + e_{SS} = 456 \quad (\text{eq. 2})$$

$$e_{LS} + e_{SS} = 410 \quad (\text{eq. 3})$$

$$e_{LL} + e_{SL} = 108. \quad (\text{eq. 4})$$

$$r = 46 \quad (\text{eq. 5})$$

There are here 5 equations and 5 unknowns, but notice that these are not all independent equations. In fact, it can be checked that

$$(\text{eq. 1}) + (\text{eq. 2}) = (\text{eq. 3}) + (\text{eq. 4}).$$

This is to be expected since all the water that evaporates eventually falls back as precipitation. We need to find another relationship among these rates. For that purpose we will make the assumption that three-fourths of the evapotranspiration from the land precipitates back on the land. (Is this a reasonable estimation?) In other words, by a rough estimate we have:

$$e_{LL} = 3e_{LS}. \quad (\text{eq. 6})$$

Solving equations 1 to 6 we obtain:

$$e_{LS} = 15.5$$

$$e_{SS} = 394.5$$

$$e_{SL} = 61.5$$

$$e_{LL} = 46.5$$

$$r = 46.$$

There are several relations among these quantities that must always hold, even after some hypothetical change in the evapotranspiration rate. First, by definition we have:

$$p_L = e_{LL} + e_{SL}$$

$$p_S = e_{LS} + e_{SS}.$$

Also, under the steady-state assumption, the total stocks of water on sea and on land remain constant. Conservation of the sea water gives the equation:

$$p_S + r = e_{SS} + e_{SL};$$

and conservation of water on land gives the equation:

$$p_L = r + e_{LL} + e_{LS}.$$

If evapotranspiration from earth decreases by 20%, we have the following changes (primed letters represent the new values):

$$e'_{SS} = e_{SS};$$

$$e'_{SL} = e_{SL};$$

$$e'_{LL} = 0.8e_{LL};$$

$$e'_{LS} = 0.8e_{LS}.$$

A little algebra now gives

$$p'_L - p_L = -0.2e_{LL} = -9.3 \times 10^{12} \text{ cubic meters per year};$$

$$r' - r = 0.2e_{LS} = 3.1 \times 10^{12} \text{ cubic meters per year.}$$

The result is that r increases by about 7% and p_L decreases by about 9%.

11.2.5 Cooling off

We have so far considered box models involving matter flows. A similar accounting of inflow and outflow of energy instead of matter is what thermodynamics is mainly about. For a very nice and good humored overview of classical thermodynamics see *Understanding Thermodynamics*, by H. C. Van Ness. Dover, 1983.

Problem 11.2.5. At what rate is water used to cool a 1000-megawatt coal-fired power plant?

We first need to have some idea of how a power plant operates. (See the figure on the next page.) There are four primary devices in the power cycle. The boiler serves to convert liquid water into steam at a high pressure and a high temperature. This requires heat from some high-temperature source. The steam is fed to a turbine which drives an electric generator. Through the turbine steam expands causing the turbine blades to rotate, and then exhausts at a low pressure. At this point, heat has been converted to mechanical energy.

The next step is the conversion of mechanical energy to electric. This is accomplished using the principle that a variable magnetic field generates current on a metal wire immersed in that field. To take advantage of this fact, the rotating turbine shaft is wrapped with conducting wires and surrounded by a strong magnetic field. This is what takes place inside the generator.

There is no limit in principle to how efficiently mechanical energy can be converted to electric energy. On the other hand, there is a fundamental thermodynamical limit on the conversion of heat into mechanical or any other type of work, which was discovered in 1824 by Carnot. It says, in the present context, that the maximum efficiency of the heat-to-mechanical energy conversion is given by the equation

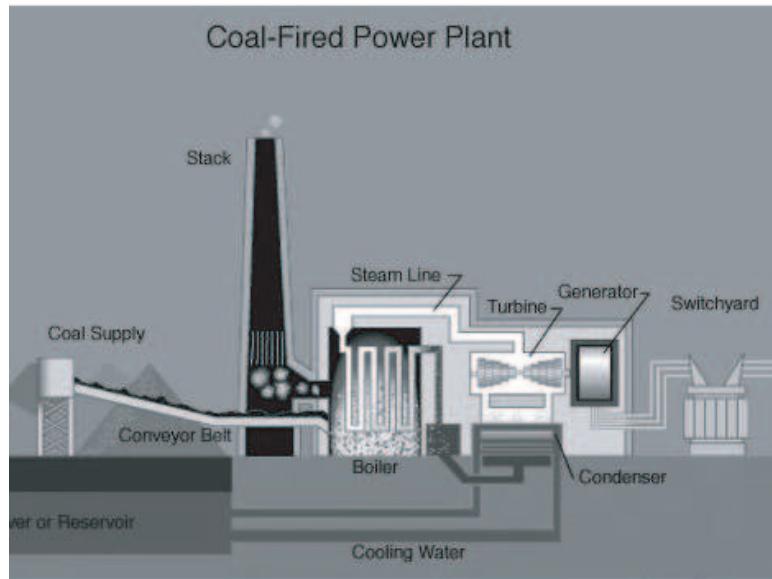
$$\eta_{\max} = \frac{T_H - T_C}{T_H},$$

where the hotter temperature, T_H , is the temperature of the boiler and the cooler temperature, T_C , is the temperature of the condenser. Therefore the greater the gap of temperature across the turbine the greater the efficiency at which it can operate.

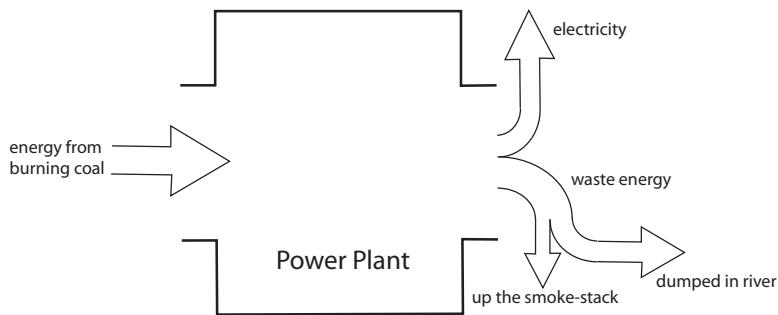
The actual efficiency of such a power plant will be less than the ideal, η_{\max} . Inefficiencies in both conversion processes, resulting from mechanical friction, electrical resistance, loss of heat up the smoke stack, etc., result in energy loss.

For a typical coal-fired electric generating plant T_H is about 800 K, and T_C is about 300 K. Thus the ideal efficiency of conversion is $\eta_{\max} = 500/800 = 62.5\%$. The actual conversion efficiency for a modern coal-fired electricity generating plant is about 40%, which means that

$$\frac{\text{electric power output}}{\text{rate of heat input from coal burning}} = 0.40.$$



(The above figure is taken from the website <http://www.tva.gov/power/coalart.htm> maintained by the Tennessee Valley Authority.) The energy budget of our power plant can be described as follows. Energy obtained from burning coal is partly transformed into electric energy and partly wasted as heat going up the smoke-stack as well as heat that is transferred to the river water as it is used to keep the condenser at its operating temperature of 300 K. A box diagram is shown next.



The difference between the heat input and the electric output is waste heat. The rate

at which this waste heat is produced, R , is

$$\begin{aligned}
 R &= (\text{rate of heat input}) - (\text{rate of electrical energy output}) \\
 &= \frac{(\text{electric power output})}{0.40} - (\text{electric power output}) \\
 &= 1.5 \times (\text{electric power output}) \\
 &= 1.5 \times 1000 \text{ megawatt} \\
 &= 4.7 \times 10^{16} \text{ joules per year.}
 \end{aligned}$$

(We have used above that 1 joule equals 1 watt-sec.)

Typically, about 15% of this waste heat is removed via the smoke-stack, in the form of hot effluent gases. The remaining 85% is the heat that must be discharged from the turbine by some cooling process. This amounts to 4.0×10^{16} joules per year.

We are assuming that for the cooling process, cool water flowing past the power plant and through the turbine condenser is warmed by the waste heat and then discharged to the environment. Let us say that cooling water enters at an average temperature of 290 K. Then it will typically be heated by about 10 K (to 300 K) as it passes through the turbine condenser.

We can now calculate the rate at which water must flow through the system. The key fact is this: it takes 1 cal, or 4.18 joules, to heat 1 gram of water 1 K. Thus 4.0×10^{16} joules per year will heat $\frac{4.0 \times 10^{16}}{4.18} = 9.6 \times 10^{15}$ grams of water 1 K per year. If the water is 10 K hotter after passing through the condenser, then we need 9.6×10^{14} grams of water per year. This amounts to about 30 cubic meters of water per second.

11.2.6 Stoichiometry of Burning Fossil Fuels

Stoichiometry is concerned with the relative amounts of the elements that constitute a chemical substance. The expressions H_2O and $HO_{0.5}$ are equivalent stoichiometric formulas for water. Note that one mole of H_2O weighs $2 + 16 = 18$ grams, whereas one mole of $HO_{0.5}$ weighs $1 + 8 = 9$ grams.

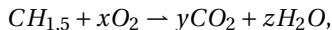
Problem 11.2.6. *In 1980, how much O_2 was removed from the atmosphere due to the combustion of fossil fuel on Earth, and how much CO_2 and H_2O were produced in the combustion process?*

The primary elemental constituents of the three major types of fossil fuels (natural gas, petroleum, and coal) are carbon and hydrogen. When fossil fuel is burned, oxygen from the atmosphere combines with the carbon to make CO_2 and with the hydrogen to make H_2O . In addition, coal contains some water (typically 10-15% by weight), which is released to the atmosphere upon combustion of the coal. All three types of fossil fuel contain various other substances such as ash, sulfur, and trace metals in even lower concentrations.

We need to consider petroleum, coal, and natural gas separately.

Here is some pertinent information from the appendix of Harte's book regarding petroleum (crude): 98% of its weight consists of $CH_{1.5}$; the world consumption in 1980 was 135×10^{18} joules, and its heat content is 43×10^6 joules per kilogram.

The combustion of $CH_{1.5}$ follows the overall reaction



where x, y, z are the stoichiometric constants, which we need to determine. These constants provide an answer to the problem: for each mole of $CH_{1.5}$ x moles of O_2 is consumed, and y and z moles of CO_2 and H_2O , respectively, are produced.

To determine x, y, z , we equate the number of moles of each element, C, O, H , on the left and right sides of the reaction:

$$1 = y \quad (C)$$

$$2x = 2y + z \quad (O)$$

$$1.5 = 2z. \quad (H)$$

This gives



To determine the number of moles of $CH_{1.5}$ burned worldwide in 1980 we calculate:

$$\text{weight fraction of } CH_{1.5} \text{ in crude composition} \times \frac{\text{world consumption (joules)}}{\text{heat content (joules per kilogram)}}.$$

This number is

$$0.98 \times \frac{135 \times 10^{18}}{43 \times 10^6} \text{ kilograms} = 3.08 \times 10^9 \text{ tonnes.}$$

Since one mole of $CH_{1.5}$ weighs $12 + 1.5 = 13.5$ grams, the amount of $CH_{1.5}$ burned is

$$\frac{3.08 \times 10^{15} \text{ grams}}{13.5 \text{ grams}} = 2.28 \times 10^{14} \text{ moles of } CH_{1.5}.$$

Therefore, the amounts of O_2 , CO_2 , and H_2O consumed or released into the atmosphere due to petroleum burning are:

$$n(O_2) = 1.375 \times 2.28 \times 10^{14} = 3.14 \times 10^{14} \text{ moles (consumed)}$$

$$n(CO_2) = 2.28 \times 10^{14} \text{ moles (released)}$$

$$n(H_2O) = 0.75 \times 2.28 \times 10^{14} = 1.71 \times 10^{14} \text{ moles (released).}$$

We repeat the analysis, now for natural gas. The composition of natural gas in molar fractions is: CH_4 (75%), C_2H_6 (6%), C_3H_8 (4%), C_4H_{10} (2%), and C_5H_{12} (1%). The remaining 12% is noncombustible. Thus one mole of natural gas consists of:

$$0.75 \times 1 + 0.06 \times 2 + 0.04 \times 3 + 0.02 \times 4 + 0.01 \times 5 = 1.12 \text{ moles of } C$$

$$0.75 \times 4 + 0.06 \times 6 + 0.04 \times 8 + 0.02 \times 10 + 0.01 \times 12 = 4 \text{ moles of } H.$$

Thus, the effective formula for the combustible portion of natural gas is $C_{1.12}H_4$, and this makes up 88% of natural gas in moles. After finding the stoichiometric constants as before, we obtain the reaction formula



The world consumption of natural gas in 1980 was 60×10^{18} joules and the heat content at standard temperature and pressure is 3.9×10^7 joules per cubic meter. This gives 1.54×10^{12} cubic meters.

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One mole of any gas at standard temperature and pressure comprises 22.4 liters, or 22.4×10^{-3} cubic meters. We will return to this point later. Accepting it for now, we obtain that 1m^3 of any gas at STP contains 44.6 moles. Therefore, the world consumption of natural gas in moles was $44.6 \times 1.54 \times 10^{11} = 6.9 \times 10^{13}$ moles of natural gas. Multiplying by 0.88 (the combustible fraction) gives 6.0×10^{13} moles of $C_{1.12}H_4$. It follows that the amounts of O_2 , CO_2 and H_2O consumed or released by burning natural gas are:

$$n(O_2) = 2.12 \times 6.0 \times 10^{13} = 1.27 \times 10^{14} \text{ moles (consumed)}$$

$$n(CO_2) = 1.12 \times 6.0 \times 10^{13} = 0.67 \times 10^{14} \text{ moles (released)}$$

$$n(H_2O) = 2 \times 6.0 \times 10^{13} = 1.20 \times 10^{14} \text{ moles (released).}$$

I leave the calculation for coal to you. Notice that 13% of coal is water, which is liberated to the atmosphere upon combustion and must be included in the calculation. The result for coal is

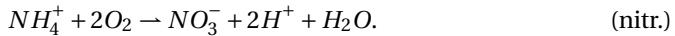
$$n(O_2) = 2.16 \times 10^{14} \text{ moles (consumed)}$$

$$n(CO_2) = 1.80 \times 10^{14} \text{ moles (released)}$$

$$n(H_2O) = 0.94 \times 10^{14} \text{ moles (released).}$$

11.2.7 Natural Acidity of Biological Processes

Many organisms are able to change ammonium nitrogen (NH_4^+) to nitrate nitrogen (NO_3^-) by the overall reaction



This process, called nitrification, is carried out by bacteria that live in the soil. Common sources of ammonium in the soil result from decaying plants and organic matter, or ammonium can come from the application of manure or nitrogen fertilizers. The nitrification process is a source of acidity.

Problem 11.2.7. *In typical freshwater lakes, the nitrification rate averages about 10^{-4} moles of N per liter per year. This produces an influx of H^+ in the lake that increases the acidity of the lake water. Assume the residence time of the water in the lake is half a year. For comparison, suppose that the same acidity results from the lake receiving inflow of water with high pH due, say, to acid rain. What pH should the rain water have that will cause the lake to have the same acidity as produced by the nitrification process?*

It will be necessary to explain first some basic facts about acids. An acid may be defined as a hydrogen-containing substance that dissociates in water to produce hydrogen ions H^+ (actually hydronium ions, H_3O^+). Pure water contains hydrogen ions in concentration 1×10^{-7} moles per liter, and hydroxide ions, OH^- in the same concentration. These ions are formed by dissociation of water:



When a small amount of acid is added to pure water the concentration of hydrogen ion is increased. The concentration of hydroxide ion then decreases. Acidic solutions contain hydrogen ion in large concentration and hydroxide ion in very small concentration.

Instead of saying that the concentration of hydrogen ion in pure water is 1.0×10^{-7} M (moles per liter), we say that the *pH* of pure water is 7. In general, the *pH* of a solution is defined as the number $-\log[H^+]$, where $[H^+]$ denotes the concentration of hydrogen ion (in moles per liter) and \log is the base 10 logarithm. In other words,

$$[H^+] = 10^{-\text{pH}}.$$

The following table gives the approximate *pH* level of a few substances.

pH scale	Substances	acid/base
0		↑ increasing acidity
1	battery acid	
2.4	lemon juice	
3	vinegar, mayonnaise	
3.4	California Chardonnay	
4.5		
5.5	bread	
6	milk	
7		neutral
7.8	egg whites	↓ increasing alkalinity
8		
9	baking soda, sea water	
10	soap	
10.5	milk of magnesia	
11		
12		
12.5	ammonia	
13		
13.5	lye	
14		

We can now get back to the problem. From the nitrification reaction (nitr.) we see that for every mole of NH_4^+ that is nitrified to NO_3^- , two moles of H^+ are produced. Hence, if 10^{-4} moles of N per liter are nitrified each year, then 2×10^{-4} moles of H^+ per liter will also be produced each year. Let V denote the volume of the lake, in liters. The product

$$2 \times 10^{-4} \times V \text{ moles per year}$$

is the inflow of H^+ due to nitrification.

Suppose now that instead of nitrification the cause of acidity is the inflow of acidic water, with a *pH* of a , to be determined. This means that $[H^+] = 10^{-a}$ moles per liter of the inflow water. This inflow takes place at a rate $F_W = V/T$ (liters per year), where T is the residence time of water in the lake, assume to be 0.5 year. The inflow of H^+ thus happens at a rate of

$$V[H^+]/T = V \times 10^{-a}/0.5.$$

We wish to find a so that this value equals $2 \times 10^{-4} \times V$. Therefore

$$2 \times 10^{-4} V = V \times 10^{-a}/0.5$$

This shows that $a = 4$, that is, a *pH* of 4.

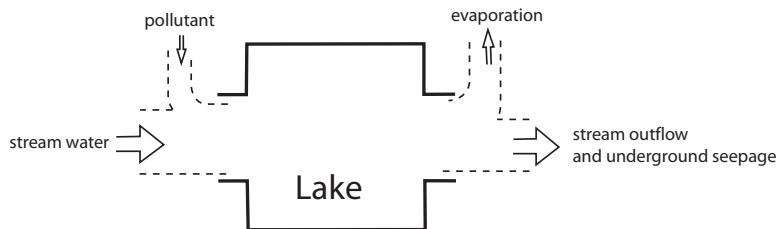
11.2.8 Pollution Buildup in a Lake

We have so far considered systems in steady state. If this condition is not present, then the stock, M , of a substance will grow or decrease in time at a rate equal to

$$\frac{dM}{dt} = F_{\text{in}} - F_{\text{out}}.$$

Problem 11.2.8. A lake has a volume of 10^6 cubic meters and a surface area of 6×10^4 square meters. Water flows into the lake at an average rate of 0.005 cubic meters per second. The amount of water that evaporates yearly from the lake is equivalent in volume to the lake's top meter of water. Initially, the lake water is pristine, but at a certain time a soluble, noncodistilling pollutant is discharged into the lake at a steady rate of 40 tonnes per year. Derive a formula for the concentration of pollutant in the lake as a function of time since the pollutant discharge began.

A *noncodistilling* pollutant is a substance that does not evaporate away with evaporating water. Therefore, evaporation of lake water is not an exit pathway for the pollutant. However, if the lake water flows out of the lake in an outlet stream or via underground seepage, that water outflow will remove pollutant.



The volume of the lake is assumed constant, so the rate of outflow stream and seepage must equal the difference between the rate of inflow and rate of water lost to evaporation. (We disregard the change in volume due to the pollutant. To get a sense of how much error is involved in this approximation, an amount of water of same weight as the pollutant added in a year, 40 tonnes, would occupy a volume of 40 cubic meters, which is less than 0.1% of the 60000 cubic meters of water that evaporates in a year.) So we have the following information (recall that 1 cubic meter of water weighs 1 metric ton):

$$\text{volume of lake} = 10^6 \text{ m}^3$$

$$\text{rate of evaporation} = 6 \times 10^4 \text{ m}^3/\text{yr.}$$

$$\text{inflow of water} = 0.005 \times (365 \times 24 \times 60 \times 60) = 1.6 \times 10^5 \text{ m}^3/\text{yr.}$$

$$\text{outflow stream and under ground seepage} = 1.6 \times 10^5 - 6 \times 10^4 = 10^5 \text{ m}^3/\text{yr.}$$

Let $x(t)$ represent the concentration of pollutant in the lake at time t as a fraction of weight. We set $t = 0$ as the time when pollutant started to be dumped in the lake. Thus $x(t) = M(t)/M_w$, where $M(t)$ is total amount of pollutant (in tonnes), M_w is the total amount of water (in tonnes), which is 10^6 tonnes, and $x(0) = 0$. The flows of pollutant

are

$$F_{\text{in}} = 40 \text{ tonnes per year}$$

$$F_{\text{out}} = \text{outflow of water by stream and seepage} \times \text{fraction of pollutant} = 10^6 \times x(t).$$

Therefore,

$$\frac{dx}{dt} = 4 \times 10^{-5} - 0.1x.$$

The solution to the initial value problem $\dot{x} = ax + b$, $x(0) = x_0$, was given in an earlier exercise. It is:

$$x(t) = \frac{b}{a}(e^{at} - 1) + x_0 e^{at}.$$

In the present case,

$$x(t) = 4.0 \times 10^{-4}(1 - e^{-0.1t}).$$

Note that, at equilibrium ($t \rightarrow \infty$) x approaches 400 parts per million.

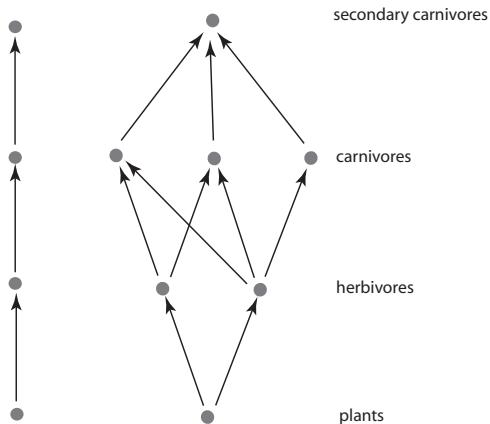
11.2.9 Biomagnification of Trace Substances

Problem 11.2.9. *How does biomagnification of a trace substance occur? Specifically, identify the critical ecological and chemical parameters determining bioconcentrations in a food chain. In terms of these parameters, derive a formula for the concentration of a trace substance in each link of a food chain.*

Imagine a young fish growing up in a lake and eating nothing but plankton. As the fish grows from, say, 10 g at birth to its average weight at death of 10^3 g, all of its newly acquired flesh and bone will be derived from the plankton it eats. To add on 990 g of tissue, it will have to eat far more than 990 g of plankton, because of excretory and metabolic losses. Excretory losses, in the sense used here, include the sloughing off of old tissue as it is replaced with new. The typical growing fish eats 10 g of plankton to grow by about 1 g of body weight. In the ecological literature this factor of 10% (the ratio of the weight it gains to the weight of food it eats) is called an *incorporation efficiency*. The remaining 90% of the food the fish eats is excreted or metabolized.

Suppose, now, that the plankton contains a trace substance, such as DDT or mercury. If a greater proportion of the trace substance than of the plankton is retained in the fish rather than excreted and metabolized, then the concentration of the trace substance in the animal will build up to a level greater than that in the plankton. Similarly, if a population of osprey prey upon the fish, they too may preferentially retain the trace substance in their food; over the lifetime of the osprey, the concentration of the substance can build up to an even greater level than that in the fish. The fraction of ingested trace substance retained by an organism is called the *retention factor*.

The next figure shows two food webs with four trophic levels (not counting the sun). The linear web is a food chain.



We would like to devise a mathematical model to study the magnification of trace substances along the various trophic levels of a food chain. The model should incorporate the following features.

- 1. Preferential Retention of the Substance in the Body.** In the extreme case, the rate of bioconcentration is greatest when all the trace substance an animal ingests is stored in body tissue and none is metabolized or excreted.
- 2. Fraction of Ingested Food Incorporated into New Tissue.** If an animal is very inefficient in building new tissue out of its food source, it must consume a lot of food to grow by any specified amount. That larger amount of ingested food is accompanied by a larger amount of trace substance. Thus, for a given retention factor, the lower the incorporation efficiency, the greater the rate of bioconcentration.
- 3. Ratio of Weight at Death to Weight at Birth.** For a given retention factor and incorporation efficiency, the more weight an animal puts on during its lifetime, compared to its weight at birth, the greater is the percentage increase in the concentration of a trace substance over the lifetime of the organism. Note that while this ratio, the *relative growth factor*, is sometimes correlated with the lifetime of the organism, it need not be. Fish generally don't live as long as humans, but their proportional weight gain is much larger. If an organism is fully grown well before death (like humans or birds, but not fish or trees), and if that organism lives many years in its fully grown state, then during these mature years its intake of the trace substance continues but its body weight does not change. Therefore, The longer the period in which the organism is fully grown, the greater the concentration of the trace substance in the organism at death. However, that effect is already described by the incorporation efficiency, which, if given as an average over the lifetime of the organism, will reflect a possible lack of growth during later years.
- 4. Location in the Food Chain.** The osprey bioconcentrates the trace substance from the fish it eats and, if other factors are equal, accumulates a higher concentration than that in the fish. The higher in a food chain an organism feeds, the greater is the concentration effect for that organism.

5. **Environmental Contamination.** The concentration of the trace substance in the plankton reflects that in the water. The contamination of soil and water initiates the food-chain effect and its amount is therefore an important determinant of the ultimate concentration in all organisms.

From this qualitative picture we would like to build a plausible mathematical model to determine the quantitative importance of the various factors enumerated above. Consider N populations, each in a steady state, whose feeding pattern is described by a linear food chain. Ignore immigration and emigration. Let X_1, \dots, X_N be the biomasses of the populations, where X_j eats X_{j-1} , for each $j \geq 2$. None of the N populations feed on X_N ; dead individuals from that population are decomposed by organisms not included among the N populations here.

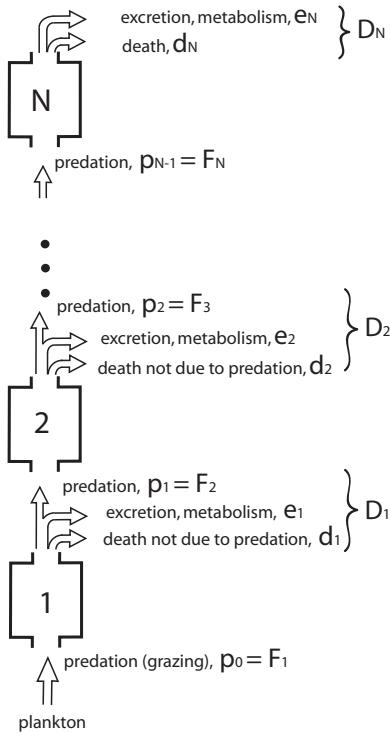
Assuming that D_i is the total rate at which biomass exits from the i th population. This total rate is the sum of metabolism plus excretion, e_i , predation, p_i , and other causes of death, d_i :

$$D_i = e_i + p_i + d_i. \quad (\text{eq. 1})$$

The total inflow rate is F_i , consisting entirely of ingested food. Note that birth is not an inflow; the process of birth adds no biomass to the population, but only divides the existing biomass into smaller pieces. The steady-state assumption is equivalent to

$$F_i = D_i \quad (\text{eq. 2})$$

for $i = 1, \dots, N$.



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All rate constants, D_i, e_i, p_i, d_i , and F_i are in units of biomass per unit time. The predation from level i is the input to level $i + 1$, and so

$$p_i = F_{i+1}. \quad (\text{eq. 3})$$

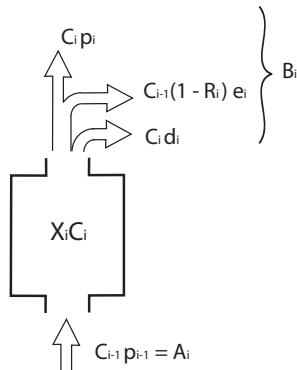
The rate at which ingested food is not metabolized or excreted is $p_i + d_i$, and therefore the incorporation efficiency, E_i , for each population is

$$E_i = \frac{p_i + d_i}{F_i}. \quad (\text{eq. 4})$$

At time $t = 0$, assume a trace substance is added to the environment (e.g., the water or soil in which population 1 grows) so that a constant environmental contamination, characterized by a concentration of C_0 , is maintained for all time thereafter. Denote the concentration of pollutant at time t in each population by $C_i(t)$. C_i has units of mass of trace substance per unit biomass. The amount of trace substance in the i th population at time t is $M_i(t) = X_i C_i(t)$.

Define A_i and B_i to be the inflow and outflow of the trace substance (in units of mass per unit time) to each population. The inflow rate, A_i , to the i th population is determined by the predation rate of i on $i - 1$ and by the concentration of trace substance in the $(i - 1)$ population, C_{i-1} . In particular,

$$A_i = p_{i-1} C_{i-1}. \quad (\text{eq. 5})$$



The rate of loss of the trace substance from the i th population can be expressed as a sum of two terms. The first equals the concentration, C_i , times the rate of outflow (by predation or other forms of death) of trace-substance-containing biomass from that population. The second is proportional to C_{i-1} times the metabolism-plus-excretion rate, with proportionality constant equal to, or a fraction less than, one. (Note that C_{i-1} rather than C_i enters into the loss rate here because excrement has a concentration of trace substance governed by that of the food rather than that of the body as a whole.) That fraction is one minus a retention factor, R_i , where R_i is the fraction of ingested trace substance retained in the body. In equation form, the outflow rate is

$$B_i + C_i(p_i + d_i) + C_{i-1}(1 - R_i)e_i. \quad (\text{eq. 6})$$

Equation 6 states that predation and other types of death ($p_i + d_i$) lead to a loss of trace substance from the population equal to 100% of whatever is in the bodies of dying organisms; it also states that metabolism and excretion lead to the loss of only a fraction, $(1 - R_i)$, where R_i is the retention factor for the i th population.

Although the X_i (as well as e_i , d_i , p_i) are assumed constant, note that we do not yet suppose that the concentrations of the trace substance are at steady state. So for now those concentrations are possibly non-constant functions of time, $C_i(t)$. (We suppose that $C_0(t)$ is a known function, from which the other concentrations are to be determined.)

From equations (1) through (5) we obtain, for $i = 1, 2, \dots, N$,

$$A_i(t) = C_{i-1}(t)p_{i-1} \quad (\text{eq. 7})$$

$$B_i(t) = [C_i(t)E_i + C_{i-1}(t)(1 + R_i)(1 - E_i)] p_{i-1}. \quad (\text{eq. 8})$$

The rate of accumulation of the trace substance in population i , \dot{M}_i , is $A_i - B_i$. Thus we have for C_i the differential equation:

$$X_i \dot{C}_i(t) = C_{i-1}(t)p_{i-1} - [C_i(t)E_i + C_{i-1}(t)(1 + R_i)(1 - E_i)] p_{i-1}. \quad (\text{eq. 9.i})$$

Together, equations 9.1, ..., 9.N form a system of linear differential equations for C_1, \dots, C_N . We will see how to solve such systems later. For the moment let us finally assume that these concentrations are also at steady state, hence constant. In this case we have $A_i = B_i$ for each i . Using equations 7 and 8, we obtain after a little algebra that

$$C_i = \left[1 + R_i \frac{(1 - E_i)}{E_i} \right] C_{i-1}. \quad (\text{eq. 10})$$

Since E_i is between 0 and 1, the quantity C_i/C_{i-1} is greater than 1. Therefore, the concentration at trophic level i is greater than the concentration at level C_{i-1} for each i . Iterating equation (10) gives

$$C_i = \left[1 + R_i \frac{(1 - E_i)}{E_i} \right] \dots \left[1 + R_2 \frac{(1 - E_2)}{E_2} \right] \left[1 + R_1 \frac{(1 - E_1)}{E_1} \right] C_0. \quad (\text{eq. 11})$$

As a very crude numerical estimate, suppose that the retention rate R_i and the incorporation efficiency E_i are both 0.5. Then $C_i/C_{i-1} = 1.5$. This means that the concentration increases by 50% from population $i - 1$ to population i .

11.2.10 First Order Linear ODEs

In the previous problem we encountered a system of differential equations of the following form, where x_1, \dots, x_N are unknown functions of t , $f(t)$ is a given (known) function, and a_i, b_i are constants:

$$\begin{aligned} \dot{x}_1 &= a_1 x_1 + f(t) \\ \dot{x}_2 &= a_2 x_2 + b_1 x_1 \\ \dot{x}_3 &= a_3 x_3 + b_2 x_2 \\ &\dots \\ \dot{x}_N &= a_N x_N + b_{N-1} x_{N-1}. \end{aligned}$$

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If we know how to solve a differential equation of the form $\dot{x} = ax + f(t)$ we can solve this system inductively: first solve the first equation, then substitute the solution, x_1 , into the second and solve for x_2 , etc.

Let us consider the more general equation with specified initial value (for initial time t_0)

$$\begin{aligned}\dot{x} &= a(t)x + f(t) \\ x(t_0) &= x_0,\end{aligned}\tag{eq. 1}$$

where $a(t)$ is also allowed to depend on t .

The key remark for solving this initial value problems is that the function of t defined by

$$I(t) = \exp\left(-\int_{t_0}^t a(s)ds\right)$$

satisfies the equation

$$\dot{I} = -a(t)I(t),$$

as you can show by an application of the chain rule. We call I the *integrating factor* for the differential equation.

To solve the initial value problem, first multiply both sides of the equation $\dot{x} - a(t)x = f(t)$ by $I(t)$ and observe that

$$\begin{aligned}fI &= \dot{x}I - x a I \\ &= \dot{x}I + x \dot{I} \\ &= \frac{d}{dt}(xI).\end{aligned}$$

Note that, by the fundamental theorem of calculus and the fact that $I(t_0) = 1$, we have

$$\begin{aligned}\int_{t_0}^t (x(s)I(s))' ds &= x(t)I(t) - x(t_0)I(t_0) \\ &= x(t)I(t) - x(t_0).\end{aligned}$$

Therefore, integrating both sides of the equation $fI = (xI)'$ from t_0 to t gives the solution

$$x(t) = I(t)^{-1} \left(x(t_0) + \int_{t_0}^t f(s)I(s)ds \right).$$

Suppose that $t_0 = 0$ and that a is a constant. Then

$$I(t) = e^{-at}$$

and the above general solution reduces to

$$x(t) = x(0)e^{at} + e^{at} \int_0^t e^{-sa} f(s)ds.$$

Exercise 11.2.2. Use the above general expression to solve the initial value problem:

$$\begin{aligned}\dot{x} &= cx + a + b_1 e^{-k_1 t} + \cdots + b_n e^{-k_n t} \\ x(0) &= A,\end{aligned}$$

where a, b_i, c, k_i and A are constants, for $i = 1, \dots, n$. Show that the solution is

$$x(t) = A + \frac{a}{c} (1 - e^{-ct}) + \sum_{i=1}^n \frac{b_i}{c+k_i} (1 - e^{-(c+k_i)t}).$$

Exercise 11.2.3. Solve the system of differential equations

$$\begin{aligned}\dot{x}_1 &= a_1 x_1 + b_0; \\ \dot{x}_2 &= a_2 x_2 + b_1 x_1.\end{aligned}$$

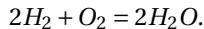
The initial conditions are $x_1(0) = x_2(0) = 0$.

11.3 Stoichiometry and Linear Algebra

A very nice reference for the material of this section is *Elementary Chemical Reactor Analysis*, by Rutherford Aris. If occasionally a phrase below sounds especially well crafted and clear, it is likely that it was lifted straight out of that excellent book. (The more rigid and formalistic paragraphs are probably my own, though.)

The strict meaning of the word “stoichiometry” is measurement of the elements, but it is commonly used to refer to all sorts of calculations regarding the composition of a chemical system. Stoichiometry is essentially the bookkeeping of the material components of the chemical system.

Changes in the composition of chemical system are subject to certain restrictions. To see the nature of these restrictions let us consider again the reaction



An equation such as this can have two meanings. It may be a kinetic description of the reaction and imply that two molecules of hydrogen combine with one of oxygen to form two molecules of water. In this particular case, as suggested in an earlier discussion, the equation is not true as a kinetic description. On the other hand, it may be a stoichiometric description of the reaction, and the equation will then mean that the numbers of hydrogen and oxygen molecules combining to form water are in the ratio 2 : 1. The important restriction in this regard is that the total number of atoms of each type be the same on both sides of the equation. In other words, atoms are not created or destroyed.

It is clear that if a reaction expression is true in a kinetic sense it is also true in a stoichiometric sense, but the converse statement is false. For the moment, the kinetic meaning of a chemical equation will only concern us in passing.

From a chemical engineer’s point of view, the important thing about a reaction like the one above is that three chemical species (here hydrogen, oxygen, and water) are observed to react in certain proportions. If the engineer can account for the rate at which this takes place in terms of concentrations of the observed chemical species, he has all he needs to know about the reactions so far as making numerical predictions about the outcome of the process is concerned. If a chemical equation cannot account for the detailed kinetics of the process, it is the chemist’s job to provide a kinetic description of what is taking place, and to devise a *mechanism* for a reaction. This amounts to looking for elementary reaction steps and their reaction rates. In doing so the chemist may be

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led to hypothesize certain intermediate species which are present in only trace quantities.

In order to describe the stoichiometric restrictions in general (whether or not it corresponds to a true kinetic description of a process), we first need to set some convenient notation. We start with a set of s chemical species and denote them X_1, X_2, \dots, X_l . Thus if $X_1 = H_2O$, $X_2 = H_2$, and $X_3 = O_2$, the reaction shown above would be $2X_2 + X_3 = 2X_1$. It is convenient to write all the chemical species on one side of the equation and to give a positive sign to the species which are regarded as the products of the reaction:

$$2X_1 - 2X_2 - X_3 = 0.$$

This convention should not be given undue importance, but it is usually possible to observe it, at least for the main reaction.

The numbers 2, -2 and -1 in the previous equation are called the *stoichiometric coefficients*. A natural way to write the general equation is

$$\sum_{i=1}^l \alpha_i X_i = 0.$$

Thus X_i denotes the i th chemical species and α_i is its stoichiometric coefficient in the given reaction. Subject to the above convention it is convenient to call the species with positive stoichiometric coefficients the *products* of the reaction and those with negative coefficients the *reactants*. The products are formed from the reactants by the *forward reaction*, while the reverse reaction converting the products into the reactants will be called the *back reaction*.

Both forward and back reactions are usually going on simultaneously and equilibrium is reached when they go at equal and opposite rates. It is sometimes useful to include an inert chemical species in the set of X_i , and since it does not take part in the reaction it is given stoichiometric coefficient 0. An *entire* reaction is thus one whose behavior can be fully described in terms of the concentrations of the species X_1, \dots, X_l .

The important thing about the stoichiometric coefficient of a reaction is their ratio rather than their absolute magnitude. Thus the reaction for the formation of water could just as well be written $H_2O - H_2 - \frac{1}{2}O_2 = 0$. We can say therefore that the stoichiometric coefficients of a reaction are given up to a constant multiplier, for the equations $\sum \lambda \alpha_i X_i = 0$ has exactly the same meaning as $\sum \alpha_i X_i = 0$.

A remark about notation: although expressions such as $2H_2 + O_2 = 2H_2O$, which represent reactions as equations, are widely used in the chemistry literature, it will be for us a possible source of confusion and will be often (but not always) avoided. A reaction will more often be expressed by the “harpoon” notation, $2H_2 + O_2 \rightarrow 2H_2O$, or by $2H_2 + O_2 \rightleftharpoons 2H_2O$, when the direction of reaction is not of immediate concern or when we need to refer explicitly to the forward and back reactions. Mathematically, all that really matters to characterize a reaction is the expression $2H_2O - 2H_2 - O_2$, which we regard as a vector. This vector is sometimes described by its coordinates, (2, -2, -1). Viewing the reaction expression as a vector, the equation $2H_2 + O_2 = 2H_2O$ is simply a wrong identity.

One feature that distinguishes chemical processes from the more general types mentioned earlier is that the substances undergoing a chemical transformation are composed of more elementary units, or ‘atoms,’ and the quantities of individual atoms must be conserved over the course of the transformation. We wish now to formalize this idea. The stoichiometric description of a process involves:

1. a list of participating substances, or *molecules*, (or species) of the process:

$$X_1, X_2, \dots, X_l;$$

2. a list of elements, or *atoms*:

$$E_1, E_2, \dots, E_N.$$

The atomic composition of substance X_j can be written as

$$X_j = E_1^{a_{1j}} E_2^{a_{2j}} \cdots E_N^{a_{Nj}},$$

where the numbers a_{ij} are non-negative (possibly 0) integers.

Example. Suppose that the process we wish to study is the partial combustion of methane. In standard chemical notation this is described as follows: CH_4 (methane) combines with O_2 (oxygen), producing CO (carbon monoxide), H_2O (water), and H_2 (hydrogen). In the above notation, there are 6 molecules:

$$X_1 = CH_4, X_2 = O_2, X_3 = CO_2, X_4 = CO, X_5 = H_2O, X_6 = H_2;$$

These are composed of 3 different types of atoms:

$$E_1 = C, E_2 = O, E_3 = H.$$

In this notation, the methane molecule for example is $E_1^1 E_2^0 E_3^4$, which we often simplify as $E_1 E_3^4$.

By a *mixture* we will mean a linear combinations of the substances with non-negative coefficients:

$$x_1 X_1 + x_2 X_2 + \cdots + x_l X_l.$$

How should the expression $x_1 X_1 + \cdots + x_l X_l$ be interpreted? The interpretation may vary somewhat with the context, but we will generally think of it as describing the amount or concentration of each substance inside some region in space, which may be a closed or open vessel, (a test tube, say) or simply a small volume in space delimited by an imaginary boundary surface, inside of which molecules will be at close enough distance to interact. In this case the coefficients x_i assume integer values. So, the amount of each species X_i is specified by the coefficient x_i . In all cases, whether the x_i are integer quantities or not, we usually write them in number of moles rather than by their mass.

It is important to note that when we write an expression such as $3.7CH_4 + 2.5O_2 + 1.2H_2$, the symbols CH_4 , O_2 and H_2 (methane, oxygen and hydrogen) do not stand for numerical quantities. We treat these symbols the same way we treat expressions like $xi + yj + zk$ in analytic geometry. Thus the symbols for molecules and atoms will be regarded as unit vectors in some coordinate space. If there are l molecular species, then the coordinate space is the l -dimensional space \mathbb{R}^l . This is, by definition, the set of all l -tuples of real numbers. The notations (x_1, \dots, x_l) and $x_1 X_1 + \cdots + x_l X_l$ represent the same point. Therefore X_i corresponds to the basis vector:

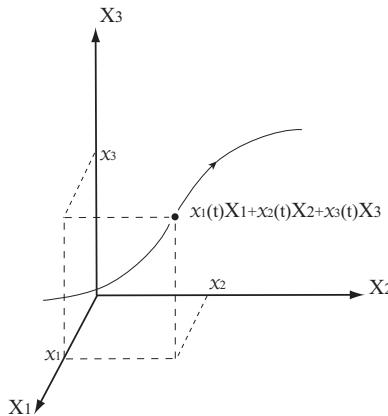
$$X_i = (0, \dots, 0, 1, 0, \dots, 0)$$

having 1 at the i -th position and 0 everywhere else.

During a process, the composition of a mixture may change due to chemical reactions or transport across the boundary of the vessel. So the mixture coefficients are generally functions of time, $x_i(t)$. The time evolution of the system thus corresponds to a parametric curve (parametrized by time, t) in the space of mixtures:

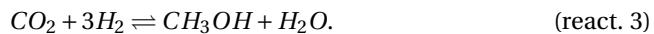
$$t \rightarrow x_1(t)X_1 + x_2(t)X_2 + \cdots + x_l(t)X_l.$$

This is shown in the next figure for a system involving three species.



11.3.1 Linear Independence

Consider the reactions:



Reaction 3 does not tell us any more about the system than is contained in the two other reactions. These reactions are not independent of each other, as the third is the sum of the first two. The precise mathematical description of dependence involves the reaction vectors. Thus the vectors

$$\mathbf{R}_1 = CH_3OH - CO - 2H_2,$$

$$\mathbf{R}_2 = H_2O + CO - CO_2 - H_2,$$

$$\mathbf{R}_3 = CH_3OH + H_2O - CO_2 - 3H_2,$$

are *linearly dependent* since

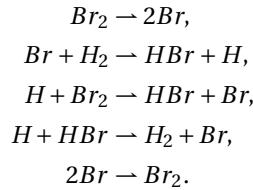
$$\mathbf{R}_3 = \mathbf{R}_1 + \mathbf{R}_2.$$

The general definition of linear independence is this: let $\mathbf{R}_1, \dots, \mathbf{R}_m$ be a set of vectors in \mathbb{R}^l . Then they are said to be linearly independent if the expression

$$c_1\mathbf{R}_1 + \cdots + c_m\mathbf{R}_m = 0$$

can only hold if the numbers c_1, \dots, c_m are all zero.

As another example, consider the set of reactions that is said to be the kinetic description of the formation of hydrogen bromide. These are:



How many independent reactions are there in this set? Clearly the first and fifth are dependent (one reaction vector is the negative of the other). The same is true for the second and fourth. Therefore there cannot be more than 3 independent reactions. One way to check that there are exactly three is to use the method of row reduction. We first set the basis vectors:

$$X_1 = Br_2, X_2 = Br, X_3 = H_2, X_4 = H, X_5 = HBr.$$

Then the reaction vectors are:

$$\begin{aligned} \mathbf{R}_1 &= -X_1 + 2X_2, \\ \mathbf{R}_2 &= -X_2 - X_3 + X_4 + X_5, \\ \mathbf{R}_3 &= -X_1 + X_2 - X_4 + X_5, \\ \mathbf{R}_4 &= X_2 + X_3 - X_4 - X_5, \\ \mathbf{R}_5 &= X_1 - 2X_2. \end{aligned}$$

It is convenient to detach the stoichiometric coefficients and write them in matrix form with the coefficients of each reaction vector as a row:

$$\begin{matrix} -1 & 2 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 \\ -1 & 1 & 0 & -1 & 1 \\ 0 & 1 & 1 & -1 & -1 \\ 1 & -2 & 0 & 0 & 0 \end{matrix}$$

If we permute the rows, multiply a row by a nonzero number, or add to a row a linear combination of the other rows, the number of linearly independent equations is not changed. We can use these operations to simplify the above matrix until it takes a form that makes the answer (the number of independent equations) clear.

By replacing (1) the fifth row with the sum of the fifth and first rows, and (2) the fourth row with the sum of the fourth and second rows, we obtain:

$$\begin{matrix} -1 & 2 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 \\ -1 & 1 & 0 & -1 & 1 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{matrix}$$

We now (3) replace the first row with the negative of itself, and (4) replace the third row with the sum of the third and the new first row:

$$\begin{array}{ccccc} 1 & -2 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 \\ 0 & -1 & 0 & -1 & 1 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{array}$$

Next, we (5) replace the second row with its negative, and (6) replace the third row with the sum of the new second with the third:

$$\begin{array}{ccccc} 1 & -2 & 0 & 0 & 0 \\ 0 & 1 & 1 & -1 & -1 \\ 0 & 0 & 1 & -2 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{array}$$

Ignoring the two trivial last rows, we obtained a matrix which has ones on the diagonal and zeros below the diagonal. Going back to the respective vectors:

$$\begin{aligned} \mathbf{S}_1 &= X_1 - 2X_2 \\ \mathbf{S}_2 &= X_2 + X_3 - X_4 - X_5 \\ \mathbf{S}_3 &= X_3 - 2X_4. \end{aligned}$$

Exercise 11.3.1. Show that the vectors $\mathbf{S}_1, \mathbf{S}_2$ and \mathbf{S}_3 are linearly independent by using the definition. That is, show that the equation

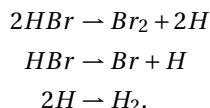
$$c_1 \mathbf{S}_1 + c_2 \mathbf{S}_2 + c_3 \mathbf{S}_3 = 0$$

only holds if $c_1 = c_2 = c_3 = 0$.

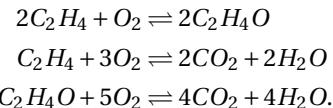
We could have simplified the last matrix further by subtracting the third row from the second and making the result the new second row, and then replacing the first row with the sum of itself plus twice the (new) second row. The result is:

$$\begin{array}{ccccc} 1 & 0 & 0 & 2 & -2 \\ 0 & 1 & 0 & 1 & -1 \\ 0 & 0 & 1 & -2 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{array}$$

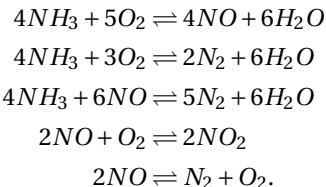
The first three rows correspond, respectively, to the following three reactions (now obviously independent since no two of them contain all the substances involved in the remaining reaction):



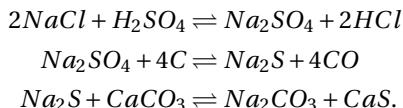
Exercise 11.3.2. How many of the following 6 reactions are independent?



Exercise 11.3.3. How many of the following 12 reactions are independent?



Exercise 11.3.4. How many of the following 6 reactions are independent?



11.3.2 Dimension

Given a set of vectors $\mathbf{R}_1, \dots, \mathbf{R}_m$ in \mathbb{R}^l , the collection of all the other vectors that can be obtained from these by linear combinations constitutes a linear subspace of \mathbb{R}^l . The number of linearly independent vectors among the \mathbf{R}_i is the *dimension* of that subspace.

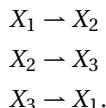
In the example given above, $\mathbf{R}_1, \dots, \mathbf{R}_5$ span a 3-dimensional subspace of \mathbb{R}^5 . This is the same subspace spanned by the vectors $\mathbf{S}_1, \mathbf{S}_2, \mathbf{S}_3$ obtained from the \mathbf{R}_i by using row reduction.

We sometimes refer to this dimension as the *rank* of the stoichiometric matrix (the matrix of the stoichiometric coefficients) derived from the vectors \mathbf{R}_i .

If a chemical process involves l different substances which are known to be involved in k reactions, $\mathbf{R}_1, \dots, \mathbf{R}_k$, then we will call the linear subspace of \mathbb{R}^l spanned by these reactions the *reaction space* of the process.

Exercise 11.3.5. Calculate the dimension of the reaction space for the reaction mechanisms defined in the previous three exercises.

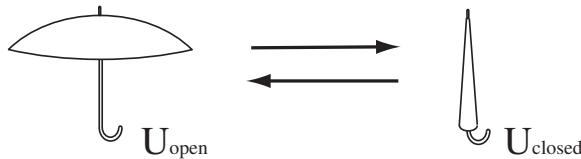
Exercise 11.3.6. Find the dimension of the reaction space involving substances X_1, X_2, X_3 , for the system of (isomerization) reactions:



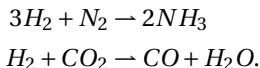
An isomerization process is illustrated by the pair of reactions $U_{\text{open}} \rightleftharpoons U_{\text{closed}}$ pictured below. Notice that the two molecules, $U_{\text{open}}, U_{\text{closed}}$, have the same mass and atomic composition. Nevertheless these are very different molecules. A vessel filled with one

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mole of molecule U_{open} would for example occupy a much greater volume than one mole of U_{closed} .



Exercise 11.3.7. Suppose that a chemical process involves the two reactions



A mixture of 68.4% H_2 , 22.6% N_2 , and 9% CO_2 reacts until 15% NH_3 and 5% H_2O are formed. (These are mole percentages.) What are then the percentages of H_2 and N_2 ?

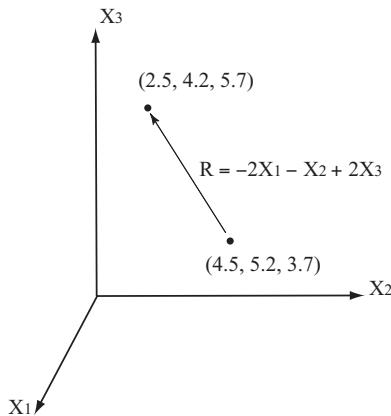
11.3.3 Degree of Advancement of a Reaction

Let $\mathbf{x}_{\text{initial}} \in \mathbb{R}^l$ be a point with non-negative coordinates representing an initial composition (in moles) of a mixture of l substances. Suppose that the mixture undergoes a reaction represented by the vector \mathbf{R} . Then at any given moment the new mixture composition, \mathbf{x}_{new} , must differ from $\mathbf{x}_{\text{initial}}$ by a multiple of \mathbf{R} , that is

$$\mathbf{x}_{\text{new}} = \mathbf{x}_{\text{initial}} + s\mathbf{R},$$

where s is some (possibly negative) number. The number s is called the *molar extent*, or *degree of advancement* of the reaction.

Say, for example, that the reaction is $2X_1 + X_2 \rightarrow 2X_3$, where $X_1 = H_2$, $X_2 = O_2$, and $X_3 = H_2O$. Let the initial composition of a mixture of oxygen (gas), hydrogen (gas), and water (liquid) be $\mathbf{x}_{\text{initial}} = (4.5, 5.2, 3.7)$; that is, the mixture contains 4.5 moles of hydrogen, 5.2 of oxygen, and 3.7 of water. Suppose that the reaction proceeds to the extent that 1 mole of oxygen is consumed. Then of necessity 2 moles of hydrogen will be consumed and 2 of water will be produced. This means that $\mathbf{x}_{\text{new}} = (4.5, 5.2, 3.7) + (-2, -1, 2) = (2.5, 4.2, 5.7)$. In this case, the molar extent of the reaction is 1.



If at a given moment the amount of hydrogen is, say, 6.1 moles, then of necessity the composition of the other substances, X_2, X_3 , can be obtained from the equation

$$(6.1, x_2, x_3) = (4.5, 5.2, 3.7) + s(-2, -1, 2),$$

for some s . From the amount of hydrogen we obtain $6.1 = 4.5 - 2s$, that is, $s = -0.8$. Therefore the reaction went in reverse, by the extent 0.8 moles. The new amounts of oxygen and water are $x_2 = 5.2 - 0.8 \times (-1) = 6$ and $x_3 = 3.7 - 0.8 \times 2 = 2.1$ moles, respectively.

We need not limit ourselves to only one reaction. If there are k reactions involved, $\mathbf{R}_1, \dots, \mathbf{R}_k$, we can introduce k advancement parameters, s_1, \dots, s_k , and represent any new composition as

$$\mathbf{x}_{\text{new}} = \mathbf{x}_{\text{initial}} + s_1 \mathbf{R}_1 + \dots + s_k \mathbf{R}_k.$$

Notice, however, that unless $\mathbf{R}_1, \dots, \mathbf{R}_k$ are independent reactions, the numbers s_1, \dots, s_k are not uniquely determined from the initial and new values of the mixture composition.

11.3.4 Atomic Composition

A chemical process that takes place in a closed reactor (that is, without exchange of substances between the reactor and the environment) is constrained by the property that the molar amount (or, equivalently, the number of atoms) of each participating atomic species does not change during the process. If you go back to any example of a chemical reaction given so far in these notes, you will see that the number of atoms of each element is the same on both the left and the right sides of a reaction $\alpha_1 X_1 + \dots + \alpha_l X_l \rightarrow \beta_1 X_1 + \dots + \beta_l X_l$. We explain now one way in which this remark can be used in a systematic way to sharpen our characterization of the set of points in \mathbb{R}^l that are accessible to the evolving process.

Suppose that there are l types of molecules and N types of atoms. We have introduced above the space of mixtures \mathbb{R}^l . If we wish to regard only the amounts of each kind of atom in a mixture, it is natural to consider as well the space \mathbb{R}^N , with basis E_1, \dots, E_N . Define the *atomic composition* function $\mathcal{E} : \mathbb{R}^l \rightarrow \mathbb{R}^N$ as follows: on each molecule, $X_j = E_1^{a_{1j}} E_2^{a_{2j}} \cdots E_N^{a_{Nj}}$,

$$\mathcal{E}(X_j) = a_{1j} E_1 + a_{2j} E_2 + \dots + a_{Nj} E_N.$$

We extend this definition to an arbitrary mixture by linearity. This means:

$$\mathcal{E}(x_1 X_1 + \dots + x_l X_l) = x_1 \mathcal{E}(X_1) + x_2 \mathcal{E}(X_2) + \dots + x_l \mathcal{E}(X_l).$$

Thus defined, \mathcal{E} is a linear map from \mathbb{R}^l to \mathbb{R}^N . If we represent points in \mathbb{R}^l and \mathbb{R}^N as column vectors, \mathcal{E} takes the matrix form

$$\mathcal{E}(X_j) = \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1j} & \cdots & a_{1l} \\ a_{21} & a_{22} & \cdots & a_{2j} & \cdots & a_{2l} \\ \vdots & \vdots & \cdots & \vdots & \cdots & \vdots \\ a_{N1} & a_{N2} & \cdots & a_{Nj} & \cdots & a_{Nl} \end{pmatrix} \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix} = \begin{pmatrix} a_{1j} \\ a_{2j} \\ \vdots \\ a_{Nj} \end{pmatrix} = a_{1j} E_1 + \dots + a_{Nj} E_N.$$

We can now express the idea of conservation of molar amounts of atomic species in the following way.

Principle 11.3.1 (Atomic Balance). *In a closed system, any changes in the composition of a mixture should not alter its atomic composition. In other words, if $A, B \in \mathbb{R}^l$ are the vectors representing the mixture composition at two different moments, then $\mathcal{E}(A) = \mathcal{E}(B)$. Equivalently, reaction vectors are contained in the kernel of the linear map \mathcal{E} . (I.e., the reaction space is contained in the stoichiometric space.)*

This means that if at a given moment in time the mixture has composition specified by the vector $A_0 = (x_1, \dots, x_l)$, then no matter what chemical transformations take place, as long as we are dealing with a closed system, the curve described above must remain inside the set

$$\{A \in \mathbb{R}^l \mid \mathcal{E}(A) = A_0\}.$$

We call this set the *stoichiometric space* through A_0 .

Example. Suppose that a closed system contains a mixture of three substances (gases): $X_1 = CO_2$, $X_2 = CO$, and $X_3 = O_2$. There are only two types of atoms: $E_1 = C$ and $E_2 = O$. Thus the atomic composition map $\mathcal{E} : \mathbb{R}^3 \rightarrow \mathbb{R}^2$ is obtained as follows, where we use that $\mathcal{E}(CO_2) = C + 2O$, $\mathcal{E}(CO) = C + O$, and $\mathcal{E}(O_2) = 2O$:

$$\begin{aligned}\mathcal{E}(x_1 X_1 + x_2 X_2 + x_3 X_3) &= x_1 \mathcal{E}(X_1) + x_2 \mathcal{E}(X_2) + x_3 \mathcal{E}(X_3) \\ &= x_1(E_1 + 2E_2) + x_2(E_1 + E_2) + x_3(2E_2) \\ &= (x_1 + x_2)E_1 + (2x_1 + x_2 + 2x_3)E_2.\end{aligned}$$

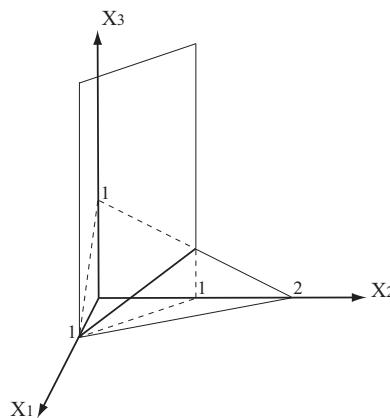
In matrix form,

$$\mathcal{E} = \begin{pmatrix} 1 & 1 & 0 \\ 2 & 1 & 2 \end{pmatrix}.$$

If the initial mixture contains an amount a_1 of atoms of type E_1 , and a_2 of type E_2 , then the atomic balance principle says that the composition of the mixture must remain in the space defined by the two equations:

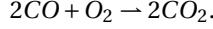
$$\begin{aligned}x_1 + x_2 &= a_1 \\ 2x_1 + x_2 + 2x_3 &= a_2.\end{aligned}$$

This system represents the intersection of two planes in \mathbb{R}^3 . Let us say that $a_1 = 1$ and $a_2 = 2$ (in moles, say). Then you can check that the planes and line of intersection are as in the next figure.



Therefore, any chemical process involving only the substances CO_2 , CO and O_2 with the amounts of C and O specified is described by a motion along this line of intersection. The motion won't be a simple uniform translation, of course. The precise function of time (parametrization) of the curve that describes it will depend on the reaction mechanism governing the process, and this mechanism has not been specified yet.

Exercise 11.3.8. Show that, up to a scalar multiple (possibly negative) the only possible reaction for this example is given by



Example. For a somewhat more complicated example consider the following substances, which are involved in the process of partial combustion of methane (CH_4):

$$X_1 = CH_4, X_2 = O_2, X_3 = H_2O, X_4 = CO, X_5 = H_2.$$

There are three different types of atoms:

$$E_1 = C, E_2 = H, E_3 = O.$$

Thus the atomic composition map has domain \mathbb{R}^5 and target space \mathbb{R}^3 . We expect the dimension of the stoichiometric space to be $5 - 3 = 2$. To see if this is indeed the case, we first need to determine \mathcal{E} .

For this example, we have:

$$\begin{aligned}\mathcal{E}(X_1) &= E_1 + 4E_2 \\ \mathcal{E}(X_2) &= 2E_3 \\ \mathcal{E}(X_3) &= 2E_2 + E_3 \\ \mathcal{E}(X_4) &= E_1 + E_3 \\ \mathcal{E}(X_5) &= 2E_2.\end{aligned}$$

Therefore,

$$\begin{aligned}\mathcal{E}(x_1 X_1 + \dots + x_5 X_5) &= x_1 \mathcal{E}(X_1) + \dots + x_5 \mathcal{E}(X_5) \\ &= x_1(E_1 + 4E_2) + x_2(2E_3) + x_3(2E_2 + E_3) + x_4(E_1 + E_3) + x_5(2E_2) \\ &= (x_1 + x_4)E_1 + (4x_1 + 2x_3 + 2x_5)E_2 + (2x_2 + x_3 + x_4)E_3.\end{aligned}$$

In matrix form,

$$\mathcal{E} = \begin{pmatrix} 1 & 0 & 0 & 1 & 0 \\ 4 & 0 & 2 & 0 & 2 \\ 0 & 2 & 1 & 1 & 0 \end{pmatrix}.$$

Denoting by a_1, a_2, a_3 the amounts of E_1, E_2, E_3 (in moles), we obtain the linear system

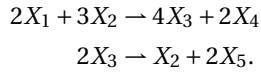
$$\begin{aligned}x_1 + x_4 &= a_1 \\ 4x_1 + 2x_3 + 2x_5 &= a_2 \\ 2x_2 + x_3 + x_4 &= a_3.\end{aligned}$$

These are 3 linear equations in 5 unknowns, and we should expect it to describe a 2-dimensional subspace of \mathbb{R}^5 . To obtain a parametric representation of this plane, we can solve for x_1, x_2, x_3 in terms of the a_i and x_4, x_5 . The result is:

$$\begin{aligned}x_1 &= a_1 - x_4 \\x_2 &= \frac{1}{4}(4a_1 - a_2 + 2a_3) - \frac{3}{2}x_4 + \frac{1}{2}x_5 \\x_3 &= \frac{1}{2}(a_2 - 4a_1) + 2x_4 - x_5.\end{aligned}$$

The stoichiometric plane can thus be regarded as the (x_4, x_5) -plane.

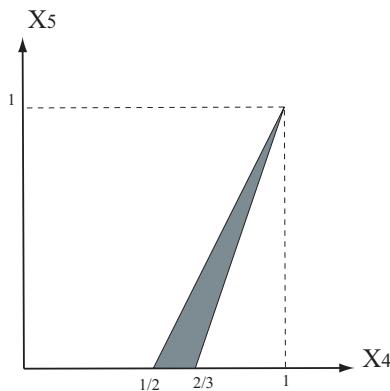
Exercise 11.3.9. Show that any reaction involving X_1, \dots, X_5 as in the above example is a linear combination of



We haven't taken into account the requirement that the x_i be non-negative. Let us see what subset of the stoichiometric plane these conditions give if we have $a_1 = 1$, $a_2 = 2$, $a_3 = 1$. From the inequalities $x_i \geq 0$, $i = 1, 2, \dots, 5$, we get the following system of inequalities for x_4, x_5 :

$$\begin{aligned}1 - x_4 &\geq 0 \\2 - 3x_4 + x_5 &\geq 0 \\-1 + 2x_4 - x_5 &\geq 0 \\x_4 &\geq 0 \\x_5 &\geq 0.\end{aligned}$$

Exercise 11.3.10. Show that the solution set to this system of inequalities is the triangular region given in the figure below.



11.3.5 Mass Balance

We have so far specified quantities of substances and elements in moles, but we might also want to consider their masses. Suppose that the various elements E_i have masses m_i (say, in grams per mole). Therefore the total mass of a mixture having atomic composition $a_1 E_1 + \dots + a_N E_N$ is $a_1 m_1 + \dots + a_N m_N$. Let us introduce a linear function $\mathcal{M} : \mathbb{R}^N \rightarrow \mathbb{R}$ by

$$\mathcal{M}(a_1 E_1 + \dots + a_N E_N) = a_1 m_1 + \dots + a_N m_N.$$

Then the mass of a mixture $K = x_1 X_1 + \dots + x_l X_l$ is the value of \mathcal{M} for the atomic composition vector $\mathcal{E}(K)$. In other words, we obtain the mass of K by evaluating K on the composition function $\mathcal{M} \circ \mathcal{E}$. In particular, if $\mathcal{E}(K(t))$ remains constant as the mixture $K(t)$ changes in time (as it does for a closed system by the principle of atomic balance), then the total mass $\mathcal{M}(\mathcal{E}(K(t)))$ also remains constant in t .

11.4 Reaction Mechanisms

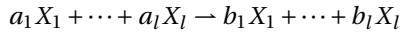
We have so far used reaction equations to indicate changes in the composition of mixtures of substances without being concerned whether the equation referred to some basic physical process involving binding and dissociation of individual molecules, or simply a description of the overall change in the mixture composition. The overall reaction may be the result of a collection of simpler and more fundamental processes. These processes are represented by the elementary reaction steps and their reaction rates. Put together, these reaction steps and rates specify a particular reaction mechanism for the process, which can then be used to determine the process's time evolution.

This section explains these things in more detail.

11.4.1 Elementary Reaction Steps

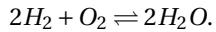
Before being more specific, let us stop for a moment to consider on an intuitive level what we would like to mean by the idea of an elementary reaction of a reaction mechanism.

Let a general reaction, involving substances, or molecules, X_1, \dots, X_l , be given by



where the coefficients a_i, b_i are non-negative integers. We call the number $a_1 + \dots + a_l$ the *length* of the reaction. The reaction will be said to be of first order, second order, etc, if its length is less than or equal to 1, 2, etc.

Now, what should we mean by a ‘reaction mechanism’? Consider the overall reaction of oxidation of hydrogen:

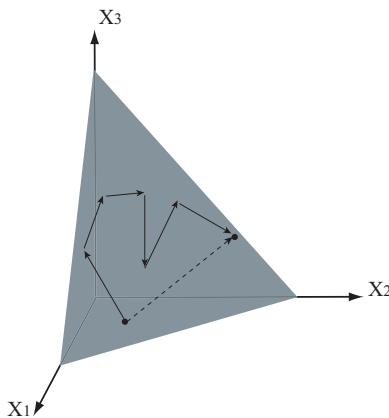


A detailed mechanism for this process is imagined to involve a large number of simpler reactions, such as $H_2 + O_2 \rightleftharpoons 2HO$, $OH + H_2 \rightleftharpoons H_2O + H$, among many others. Notice that these reactions are more elementary than the first one in one important respect: for $2H_2 + O_2 \rightarrow 2H_2O$ to occur in one step, three molecules must come together in close proximity (collide), with sufficient energy and at a brief enough interval of time in order to interact. In other words, it is a reaction of length 3. The other two reactions, on the other hand, have length 2, so their chances of actually taking place would seem greater.

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A reaction mechanism is an enumeration of what is believed to be the physically elementary steps through which the overall reaction will proceed.

The next figure represents a sequence of elementary reactions as given by their reaction vectors. There are only three substances in this case. We think of the elementary steps as individual “reaction events” that add up to the overall reaction represented by the broken line vector. (The gray triangle represents stoichiometric space, that is, the kernel of the linear map \mathcal{E} .)



Formally, a reaction mechanism will mean for us the specification of the following ingredients:

1. A list of participating substances: X_1, \dots, X_l ;
2. A list of elementary reactions, $\mathbf{R}_1, \dots, \mathbf{R}_k$, which will often be directly represented by their reaction vectors or the corresponding stoichiometric coefficients. (The coefficients $a_1, \dots, a_l, b_1, \dots, b_l$ are unambiguously specified by the reaction vector only if we suppose that $a_i b_i = 0$ for each i ; that is, if either a_i or b_i is zero for each i so that no molecular species shows up on both sides of the reaction.)
3. A list of reaction rates: r_1, \dots, r_k , one for each reaction. (This is explained later.)

The actual determination of a reaction mechanism is typically a very complicated detective job involving theory and experiment. One can propose different hypothetical mechanisms for a given process and then select the one which best accounts for the empirical data obtained in the lab. For doing this selection it is helpful to be able to mathematically derive as much theoretical information as possible from each hypothetical mechanism.

Typically, an elementary reaction has the property of being itself and its reverse reaction both of order two. Reactions of order 3 may be considered elementary if one of the reactants is a catalyst. More on this later. For now, a catalytic reaction will typically take the form $X + X' + M \rightarrow Y + Y' + M$ where M , which appears on both sides of the reaction arrow, is the catalyst.

The reaction rates for elementary reaction steps are also expected to take relatively simple analytic expressions. We will often assume that these rates are given by the so-called *mass-action law*. More on this later.

One way in which mathematics can help to specify the set of elementary reactions is in providing ways to answer the following general question:

Question 11.4.1. Suppose it is given a list of substances that we believe to take part in a chemical process under study. How can we find **all** possible reactions, subject to the atomic balance requirement, involving molecules from that list?

We illustrate this point with a few examples. Suppose we are given the following list of substances; see the example on partial combustion of methane. (We are now adding CO_2 to the list.)

$$X_1 = CH_4, X_2 = O_2, X_3 = H_2O, X_4 = CO, X_5 = H_2, X_6 = CO_2.$$

As in the earlier example, we write $E_1 = C$, $E_2 = H$, $E_3 = O$. We wish to find the possible reactions, and in particular, candidates for elementary reactions, that can be written using this list.

We write a reaction vector in the form $\mathbf{R} = z_1 X_1 + \dots + z_6 X_6$, where $z_i = b_i - a_i$. We know that \mathbf{R} should lie in the kernel of \mathcal{E} . To determine this kernel, observe that

$$\mathcal{E}(z_1 X_1 + \dots + z_6 X_6) = (z_1 + z_4 + z_6)E_1 + (4z_1 + 2z_3 + 2z_5)E_2 + (2z_2 + z_3 + z_4 + 2z_6)E_3.$$

Therefore, the z_i must solve the linear system:

$$\begin{aligned} z_1 + z_4 + z_6 &= 0 \\ 4z_1 + 2z_3 + 2z_5 &= 0 \\ 2z_2 + z_3 + z_4 + 2z_6 &= 0. \end{aligned}$$

The solution set is a linear space of dimension 3. Choosing z_4, z_5, z_6 as the independent variables, we solve for z_1, z_2, z_3 :

$$\begin{aligned} z_1 &= -z_4 - z_6 \\ z_2 &= -\frac{3}{2}z_4 + \frac{1}{2}z_5 - 2z_6 \\ z_3 &= 2z_4 - z_5 + 2z_6. \end{aligned}$$

Taking for (z_4, z_5, z_6) the values $(1, 0, 0)$, $(0, 1, 0)$, $(0, 0, 1)$, we obtain (after eliminating denominators) the following linearly independent solution vectors:

$$\begin{aligned} \mathbf{u}_1 &= (-2, -3, 4, 2, 0, 0) \\ \mathbf{u}_2 &= (0, 1, -2, 0, 2, 0) \\ \mathbf{u}_3 &= (-1, -2, 2, 0, 0, 1). \end{aligned}$$

These three vectors constitute a basis for the kernel of \mathcal{E} . Therefore an arbitrary reaction that satisfies the atomic balance condition must have reaction vector

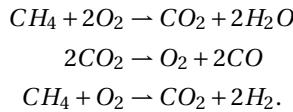
$$\mathbf{R} = \alpha_1 \mathbf{u}_1 + \alpha_2 \mathbf{u}_2 + \alpha_3 \mathbf{u}_3,$$

where the coefficients are arbitrary (except for the condition that we want the reaction coefficients to be integers). After substitution, we obtain:

$$\mathbf{R} = (-2\alpha_1 - \alpha_3)X_1 + (-3\alpha_1 + \alpha_2 - 2\alpha_3)X_2 + (4\alpha_1 - 2\alpha_2 + 2\alpha_3)X_3 + 2\alpha_1 X_4 + 2\alpha_2 X_5 + \alpha_3 X_6.$$

Any reaction is obtained from this vector by substituting for α_i rational numbers (not necessarily non-negative), eliminating denominators, and then separating positive and negative terms to form the right and left sides of the reaction, respectively.

Each choice of $(\alpha_1, \alpha_2, \alpha_3)$ yields a reaction equation. A somewhat arbitrary choice of values, $(0, 0, 1)$, $(-1, 0, 2)$, and $(0, 1, 1)$, gives respectively,



Other reactions can be obtained from these by linear operations. We may think of these three reactions as forming a basis for the space of all reactions involving these 6 substances.

Exercise 11.4.1. *Is there any elementary reaction that can be generated by linear combinations of the above three? (For the sake of this exercise, \mathbf{R} is elementary if both \mathbf{R} and $-\mathbf{R}$ have order at most 2.)*

We wish in the next exercise to describe the possible reactions that can occur in a polymerization process. The monomer is represented by A and we wish to consider all reactions involving the substances X_1, X_2, \dots, X_l , where $X_i = A^i$, a polymer containing i monomers.

Exercise 11.4.2. *How many elementary reaction can be written only involving polymers A^i , for $i = 1, \dots, l$?*

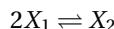
For the purposes of this exercise we say that a reaction with vector $(b_1 - a_1)X_1 + \dots + (b_l - a_l)X_l$ is elementary if:

1. a_i and b_i are non-negative for each i ;
2. either a_i or b_i is zero, for each i ;
3. $a_1 + \dots + a_l \leq 2$;
4. $b_1 + \dots + b_l \leq 2$.

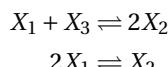
Since there is only one type of “atom” (monomer), there is only one equation that defines the stoichiometric space. The equation is

$$(b_1 - a_1) + 2(b_2 - a_2) + \dots + l(b_l - a_l) = 0.$$

Exercise 11.4.3. *Show that the elementary reactions involving polymers of length at most l and a single type of monomer are: For $l = 2$:*



For $l = 3$:



What are the reactions for $l = 4$? Can you find the number of reactions for arbitrary l ?

Exercise 11.4.4. *Find all the elementary reactions involving the substances: $H_2, O_2, H_2O, OH, O, H, H_2O_2, HO_2$.*

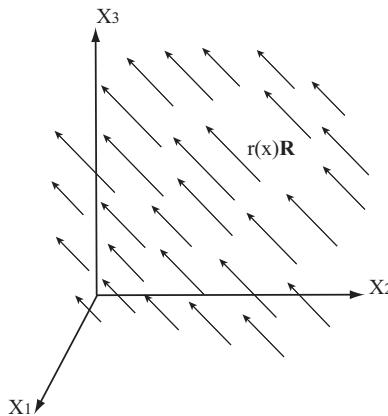
11.4.2 Reaction Rates

Recall the meaning of the reaction vector \mathbf{R} for a reaction involving l substances: assuming no fluxes of matter in and out of the system (a closed system) and no other reactions taking part in the process, then a mixture which at any given moment has a composition specified by $\mathbf{x} = (x_1, \dots, x_l) \in \mathbb{R}^l$ (for x_i non-negative), will at any other moment have a composition $\mathbf{x} + s\mathbf{R}$, for some number $s \geq 0$. (If the reverse reaction, $-\mathbf{R}$, also occurs, the molar extent s can be negative as well.)

Here and later we denote by \mathbb{R}_+^l the subset of \mathbb{R}^l consisting of all \mathbf{x} with non-negative coordinates.

The vector \mathbf{R} gives the direction of change in the mixture composition, but it says nothing about the speed at which that change is taking place. We make now the theoretical assumption that it is possible, at least in principle, to determine for a given reaction a *rate function* r that specifies that speed. Then r is to be a function of \mathbb{R}_+^l and possibly of other parameters, such as temperature and pressure; it will be written, typically, as $r(\mathbf{x})$, or as $r(x_1, \dots, x_l)$, or $r(\mathbf{x}, T, P)$, or in some other similar form. We ignore for now any dependence on parameters.

By definition, r is the rate of change of the molar extent in time, when the mixture composition is \mathbf{x} : $r(\mathbf{x}) = \frac{ds}{dt}$. If r is known, then the change in \mathbf{x} due to the reaction is completely determined by the vector field $r\mathbf{R}$ on \mathbb{R}_+^l . This vector field is shown in the next figure.



Another way to interpret the vector field $r\mathbf{R}$ is by saying that over a small interval of time of length $\Delta t = t_{\text{final}} - t_{\text{initial}}$, the change in \mathbf{x} is given by

$$\mathbf{x}_{\text{final}} = \mathbf{x}_{\text{initial}} + r(\mathbf{x}_{\text{initial}})\Delta t\mathbf{R} + o(\Delta t).$$

The notation $o(\Delta t)$ represents a small error that goes 0 with Δt and is small compared to Δt . More precisely, it represents an unspecified function whose only relevant property is that $o(\Delta t)/\Delta t \rightarrow 0$ as $\Delta t \rightarrow 0$.

More generally, suppose that k reactions participate in the process, whose reaction vectors are $\mathbf{R}_1, \dots, \mathbf{R}_k$. Our fundamental mathematical assumption concerning the kinetic properties will be that it is possible, at least in principle, to define rate functions r_1, \dots, r_k , one for each reaction, in such a way that the change of \mathbf{x} during a short interval

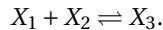
of time of length Δt is the sum of the $\Delta s\mathbf{R}$ contributed by each reaction, up to a small error of the order $o(\Delta t)$:

$$\mathbf{x}_{\text{final}} = \mathbf{x}_{\text{initial}} + r_1(\mathbf{x}_{\text{initial}})\Delta t \mathbf{R}_1 + \cdots + r_k(\mathbf{x}_{\text{initial}})\Delta t \mathbf{R}_k + o(\Delta t).$$

Dividing this expression by Δt and passing to the limit as $\Delta t \rightarrow 0$ gives the differential equation (in vector form):

$$\dot{\mathbf{x}} = \sum_{i=1}^k r_i(\mathbf{x}) \mathbf{R}_i.$$

Let us look at one example. Suppose that the process involves substances X_1, X_2, X_3 , and a pair of reactions



whose rate functions are: $r_1 = ax_1 x_2$ for the forward reaction and $b x_3$ for the reverse reaction, where a and b are constants.

First note that the reaction vector for the forward reaction is $\mathbf{R} = -X_1 - X_2 + X_3 = (-1, -1, 1)$. (Recall that in this expression the X_i represent standard basis vectors.) For the reverse reaction the vector is $-\mathbf{R}$. Therefore

$$\begin{aligned} (\dot{x}_1, \dot{x}_2, \dot{x}_3) &= \dot{\mathbf{x}} \\ &= r_1 \mathbf{R} + r_2(-\mathbf{R}) \\ &= (ax_1 x_2 - bx_3)(-1, -1, 1) \\ &= (-ax_1 x_2 + bx_3, -ax_1 x_2 + bx_3, ax_1 x_2 - bx_3) \end{aligned}$$

Written as a system of ordinary differential equations, this is:

$$\begin{aligned} \dot{x}_1 &= -ax_1 x_2 + bx_3 \\ \dot{x}_2 &= -ax_1 x_2 + bx_3 \\ \dot{x}_3 &= ax_1 x_2 - bx_3. \end{aligned}$$

To this system it may be added initial values: $x_1(0) = q_1, x_2(0) = q_2, x_3(0) = q_3$.

Exercise 11.4.5. Find an expression for the equilibrium concentrations, that is, the values of x_1, x_2, x_3 when $\dot{\mathbf{x}} = 0$, for the system of the previous example.

Exercise 11.4.6. Solve the above initial value problem. Here are a few suggested steps for doing it.

1. Notice first that $\dot{x}_1 = \dot{x}_2 = -\dot{x}_3$. Therefore $x_1 - x_2$ and $x_1 + x_3$ are constant in time. It follows that $x_2(t) = x_1(t) + q_2 - q_1$. A similar expression for x_3 in terms of x_1 and the initial values holds.
2. Replacing the expressions for x_2 and x_3 obtained above into the first differential equation gives a differential equation in x_1 only, which is of the form

$$\dot{x}_1 = Ax_1^2 + Bx_1 + C.$$

Determine the precise form of the constants A, B, C , in terms of a, b, q_1, q_2, q_3 .

3. Suppose that $a = b = 1, q_1 = 4, q_2 = 3, q_3 = 0$. Solve for $x_1(t), x_2(t), x_3(t)$.

You should get for x_1 :

$$x_1(t) = \frac{6e^{4t} + 2}{3e^{4t} - 1}.$$

11.4.3 The Law of Mass Action

Before we play with other examples of writing the differential equations from a given reaction mechanism, let us stop to consider one type of rate function that will show up very frequently. This is the so-called *mass action law*.

Suppose an elementary reaction of the general form



(For elementary reactions the sum $a_1 + \cdots + a_l$ rarely exceeds 2.) Then the mass action law rate is defined by the expression

$$r(\mathbf{x}) = k x_1^{a_1} x_2^{a_2} \cdots x_l^{a_l}.$$

The constant k will typically depend on parameters such as temperature and pressure, but not on the concentrations x_1, \dots, x_l . The dependence of k on the temperature is often adequately described by the form proposed by Arrhenius in the 19 century:

$$k = A \exp\left(-\frac{E}{RT}\right).$$

Here E is called the *activation energy*, R is the so-called *gas constant*, and A (appropriately enough) is the *pre-exponential factor*.

The precise form that the rate function can take for a specific reaction depends on many complicated factors having to do with the microscopic properties of the interacting molecules, such as their electronic structure and geometry. The task of relating these microscopic properties of the reaction with the macroscopic properties expressed in the rate function is the subject of so-called *collision theory*. For the most part this theory is better established for reactions involving gases and to some extent dilute liquid solutions. The mass action law is generally accepted as the appropriate rate function in these cases.

I will often use the rate function given by the mass action law uncritically. I hope to return to a more detailed discussion of it, and of collision theory in general, later in the course.

Sometimes empirical deviation from the mass action law may signal that a reaction is not elementary, and that the precise reaction mechanism involves intermediate substances and additional reaction steps.

A classical example is the formation of phosgene, $X_1 = COCl_2$, from carbon monoxide, $X_2 = CO$, and chlorine, $X_3 = Cl_2$. (Phosgene is a highly toxic, irritating and corrosive gas that can cause fatal respiratory damage when inhaled. It is used in organic synthesis, in manufacture of dyes, pharmaceuticals, herbicides, insecticides, synthetic foams, resins, and polymers. It first came into prominence during World War I, when it was used against troops, as a chemical weapon.)

If the reaction were elementary, of the form $X_2 + X_3 \rightarrow X_1$, one would expect the rate function to be $r = kx_2 x_3$, according to the mass action law, where x_2 and x_3 are, respectively, the concentrations of carbon monoxide and chlorine. In reality, the reaction rate far from equilibrium is found to be

$$r = x_2 x_3^{3/2}.$$

To explain this it has been suggested that besides the three species X_1, X_2, X_3 there are also present chlorine atoms, $X_4 = Cl$, and an intermediate $X_5 = COCl$, and that the reaction takes place in three steps that satisfy the mass action law:



It is further supposed that reactions (1) and (2) are so fast compared to (3) that they can always be held to be at equilibrium.

Let us try to determine under these assumptions what reaction rate would obtain for the overall reaction $X_2 + X_3 \rightarrow X_1$.

The differential equation associated to this mechanism is given by

$$\dot{\mathbf{x}} = (r_1^+ - r_1^-)\mathbf{R}_1 + (r_2^+ - r_2^-)\mathbf{R}_2 + (r_3^+ - r_3^-)\mathbf{R}_3,$$

where $\mathbf{R}_1 = -X_3 + 2X_4$, $\mathbf{R}_2 = -X_2 - X_4 + X_5$, $\mathbf{R}_3 = X_1 - X_3 + X_4 - X_5$, and the rate functions are given as follows (we denote by r_i^+ and r_i^- the rate functions for the reactions associated to \mathbf{R}_i and $-\mathbf{R}_i$, respectively):

$$\begin{aligned} r_1^+ &= k_1^+ x_3 \\ r_1^- &= k_1^- x_4^2 \\ r_2^+ &= k_2^+ x_2 x_4 \\ r_2^- &= k_2^- x_5 \\ r_3^+ &= k_3^+ x_3 x_5 \\ r_3^- &= k_3^- x_1 x_4. \end{aligned}$$

The assumption that the x_i are equilibrium concentrations for the first two reactions amounts to imposing $r_1^+ = r_1^-$ and $r_2^+ = r_2^-$. That is,

$$\begin{aligned} x_4^2 &= \frac{k_1^+}{k_1^-} x_3 \\ x_5 &= \frac{k_2^+}{k_2^-} x_2 x_4. \end{aligned}$$

With a little algebra now, the differential equation reduces to:

$$\dot{\mathbf{x}} = (ax_2 x_3^{3/2} - bx_1 x_3^{1/2})\mathbf{R}_3,$$

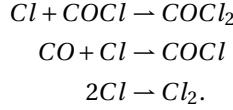
where the constants a and b are easily obtained from the k_i^+ and k_i^- .

If initially the concentration of $COCl_2$ is very small, the rate of formation of phosgene is $ax_2 x_3^{3/2}$.

Exercise 11.4.7. Show that the map \mathcal{E} associated to the substances X_1, \dots, X_5 is given by

$$\mathcal{E} = \begin{pmatrix} 1 & 1 & 0 & 0 & 1 \\ 1 & 1 & 0 & 0 & 1 \\ 2 & 0 & 2 & 1 & 1 \end{pmatrix},$$

and that the kernel of \mathcal{E} has a basis consisting of vectors: $\mathbf{S}_1 = -X_1 + X_4 + X_5$, $\mathbf{S}_2 = -X_2 - X_4 + X_5$ and $\mathbf{S}_3 = X_3 - 2X_4$. This means that any reaction involving X_1, \dots, X_5 that respects atomic balance can be linearly generated from the (possibly only fictitious) reactions:



As given above the process is described by a system of 5 differential equations, one for each x_i . There are, however, only 3 independent concentrations, so we should be able to reduce those 5 equations to only 3. That can be done by parametrizing the reaction space through the initial condition $\mathbf{x}(0) = \mathbf{q}$ using the reactions $\mathbf{S}_1, \mathbf{S}_2, \mathbf{S}_3$ defined in the previous exercise. Thus, write

$$\mathbf{x} = \mathbf{q} + s_1 \mathbf{S}_1 + s_2 \mathbf{S}_2 + s_3 \mathbf{S}_3.$$

In coordinates, this means that

$$\begin{aligned} x_1 &= q_1 - s_1; \\ x_2 &= q_2 - s_2; \\ x_3 &= q_3 + s_3; \\ x_4 &= q_4 + s_1 - s_2 - 2s_3; \\ x_5 &= q_5 + s_1 + s_2. \end{aligned}$$

Furthermore, we can express the reaction vectors $\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3$ in the basis $\mathbf{S}_1, \mathbf{S}_2, \mathbf{S}_3$ as

$$\begin{aligned} \mathbf{R}_1 &= -\mathbf{S}_3; \\ \mathbf{R}_2 &= \mathbf{S}_2; \\ \mathbf{R}_3 &= -\mathbf{S}_1 + \mathbf{S}_3. \end{aligned}$$

We can now write

$$\begin{aligned} \dot{s}_1 \mathbf{S}_1 + \dot{s}_2 \mathbf{S}_2 + \dot{s}_3 \mathbf{S}_3 &= \dot{\mathbf{x}} \\ &= (r_1^+ - r_1^-) \mathbf{R}_1 + (r_2^+ - r_2^-) \mathbf{R}_2 + (r_3^+ - r_3^-) \mathbf{R}_3 \\ &= -(r_1^+ - r_1^-) \mathbf{S}_3 + (r_2^+ - r_2^-) \mathbf{S}_2 + (r_3^+ - r_3^-) (-\mathbf{S}_1 + \mathbf{S}_3) \\ &= -(r_3^+ - r_3^-) \mathbf{S}_1 + (r_2^+ - r_2^-) \mathbf{S}_2 + (r_3^+ - r_3^- - r_1^+ + r_1^-) \mathbf{S}_3. \end{aligned}$$

Since the vectors $\mathbf{S}_1, \mathbf{S}_2, \mathbf{S}_3$ are linearly independent we can equate the respective coefficients and then express the rate functions in terms of s_1, s_2, s_3 :

$$\begin{aligned} \dot{s}_1 &= -k_3^+(q_3 + s_3)(q_5 + s_1 + s_2) + k_3^-(q_1 - s_1)(q_4 + s_1 - s_2 - 2s_3); \\ \dot{s}_2 &= k_2^+(q_2 - s_2)(q_4 + s_1 - s_2 - 2s_3) - k_2^-(q_5 + s_1 + s_2); \\ \dot{s}_3 &= k_3^+(q_3 + s_3)(q_5 + s_1 + s_2) - k_3^-(q_1 - s_1)(q_4 + s_1 - s_2 - 2s_3) - k_1^+(q_3 + s_3) + \\ &\quad k_1^-(q_4 + s_1 - s_2 - 2s_3)^2. \end{aligned}$$

The initial conditions are $s_i(0) = 0$ or $i = 1, 2, 3$. This is an initial value problem for which we have little hope of finding explicit solutions. Later, when talking about the theory of dynamical systems, we will consider how to try to extract interesting information from the equations without having to fully solve them analytically.

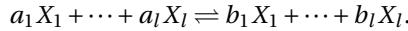
11.5 Reaction Mechanisms and Differential Equations

We have already seen how to translate a given reaction mechanism into a system of differential equations from which we can hope to obtain the time dependence of the concentrations, $x_i(t)$. Here we would like to start a more systematic study of the differential equations that arise.

We begin with a number of examples that can be solved more or less explicitly.

11.5.1 Single Pair of Forward-Back Reactions

Consider a pair of reactions



Let the rate functions be

$$\begin{aligned} r_+(\mathbf{x}) &= k_+ x_1^{a_1} \cdots x_l^{a_l} \\ r_-(\mathbf{x}) &= k_- x_1^{b_1} \cdots x_l^{b_l} \end{aligned}$$

for the forward and backward reactions, respectively. The reaction vector for the forward reaction is the constant vector

$$\mathbf{R} = \sum_{i=1}^l (b_i - a_i) X_i = (b_1 - a_1, \dots, b_l - a_l).$$

Then $\mathbf{x}(t)$ satisfies the differential equation:

$$\dot{\mathbf{x}} = (r_+(\mathbf{x}) - r_-(\mathbf{x})) \mathbf{R}$$

with initial condition $\mathbf{x}(0) = \mathbf{q}$, where $\mathbf{q} = (q_1, \dots, q_l)$ is some arbitrary vector of initial concentrations. The reaction space in this case is one-dimensional, so we know that the solution must take the form

$$\mathbf{x}(t) = \mathbf{q} + s(t) \mathbf{R},$$

where $s(t)$ is the molar extent of the reaction at time t . Therefore, rather than write a system of differential equations, one for each x_i , we may try to solve for the single function $s(t)$, from which the values of $x_i(t)$ will follow. The differential equation for $s(t)$ can be obtained by noting that, on the one hand

$$\dot{\mathbf{x}} = \dot{s} \mathbf{R}$$

and on the other

$$\dot{\mathbf{x}} = (r_+(\mathbf{q} + s(t) \mathbf{R}) - r_-(\mathbf{q} + s(t) \mathbf{R})) \mathbf{R}.$$

Therefore

$$\dot{s} = r_+(\mathbf{q} + s(t) \mathbf{R}) - r_-(\mathbf{q} + s(t) \mathbf{R}).$$

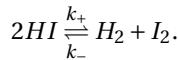
This is an initial value problem of the form

$$\begin{aligned} \dot{s} &= f(s) \\ s(0) &= 0. \end{aligned}$$

This initial value problem can in principle be solved explicitly by noting that the inverse function, $t(s)$, satisfies:

$$t = \int_0^s \frac{ds}{f(s)}.$$

Example. The decomposition of hydrogen iodite is a reversible reaction of second order given by



A 200 liter flask was filled with pure HI at 1.24 atm. and 683 K. The decomposition was followed photometrically by measuring the absorption of light by the iodine produced in the reaction. The optical density given is proportional to the iodine concentration. Immediately after the last reading was taken, the flask was chilled and was found to contain 1.17 grams of iodine (atomic weight 127). The following data were obtained:

Time t (min)	42	118	230	397	680	770	940
Optical density	0.81	2.13	3.66	5.04	6.00	6.18	6.21

We wish to see how the data obtained agree with the reaction scheme and use it to estimate the values of the reaction constants k_+ and k_- .

Let us begin by finding the initial concentrations. We set $X_1 = HI$, $X_2 = H_2$, $X_3 = I_2$, and the respective concentrations x_1, x_2, x_3 . Initially the flask is filled with pure HI , so $x_2(0) = 0$ and $x_3(0) = 0$. In order to determine $x_1(0)$ we will assume that the perfect gas equation is valid for the HI :

$$PV = nRT$$

where n is the number of moles of HI to be determined, $P = 1.24$ atm., $V = 200$ liters, $T = 683K$, and R is the gas constant:

$$R = 0.0820 \text{ (liter atmosphere) / (degree mole).}$$

Then the molar concentration is

$$x_1(0) = \frac{n}{V} = \frac{P}{RT} = \frac{1.24 \text{ atm}}{683 \text{ deg.} \times 0.0820 \text{ (l. atm.) / (deg. mole)}} = 0.022 \text{ moles per liter.}$$

So in units of moles per liter we have (notice that $\mathbf{R} = (-2, 1, 1)$):

$$x_1(t) = 0.022 - 2s(t)$$

$$x_2(t) = s(t)$$

$$x_3(t) = s(t).$$

Let us now look for the molar extent $s(t)$. The differential equation in vector form is

$$\dot{\mathbf{x}} = (k_+ x_1^2 - k_- x_2 x_3) \mathbf{R}.$$

Writing the equation in terms of s gives:

$$\dot{s} = k_+ (0.022 - 2s)^2 - k_- s^2.$$

This is an equation of the form $\dot{s} = f(s)$, where $f(s)$ is a quadratic function in s . With a little algebra it is possible to write

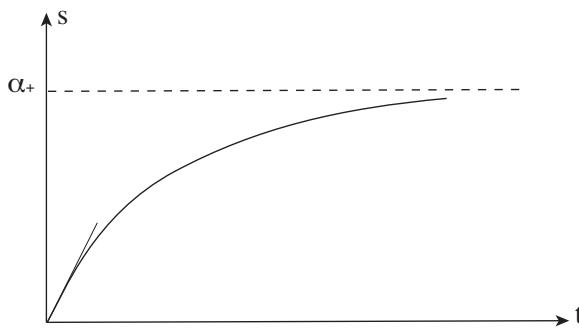
$$f(s) = A(s - \alpha_-)(s - \alpha_+)$$

where $A = 4k_+ - k_-$ and $\alpha_{\pm} = 0.022/(2 \pm \sqrt{k_-/k_+})$.

Before finding an explicit solution for the above differential equation it is useful to try to anticipate some of the qualitative features the solution should display. From the expression of $f(s)$ we find that $\dot{s} = 0$ if $s = \alpha_-$ or $s = \alpha_+$. At these values we say that the reaction is at equilibrium. At $s = 0$ the rate \dot{s} is given by

$$(4k_+ - k_-) \frac{0.022}{2 + \sqrt{\frac{k_-}{k_+}}} \frac{0.022}{2 - \sqrt{\frac{k_-}{k_+}}} = (0.022)^2 k_+ > 0.$$

Consequently, at and near $s = 0$ the function $s(t)$ grows. Moreover, \dot{s} can only change sign as it crosses α_{\pm} . Notice that $0 < \alpha_+ < |\alpha_-|$. Whether α_- is positive or negative, we have that $\dot{s} > 0$ on the interval $0 \leq s < \alpha_+$ and negative on the immediate right of α_+ . Therefore $s(t)$ grows monotonically starting at 0 with rate $\dot{s}(0) = (0.022)^2 k_+$, and toward the value $\alpha_+ = 0.022/(2 + \sqrt{k_-/k_+})$. A sketch of the graph of $s(t)$ is shown below.



Given our rough understanding of the solution, let us try to estimate the values of k_- and k_+ . Let us next plot the data so that it can be compared with the above graph. Some work is involved in writing the data in terms of s rather than the optical density.

The problem states that the optical density is proportional to the iodine concentration. Call the optical density ρ . Then $x_3 = a\rho$, where a is a proportionality constant. To determine a we use that at time 940 minutes the flask was found to contain 1.17 grams of iodine, which amounts to $1.17/127 = 9.2 \times 10^{-3}$ moles of I_2 . The concentration of I_2 is then

$$x_3(940 \text{ minutes}) = \frac{1}{2} \times \frac{9.2 \times 10^{-3} \text{ moles}}{200 \text{ liters}} = 2.3 \times 10^{-5} \text{ moles per liter.}$$

The constant a is then

$$a = \frac{2.3 \times 10^{-5}}{6.21} = 0.4 \times 10^{-5} \text{ moles per liter.}$$

We can now rewrite the table in terms of x_3 . (Recall that $x_3 = s$.)

Time t (min)	42	118	230	397	680	770	940
x_3 (10^{-5} moles per liter)	0.32	0.85	1.46	2.02	2.40	2.47	2.48

A crude estimation of k_- and k_+ can be obtained by using the values of the asymptote α_+ , about 2.5×10^{-5} liters per mole, and slope $\dot{s}(0) = (0.022)^2 k_+$ calculated using by the

first data point . This gives:

$$k_+ = \frac{0.32 \times 10^{-5}}{(0.022)^2 \times 42} = 1.6 \times 10^{-4} \text{ liters per mole per minute};$$

$$k_- = \left(\frac{0.022}{2.5 \times 10^{-5}} - 2 \right)^2 k_+ = 0.9 \times 10^3 \times k_+ = 0.15 \text{ liters per mole per minute.}$$

Let us finally look for an explicit solution. Integrating $\int A dt = \int f(s)^{-1} ds$ gives:

$$\begin{aligned} At &= \int_0^s \frac{du}{(u-\alpha_-)(u-\alpha_+)} \\ &= \frac{1}{\alpha_- - \alpha_+} \left(\int_0^s \frac{du}{u-\alpha_-} - \int_0^s \frac{du}{u-\alpha_+} \right) \\ &= \frac{1}{\alpha_- - \alpha_+} \left(\ln \left| \frac{s-\alpha_-}{\alpha_-} \right| - \ln \left| \frac{s-\alpha_+}{\alpha_+} \right| \right) \\ &= \frac{1}{\alpha_- - \alpha_+} \ln \left| \frac{(s-\alpha_-)\alpha_+}{(s-\alpha_+)\alpha_-} \right| \end{aligned}$$

Notice that $A(\alpha_- - \alpha_+) = 0.044 k_+ \sqrt{k_- / k_+}$ is positive and that for $0 \leq s < \alpha_+$

$$\frac{(s-\alpha_-)\alpha_+}{(s-\alpha_+)\alpha_-} > 0.$$

Therefore,

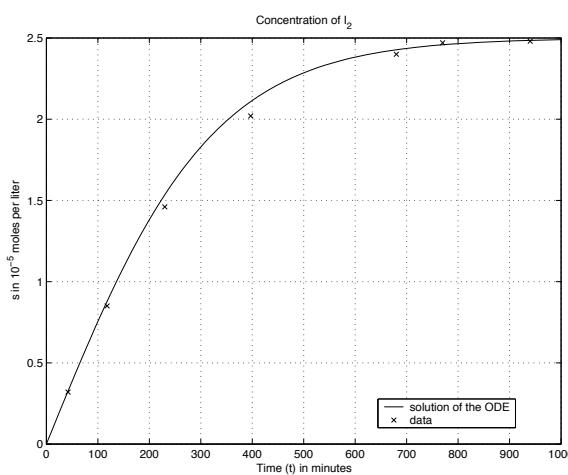
$$A(\alpha_- - \alpha_+) t = \ln \frac{(s-\alpha_-)\alpha_+}{(s-\alpha_+)\alpha_-}$$

It is now easy to solve for s . A little algebra gives:

$$s(t) = \alpha_+ \left(e^{A(\alpha_- - \alpha_+)t} - 1 \right) \left(e^{A(\alpha_- - \alpha_+)t} - \frac{\alpha_+}{\alpha_-} \right)^{-1}.$$

With our estimated values for the constants we obtain:

$$s(t) = 2.5 \times 10^{-5} \frac{e^{6.2 \times 10^{-3} t} - 1}{e^{6.2 \times 10^{-3} t} + 0.99}.$$



11.5.2 Equilibrium Concentrations

Suppose that a chemical process involves the molecular species X_1, \dots, X_l and a reaction mechanism that consists of elementary reactions (indicated by their reaction vectors) $\pm \mathbf{R}_1, \dots, \pm \mathbf{R}_k$ and respective reaction rates $r_1^\pm(\mathbf{x}), \dots, r_k^\pm(\mathbf{x})$. If all changes in \mathbf{x} are due to the reactions only (i.e., if there are no fluxes and diffusion can be neglected) then the rate of change of \mathbf{x} is given by $\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x})$, where

$$\mathbf{f}(\mathbf{x}) = (r_1^+(\mathbf{x}) - r_1^-(\mathbf{x}))\mathbf{R}_1 + \dots + (r_k^+(\mathbf{x}) - r_k^-(\mathbf{x}))\mathbf{R}_k.$$

We say that $\mathbf{x} \in \mathbb{R}_+^l$ is a *critical point* (or a *zero*) of the system of differential equations if $\mathbf{f}(\mathbf{x}) = 0$. (You should be aware that chemists seem to make finer distinctions between the terms *equilibrium* and *stationary* points, whereas the term *critical* point is rarely used by them with this precise meaning. I will observe here the terminology used by mathematicians.)

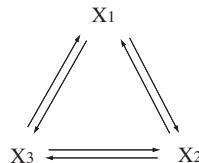
Notice that if the system reaches an equilibrium state, at which concentrations do not change in time, then that point must be a critical point of the vector field \mathbf{f} . Knowing the zeros of \mathbf{f} is thus a first step in understanding how the process evolves in time.

There is a subtlety here that I need to point out. If a point \mathbf{x} is such that $r_i^+(\mathbf{x}) = r_i^-(\mathbf{x})$ for each i , then clearly it is a critical point. But if the reaction vectors are not linearly independent, the converse is not necessarily true.

It is generally assumed, however, based on statistical physics reasoning of a sort that I do not understand, that for a system at equilibrium each of the elementary step reactions comprising the reaction mechanism appears together with its reverse reaction and is at equilibrium with it; that is, $r_i^+(\mathbf{x}) = r_i^-(\mathbf{x})$ for each i . We say in this case that *detailed balance*, or *detailed equilibrium* holds. If I say that a vector \mathbf{x} represents equilibrium concentrations I will generally mean detailed equilibrium.

Let us look at a simple example to clarify this point. Consider a process that involves three isomers X_1, X_2, X_3 , and the elementary reactions and respective rate functions given by

$$\begin{aligned}\pm \mathbf{R}_1 &= \pm(X_2 - X_1), \quad r_1^\pm; \\ \pm \mathbf{R}_2 &= \pm(X_3 - X_2), \quad r_2^\pm; \\ \pm \mathbf{R}_3 &= \pm(X_1 - X_3), \quad r_3^\pm.\end{aligned}$$



Defining $J_i = r_i^+ - r_i^-$ for $i = 1, 2, 3$, we can write the vector field associated with this mechanism as

$$\mathbf{f}(\mathbf{x}) = J_1 \mathbf{R}_1 + J_2 \mathbf{R}_2 + J_3 \mathbf{R}_3 = (J_3 - J_1)X_1 + (J_1 - J_2)X_2 + (J_2 - J_3)X_3.$$

Thus we see that \mathbf{x} is a point of detailed equilibrium if

$$J_i(\mathbf{x}) = 0 \text{ for all } i,$$

whereas \mathbf{x} is a critical point if

$$J_i(\mathbf{x}) - J_j(\mathbf{x}) = 0 \text{ for all } i \text{ and } j.$$

It is interesting to note what happens if we assume mass action kinetics and detailed balance. In this case

$$\begin{aligned} J_1 &= k_1^+ x_1 - k_1^- x_2; \\ J_2 &= k_2^+ x_2 - k_2^- x_3; \\ J_3 &= k_3^+ x_3 - k_3^- x_1. \end{aligned}$$

Defining the constants $K_i = k_i^+ / k_i^-$ for $i = 1, 2, 3$, we obtain the relations:

$$x_2 = K_1 x_1, \quad x_3 = K_2 x_2, \quad x_1 = K_3 x_3.$$

In particular, it follows that these constants must satisfy the relation

$$K_1 K_2 K_3 = 1.$$

11.6 Vocabulary

Chemical system: a region of space containing matter of various kinds. It is separated from the outside *ambient* by a *boundary*. Any influence the ambient can have on the system happens through the boundary by the exchange of *matter* and *energy* such as heat, light, etc. The system is *isolated* if there are no exchanges between it and the ambient. The ambient can have no influence on the system if it is isolated. It is a *closed system* if there are no exchanges of matter, although energy transfer is allowed. The system is *open* if both matter and energy can move across the boundary.

State quantities. The measurable quantities used to describe the *state* of the system at a given moment in time, such as pressure, temperature, volume, viscosity, electric resistivity, etc., are called *state quantities*. A state quantity is an *extensive quantity* if it is a number associated to the system as a whole having the property of being *additive*. This means that if a system consists of two non-overlapping sub-systems, the value of that quantity for the whole system is the sum of the values for the two sub-systems. Examples are mass, volume, total electric charge, etc. *Intensive quantities* are quantities which are defined at each point of the system, thus specifying a (possibly discontinuous) function of the space variables, such as concentrations of substances, density of charge, temperature, pressure, etc. (Mathematically, extensive quantities are *measures* and intensive quantities are *densities*.)

The system is *uniform* if all intensive quantities are constant functions. A *phase* is a subset of the system on which all intensive quantities are described by continuous functions. For example, a glass partially filled with water has two phases: water and air. (The density of mass is discontinuous on the transition from water to air.) A subset on which all intensive quantities are constant is a *uniform phase*.

Composition of a uniform phase. The global composition of a chemical system (either monophasic or polyphasic) is specified by the amounts of each of its *chemical species*. (Chemical species are also called *substances*.) These amounts are typically given in *moles*, which is a unit proportional to the number of molecules of a chemical species

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present in the system. If there are l substances in amounts n_1, n_2, \dots, n_l (moles) the numbers $x_i = n_i / \sum_j n_j$ is called the *molar fraction* of the respective substance.

The molar fraction, x_i , of a uniform phase can be interpreted as the probability that a molecule drawn at random from the phase will be of the chemical species i . The *concentration* of substance i in a system of volume V is the number $C_i = n_i / V$.

The total amount n_i of a chemical species is the sum of the amounts $n_{i,\alpha}$ of the same species in each of its phases. The phase is indicated by the extra sub-index ' α '.

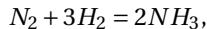
One may also consider the *mass* m_i of each chemical species in the system. If m_i is the amount of species i in units of mass, then $w_i = m_i / \sum_j m_j$ is the corresponding *mass fraction* and $\rho_i = m_i / V$ is the corresponding *mass concentration*. If M_i represents the mass of one mole of species i , then $m_i = n_i M_i$.

Mass balance in an open system. Let m_{in} be the total mass that enter the system through its boundary over an interval of time from t_1 to t_2 , and m_{out} the total mass that leaves the system through the boundary over the same interval. Under the assumption that total mass is conserved, then $\Delta m = m_{\text{in}} - m_{\text{out}}$ is the amount of mass that the system acquired during that interval. There is *accumulation* of matter if Δm is positive, and *evacuation* if negative. If $\Delta m = 0$ over any interval of time we say that the transport of matter across the boundary occurs in a *permanent mass regime*.

If, besides the total amount of matter in the system, all intensive quantities are time independent functions, we say that the system is in an *stationary state*.

Chemical reactions. The amounts n_i may change in time due to transport of the substance in and out of the system and due to chemical reaction. If the n_i change in a closed system, then some chemical reaction has occurred. The substances that decrease in amount due to a chemical reaction are called the *reactants*; those that increase in amount are the *reaction products*. There may be substances that affect the speed of a reaction but whose amounts do not change, such as *catalysts*.

In a closed or stationary system, the quantities (in moles) of each species of atoms is conserved. The changes in the molar quantities of each chemical species due only to reaction (i.e., all changes that are not due to transport of matter across the boundary) must satisfy a *reaction equation*. This is an expression such as



which is interpreted as saying that changes in the molar amounts of nitrogen gas, hydrogen gas and ammonia in the system due to this reaction involves the disappearance of one mole of nitrogen, 3 of hydrogen, and the formation of 2 moles of ammonia.

Traditionally, reactants are written on the left-hand side of the equation and products on right. The numbers in front of the molecular symbols (1 for N_2 , 2 for NH_3 , for example) are the *stoichiometric coefficients*. These numbers give no indication of the actual amount of matter involved in the equation; only their ratios are meaningful. In this sense, the previous reaction equation and $2N_2 + 6H_2 = 4NH_3$ have exactly the same meaning. The changes in the actual molar amounts of each constituent species of this reaction are thus related by the equations

$$\frac{\Delta n_{H_2}}{-3} = \frac{\Delta n_{N_2}}{-1} = \frac{\Delta n_{NH_3}}{+2} \quad (> 0).$$

11.7 A General Box Model

(Flows, divergence theorem, continuity equation with reactions, etc.; add energy?)