A simplified model for geochemical reactions in a geothermal reservoir

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Abstract

Hot water pumped out of the ground for purposes of geothermal energy extraction cools down after it is used in a heat exchanger. The now cold water contains minerals that undergo a shift in chemical equilibrium. This may cause the minerals to come out of solution and become sediments. When pumping the cold water back into the porous ground, these sediments can cause cloggings that eventually lead to a net energy loss using this source. It will require more mechanical energy to pump up the water, than we gain in geothermal energy.

In this report we aim to create a simple computer program that models the creation of these sediments. The goal is to know what minerals cause cloggings, and which do not. The program approximates the underground as a 0-dimensional tank with inflow and outflow called a Continuously Stirred Tank Reactor (CSTR). We derive a set of differential equations for both the inflow and outflow and the chemical reactions that take place. The chemistry used in this model uses data from individual reactions, which gives us differential equations for the concentrations of the minerals. These chemical reactions are very dependent on the temperature in the tank. Because the inflow water may have a different temperature than the tank, we will also make a differential equation for the temperature. Using a fourth order Runge-Kutta scheme we can numerically integrate these equations in time. To test the program we use 6 of the most common dissolution reactions in ground water.

When using the program we can see that some concentrations change a very insignificant amount and therefore do not contribute to the cloggings. These minerals were Mg^{2+} from the dissolution of dolomite and Fe^{2+} from the dissolution of magnetite.

The program works as desired, but does lack some elements, first and foremost the reactions between acids and bases, such as HCO_3^- and H^+.

Inhoudsopgave

1

Introduction

As most of the world agrees that fossil fuels cause global warming, the search for renewable energy becomes ever more important. We are already quite familiar with wind, solar and nuclear energy, but not so much with geothermal energy. Geothermal energy works using the heat of the earth's core, which has a temperature of about 5,200 °C. This heat flows outwards to the mantle and finally into the crust. If a pipe is drilled into the crust and the hot water is pumped out, the energy can be extracted using a heat exchanger. The warm water can now be used to heat homes. The great benefit of this source of energy is that it does not depend on the amount of wind or daylight. It also does not need as many safety precautions as nuclear energy.

Generally the goal is to pump up water that is 80 °C. Due to plate tectonics, the depth where water is 80°C varies greatly from location to location. In Iceland it takes only a few 100 meters or sometimes even 0 at their hot springs. In the Netherlands we would need to drill 2 kilometers deep before we reach the desired temperature. Drilling and pumping is usually not a problem for this clean energy source. The problem is what to do with the water once it has gone through the heat exchanger. We have to pump it back into the ground, where it can be reheated by the earth.

The problem here is that as the water cools down in the heat exchanger, the chemical balance is shifted and dissolved minerals become sediments. Most of the sediments formed might be caught by a filter installed at the end of the pipeline. But the sediments can also form inside the ground, where the water still has not reached a sufficiently high temperature. We cannot place a filter there. Not preventing this sedimentation underground could result in clogging.

Because the earth is porous, these pores can fill up with sediments and we would have to use more energy in the pump to get the water back underground. There will be a point where the thermal energy we obtain by this method is less than the mechanical energy used by the pump. In order to maintain efficiency we have to prevent this clogging.

In order to prevent this clogging we have to know a few things about our system. We need to know how this sediment forms and at what rate. Depending on the type of sediments and rock, some sediments may also

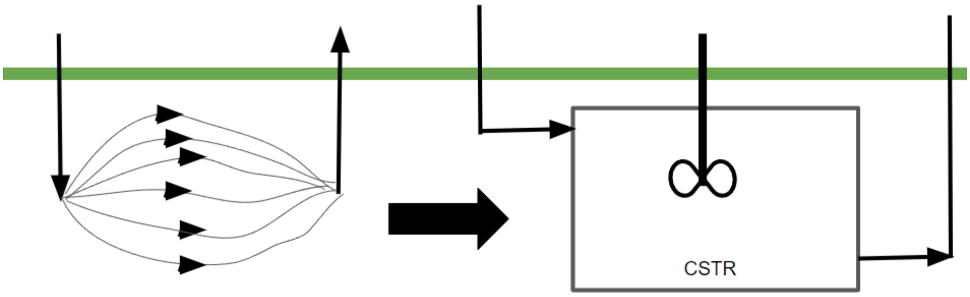

Figure 1.1: Figure to illustrate the simplification of the porous ground to the CSTR model, where the entirety of the underground is reduced to a 0 dimensional tank.

stick to the rock, or some sediments might bond together over time to form larger particles.

To know what minerals are dissolved and what minerals might precipitate, we make a model of the ground. There are three things that govern the concentration of the minerals, heat, chemistry and transport. Each of these three things affects the others. As a first model to describe water flowing through the ground and the chemical reactions inside the water we disregard the transport. This simplifies the problem so we may use the concept of a Continuously Stirred Tank Reactor (CSTR). Figure 1.1 is a schematic drawing of this transition. In the left hand drawing the ground is already simplified to a bundle of small capillary tubes, even though it is better thought of as a sponge-like rock. We simplify this sponge to a 0 dimensional tank where nothing depends on position. This is called well stirred. This is a reasonable approximation as the dispersion in the porous material would stir the minerals in the water. The inflow of the tank is the same as for the ground, namely the water that comes out of the heat exchanger. Under the ground the water would spend a certain amount of time, the residence time, before it would come back to the outflow pipe (the pump). In the tank there is no measure of time, some amount of water goes in with a certain concentration of molecules and the same amount of water goes out, but with the concentration of molecules of the entire tank. It is possible to have an average residence time by tweaking the volume of the tank and its inflow.

Of the other two parts, heat and chemistry we say that heat only influences chemistry but not vice versa. The temperature affects the chemical equilibrium of the reactions, but the heat created or used by the chemical reactions is negligible so the chemistry does not affect the heat. The temperature of the water is the same everywhere in the tank. This is also a simplification because the ground has different temperatures at different places. The temperature of the water does change as a whole if the inflowing water has a different temperature than that of the water in the tank.

The goal of this report is to create a simple model to predict the concentrations of particles in the water after being re-injected into the ground. It should be simple to use and simple to add as many reactions as we want. The foundation of the program will consist of the CSTR model and for the chemical reaction part of the model we use the works of J.D. Rimstidt [10]. By taking the data obtained from research done on individual dissolution reactions we can combine this to make a program that tracks the concentrations of multiple particles. Using this we can determine what types of minerals play a big part, and which play little to no part at all in the clogging of the porous earth.

This report will explain how the computer program is made and structured. There will be some examples of simple reactions that are analytically solvable. After creating a python program that does the time-integration we shall also test it for numerical stability and the influence of residence time on the evolution of the concentrations. The report will contain many figures containing graphs of the species concentrations.

2

Deriving differential equations

In this chapter we look at the workings of a Continuously Stirred Tank Reactor and how we may use it to approximate what happens under the ground. In the first section we derive the general equation for the CSTR. In the second section we formulate the mathematics of the reaction kinetics, how we mathematically model transient chemical reactions. The third section explains how we program both these mathematical equations into a computer using python. A set of five reversible reactions is used to demonstrate how the computer program would process the data and computations.

2.1. The CSTR equation

A CSTR is a Continuously Stirred Tank Reactor. The first word means that the tank has inflow and outflow. The inflow will be a volume of water per second containing a (fixed) concentration of species. The outflow has the same volume per second, but the concentration of species will be that of the tank. The second word, stirred, means that at all times it may be assumed that the concentration of a species and the temperature of the water is identical for every point in the reactor. The whole reactor may be seen as a point and the concentration of a species is therefore not dependent on the position. The last word, reactor, means that inside the tank different chemical reaction can take place and change the concentration of the species.

We now derive the CSTR equation [8]. We start with a total amount of molecules, N, of a certain species. In a CSTR we have three processes that could change its value. A crude differential equation would look like this.

$$\frac{dN}{dt} = \text{inflow - outflow + reaction} \tag{2.1}$$

In- and outflow

Firstly we look at only the inflow and outflow of the equation. Our tank has a volume V in m^3 and there will be a volumetric flow rate ϕ in $m^3 s^{-1}$. The equation for the change in number of particles in the tank can be written as a differential equation.

$$\frac{dN}{dt} = \dot{N}_{in} - \dot{N}_{out} \tag{2.2}$$

Where $\dot{N}_{in}$ and $\dot{N}_{out}$ have units *particles per second*. We can write N as c ·V, where V is the volume and c the concentration in the tank. We can do the same for $\dot{N}_{in}$ and $\dot{N}_{out}$ with $c_{in} \cdot \phi$ and $c_{out} \cdot \phi$. Because we say that the outflow concentration of a CSTR is the concentration in the tank itself, the equation then becomes

$$\frac{d(cV)}{dt} = c_{in}\phi - c\phi \tag{2.3}$$

If we rearrange this and say the volume does not change we get

$$\frac{dc}{dt} = (c_{in} - c)\frac{\phi}{V} \tag{2.4}$$

Temperature

In addition to just concentrations, the tank and inflowing water also have a certain temperature. If these are not equal, the temperature inside the tank will change. This is very important as the chemical equilibrium of the reactions depends heavily on temperature.

For the derivation of the temperature change we have an intermediate step. It is not possible to add temperatures. The CSTR equation 2.1 uses energy, E in J, instead of temperature and e in $J\ m^{-3}$ instead of concentration. We assume that the heat generated or used by the chemical reactions is negligible, therefore there is no reaction term. The only energy present is in the temperature of the water, which has a certain density, ρ ($kg\ m^{-3}$), and specific heat capacity, c_p ($J\ kg^{-1} K^{-1}$).

$$\begin{aligned}\frac{dE}{dt} &= e_{in}\phi_{in} - e_{out}\phi_{out} \\ \frac{d(V\rho c_p T)}{dt} &= \phi\rho c_p T_{in} - \phi\rho c_p T \\ \frac{dT}{dt} &= (T_{in} - T)\frac{\phi}{V}\end{aligned} \tag{2.5}$$

2.2. Reaction kinetics

For the making of a mathematical model for chemical reactions, we use the equations derived in *Geochemical rate models: an introduction to geochemical kinetics* by J.D. Rimstidt [10]. The goal of such a model is to know at any time how much there is of any relevant ion/molecule, a specie. For this we can calculate the reaction rate r (mole/sec). The reaction rate tells us for one chemical reaction how many moles of a specie turns into its products per unit time.

For example a reversible reaction could be A and B turning into C. But also C decaying into A and B, the reverse.

$$\mathrm{A} + \mathrm{B} \underset{-}{\overset{+}{\rightleftharpoons}} \mathrm{C} \tag{2.6}$$

In this case we call the creation of C the forwards reaction (+) and the decay of C the backwards reaction (-). The reaction rate r_+ would tell us what amount of moles of C would be created and the same amount of moles of A and B would be used per second. r_- would tell the reverse.

The value of $r_{+/-}$ is dependent on 5 things according to Collision Theory [6]: 1. The nature of the reactants 2. the concentration, c, of those reactants 3. the temperature at which the reaction occurs 4. the surface area of a solid reactant and 5. a possible catalyst. In the following model we do not take into account 4 which will be explained later, and 5 because we assume there to be no catalyst present.

A reaction happens when two molecules meet, collide, and have enough energy to actually react. If there are more molecules around (no.2) then the probability that two are near is larger. The probability that they actually hit each other increases if the molecules are larger (no.1), or the molecules may move faster when the temperature is higher (no.3). These things influence the amount of collisions that happen per second. The energy needed to react is explained later. For the equation of the reaction rate we take the concentration of the reactions separate and combine the rest into a constant $k_{+/-}$. For the example of equation 2.6 its forward reaction has two reactants and its backward reaction one reactant.

$$\begin{cases} r_+ = k_+ c_A c_B \\ r_- = k_- c_C \end{cases} \tag{2.7}$$

Up until now species were said to have a concentration. For the kinetics part, according to Rimstidt, it is said that species have an activity, denoted by the letter a. Activity should be read as "effective concentration." Activity can be converted to concentration m or c (mol/kg solvent) by the following equation.

$$a = \frac{\gamma m}{\gamma^0 m^0} \tag{2.8}$$

Here γ is called the activity coefficient and has no units. Generally $\gamma^0 = 1$ and $m^0 = 1$ mol/kg by convention. So the activity a is dimensionless. γ is incorperated into the $k_{+/-}$. So if we look at the activity of specie A we would get the following differential equation.

$$\frac{da_A}{dt} = k_- a_C - k_+ a_A a_B \tag{2.9}$$

From experimental research we have a formula for the constant $k_{+/-}$.

$$k_{+/-}(T) = A_{acid} \cdot e^{\frac{-E_{a,acid}}{RT}} a_k^{n_{acid}} + A_{neutral} \cdot e^{\frac{-E_{a,neutral}}{RT}} a_l^{n_{neutral}} + A_{base} \cdot e^{\frac{-E_{a,base}}{RT}} a_m^{n_{base}} \tag{2.10}$$

The equation consists of three parts, one for each regime of acidity: acid, neutral and base (equation 9 from Palandri et al., 2004 [9]). The A constants are called the Arrhenius pre-exponential constant and take into account the activity coefficients and the rate of molecules hitting each other. In most reactions only one or two of the three terms is used. The other A's are zero. E_a is the activation energy, the energy needed to make the reaction happen. R is the universal gas constant and T the temperature in Kelvin. The exponential term takes into account the probability that when two reactants meet, they actually react. The a^n term is included as a reaction might depend on a certain species' activity up to an exponent. This equation only gives either the k_+ or the k_-. For the entire equation there will be at most nine constants. If we use equation 2.10 to calculate k_+ then we will have to use another equation to obtain k_-.

If we set the derivative of equation 2.9 to zero and rearrange we may define a new constant K, the equilibrium constant. Even though we are looking for kinetic equations, we need to use the equilibrium values.

$$K \equiv \frac{k_+}{k_-} = \frac{a_{C,eq}}{a_{A,eq} a_{B,eq}} \tag{2.11}$$

where 'eq' stands for equilibrium. The value of K can be found using another equation which depends on temperature in Kelvin. [7]

$$^{10}\log(K) = A_1 + A_2 T + \frac{A_3}{T} + A_4\, ^{10}\log(T) + \frac{A_5}{T^2} + A_6 T^2 \tag{2.12}$$

The constants A_i are determined by data fitting[7], where we use known equilibrium constants per temperature and find out which A_i's best predict the K value. Equation 2.12 is just one way of data fitting, it is possible to extend it with more terms or a different equation entirely. Given either $k_+(T)$ or $k_-(T)$ we then use the equilibrium constant K(T) to calculate the other using equation 2.11.

In total form the equation for the reaction rate per reaction would be.

$$r_{+/-} = k_{+/-} \prod_i a_i^{n_i} \tag{2.13}$$

Here a_i is the activity of the species that are used in the reaction. n_i is the partial order of that species. If say reaction 2.6 used 2 A molecules instead of one, then the partial order n_A (exponent) of a_A would be 2 instead of 1. Summing all partial orders gives the total reaction order. The Greek letter capital Π here means a product of all a_i's so $a_1^{n_1} \cdot a_2^{n_2} \cdot a_3^{n_3} \ldots$

For every specie we can write down a differential equation per reaction like 2.9 with both the kinetics and inflow/outflow mechanics and gain a system of equations for the activities of all species due to kinetics. If we then combine this with the differential equation for the temperature we will have a complete mathematical model.

$$\begin{aligned} \frac{da_j}{dt} &= \sum_i k_i \prod_l a_l^{n_{l,i}} + (a_{j,inflow} - a_j)\frac{\phi}{V} \\ \frac{dT}{dt} &= (T_{in} - T)\frac{\phi}{V} \end{aligned} \tag{2.14}$$

Written in Matrix form it would look like this.

$$\frac{dA}{dt} = \begin{pmatrix} \frac{da}{dt} \\ \frac{dT}{dt} \end{pmatrix} = \begin{pmatrix} (k_+ a^{M_{forwards}} - k_- a^{M_{backwards}}) \cdot M_{normalized}{}^T + (a_{inflow} - a)\frac{\phi}{V} \\ (T_{in} - T)\frac{\phi}{V} \end{pmatrix} \tag{2.15}$$

With a again the vector of activities. M is the matrix formed by all partial reaction orders, the $n_{l,i}$. M$_{forwards}$ is the same matrix but only the forward going reactions, backwards vice versa. And M$_{normalised}$ is M, but every entry is either 1, forwards reaction, or -1, backwards reaction. Using initial conditions of activities and temperature together with the inflow conditions of flow rate, activities and temperature, we can integrate a system of equations like 2.14 to obtain the activity of all species through time.

2.3. The numerical procedure

As an example of how the time-integration program would use equation 2.15 we use the same set of five reversible reactions.

$$\begin{cases} \text{Calcite} \quad Ca^{2+} + HCO_3{}^{-} & \xrightleftharpoons[k_-^1]{k_+^1} CaCO_3 + H^+ \\ \text{Dolomite} \quad Ca^{2+} + Mg^{2+} + 2\,HCO_3{}^{-} & \xrightleftharpoons[k_-^2]{k_+^2} CaMg(CO_3)_2 + 2\,H^+ \\ \text{Goethite} \quad Fe^{3+} + H_2O & \xrightleftharpoons[k_-^3]{k_+^3} FeOOH + 3\,H^+ \\ \text{Magnetite} \quad 2\,Fe^{3+} + 4\,H_2O + Fe^{2+} & \xrightleftharpoons[k_-^4]{k_+^4} Fe_3O_4 + 8\,H^+ \\ \text{Hematite} \quad 3\,H_2O + 3\,Fe^{3+} & \xrightleftharpoons[k_-^5]{k_+^5} Fe_2O_3 + 6\,H^+ \end{cases} \tag{2.16}$$

In order to make the reaction set easier in later stages and add as many reactions as possible a .txt file is used as input for the program. In previous versions everything was typed by hand per ODE line. As we are looking at the kinetics of chemical reactions we need data for the equilibrium value K, Arrhenius terms for $k_{+/-}$ and the reactions themselves. All these values are put in blocks of 4 lines. One block per reaction. All necessary parameters are found in Palandri et al.[9] or in a rates library [11].

Name of reaction
chemical reaction
A_i's for equilibrium K
Arrhenius terms: pre-exponential, activation energy and activity exponent, for basic, neutral and acid parts

For the dissolution reaction of Calcite it would look like this.

```
Calcite
Ca1C1O3 + 1.0000 H+ = 1.0000 HCO3- + 1.0000 Ca+2
-analytic 4.764488e+003 1.443789e+000 -1.965495e+005 -1.855352e+003 8.937845e+006 -4.900053e-004
-arrhenius 0 0 0 6.59e4 66000 0 1.04e9 67000 1.6
```

lines 1, 3 and 4 are imported and stored in arrays. One array for the names of reactions, one array of the array containing the A_i's used in equation 2.12 and the same for the Arrhenius terms used in equation 2.10. The second line, which is the reaction equation, is done separately as not every reaction uses the same species and at the same order. All lines are put into a matrix with rows for the reactions and columns for the species. Entries of this matrix are the exponential coefficients ($n_{l,i}$ from equation 2.14) of the reaction. The mineral itself, 'Ca1C1O3' for instance, and 'H2O' are not recorded as we don't use them in kinetic equations. For the set of equations 2.16 the matrix would look like this.

$$M = \begin{array}{r|cccccc|} & Ca^{2+} & HCO_3^- & H^+ & Mg^{2+} & Fe^{3+} & Fe^{2+} \\ \hline Calcite & 1 & 1 & -1 & 0 & 0 & 0 \\ Dolomite & 1 & 2 & -2 & 1 & 0 & 0 \\ Goethite & 0 & 0 & -3 & 0 & 1 & 0 \\ Magnetite & 0 & 0 & -8 & 0 & 2 & 1 \\ Hematite & 0 & 0 & -6 & 0 & 2 & 0 \end{array}$$

$$a = \begin{pmatrix} a_{Ca^{2+}} & a_{HCO_3^-} & a_{H^+} & a_{Mg^{2+}} & a_{Fe^{3+}} & a_{Fe^{2+}} \end{pmatrix}$$

We can now split the matrix into the forwards going, positive numbers, and backwards going, negative numbers, reactions. Using the NumPy functions in Python it is very easy and fast to use matrices and arrays, one can even use a matrix as exponent. The next step would be to take the array of the species' activity and exponentiate with the forward matrix and the backwards matrix. Then we multiply each row together. For dolomite this would be backwards = $a_{H^+}^2$ and forwards = $a_{Ca^{2+}} \cdot a_{HCO_3^-}^2 \cdot a_{Mg^{2+}}$.

$$\mathrm{a}^{M_{forwards}} = \begin{pmatrix} a_{Ca^{2+}} \cdot a_{HCO_3^-} \\ a_{Ca^{2+}} \cdot (a_{HCO_3^-})^2 \cdot a_{Mg^{2+}} \\ a_{Fe^{3+}} \\ (a_{Fe^{3+}})^2 \cdot a_{Fe^{2+}} \\ (a_{Fe^{3+}})^2 \end{pmatrix} \qquad a^{M_{backwards}} = \begin{pmatrix} (a_{H^+})^1 \\ (a_{H^+})^2 \\ (a_{H^+})^3 \\ (a_{H^+})^8 \\ (a_{H^+})^6 \end{pmatrix}$$

If we now multiply with k_+ and k_- we get the components per reaction. Then we subtract the backwards reaction from the forwards reaction to get the change in activity per unit time due to a reaction, r.

$$\mathrm{r} = \begin{pmatrix} \mathrm{k}_+^{Calcite} & (a_{Ca^{2+}} \cdot a_{HCO_3^-}) & -k_-^{Calite}(\mathrm{a}_{H^+})^1 \\ \mathrm{k}_+^{Dolomite} & (a_{Ca^{2+}} \cdot (a_{HCO_3^-})^2 \cdot a_{Mg^{2+}}) & -k_-^{Dolomite}(\mathrm{a}_{H^+})^2 \\ \mathrm{k}_+^{Goethite} & (a_{Fe^{3+}}) & -k_-^{Goethite}(\mathrm{a}_{H^+})^3 \\ \mathrm{k}_+^{Magnetite} & ((a_{Fe^{3+}})^2 \cdot a_{Fe^{2+}}) & -k_-^{Magnetite}(\mathrm{a}_{H^+})^8 \\ \mathrm{k}_+^{Hematite} & ((a_{Fe^{3+}})^2) & -\mathrm{k}_-^{Hematite}(\mathrm{a}_{H^+})^6 \end{pmatrix} \qquad M_{normalized} = \begin{pmatrix} 1 & 1 & -1 & 0 & 0 & 0 \\ 1 & 1 & -1 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 & 1 & 0 \\ 0 & 0 & -1 & 0 & 1 & 1 \\ 0 & 0 & -1 & 0 & 1 & 0 \end{pmatrix}$$

For the next step we normalize the matrix M so that all entries are 1 or -1. This normalized matrix can be used to calculate how much the activity of a specie changes due to each reaction. This is done by multiplying the array created by the difference of backwards and forwards, r, with the transposed normalized matrix. We now have the total $\frac{da}{dt}$ per species due to reactions.

In the matrix, M$_{normalized}$, we can see that Fe^{3+}, the fifth column, relates to the last three reactions and as all these entries are 1 we have to add the last three rows of the r array.

Using this reaction part of the CSTR. We fill in equation 2.15. The $\frac{dA}{dt}$ will be the function used as the differential equation: $f(t,a,T) = \frac{dA}{dt}$. To integrate in time a fourth order Runge-Kutta scheme is used. This implicit method is used, as it has greater stability even when dealing with stiff equations such as these. A system of stiff differential equations is a system where the differential equations have a wide range of time scales. In chemical systems it is to be expected that some reactions are in the order of pico seconds, but others at seconds.

3

The necessity of a time-integration program

In this chapter we demonstrate that rate equations quickly become too difficult to solve analytically. We start with one relatively simple reaction which results in a system of differential equations that uses just one equation. For this system it is still possible to analytically solve the system and obtain a function for the activity. The second example is also just one reaction, but now gives a non-linear set of differential equations, that cannot be solved analytically anymore. For these systems we have to use the time-integration program we created.

3.1. Analytic solutions

As a first example I test the halite example given in section 3.1 from Atis 2020[4]. Halite is the mineral word for common table salt. In this example we treat the dissolution of salt.

$$\mathrm{NaCl\,(s)} \underset{-}{\overset{+}{\rightleftharpoons}} \mathrm{Na^+ + Cl^-} \tag{3.1}$$

of which we get the set of equations for the activity of $\mathrm{Na^+}$

$$\begin{cases} \frac{da_{Na^+}}{dt} = k_+ a_{NaCl} - k_- a_{Na^+} a_{Cl^-} \\ a_{Na^+}(t_0) = a_0 \end{cases} . \tag{3.2}$$

Already we can make a few simplifications. Firstly NaCl is a solid so a_{NaCl}=1. According to Rimstidt [10] this is because the reaction occurs at the interface between the solid and the solution and we do not take this into account. Furthermore, in this example we take it that a_{Na^+} and a_{Cl^-} are equal as they are created or used together and we give them the same initial activity . We will abbreviate their activity with the letter a. In other cases it may be that their starting activity differs, then we would have two separate differential equations.

$$\begin{cases} \frac{da}{dt} = k_+ - k_- a^2 \\ a(t_0) = a_0 \end{cases} . \tag{3.3}$$

To find the equilibrium activity we set $\frac{da}{dt}$ equal to zero and solve for $a = a_{eq}$.

$$a_{eq} = \sqrt{\frac{k_+}{k_-}} \equiv \sqrt{K} \tag{3.4}$$

using equation 2.12 we can calculate K. It is also possible to solve equation 3.3 analytically. The derivation of the solution, equation 3.5, can be found in appendix A.1.

$$a(t) = \begin{cases} a_{eq}\tanh\left(\sqrt{k_- k_+}(t+C)\right) & \text{if } a_{eq} > a_0 \\ a_{eq}\frac{1}{\tanh\left(\sqrt{k_- k_+}(t+C)\right)} & \text{if } a_{eq} < a_0 \end{cases} . \tag{3.5}$$

with

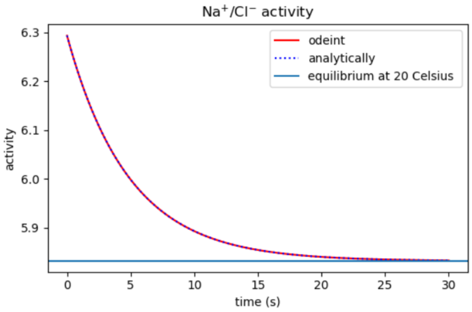

Figure 3.1: Activity of Na^+/Cl^- according to the analytic function and the integration function. Initial activity is 6.29 the equilibrium at 80°C and decreases to its equilibrium at 20°C of 5.83. Note that only one curve is visible as both solutions are so similar they are on top of each other.

	NaCl
A_1	$6.244800 \cdot 10^3$
A_2	$1.851478 \cdot 10^0$
A_3	$-2.624691 \cdot 10^5$
A_4	$-2.423205 \cdot 10^3$
A_5	$1.203027 \cdot 10^7$
A_6	$-6.099010 \cdot 10^{-4}$
$A[1/s]$	12.3
$E_a\ [J/Mole]$	7442

Table 3.1: Parameter values for equations 2.12 and 2.10 for the dissolution of Halite reaction

$$C = \frac{1}{2\sqrt{k_- k_+}} \ln\left(\frac{a_{eq} + a_0}{|a_{eq} - a_0|} \right) - t_0 \tag{3.6}$$

where we find K using equation 2.12 and k_+ by equation 2.10. Also when $a_{eq} = a_0$ or a_0 approaches a_{eq} from above or below the term $\frac{1}{|a_{eq}-a_0|}$ approaches positive infinity. And since $\lim_{x\to\infty} tanh(x) = 1$ both cases of equation 3.5 leads to a(t)= a_{eq}.

Because we know the analytical solution to be true, we could also use the time-integration program to see if it agrees. The time-integration solution is visible in figure 3.1 as odeint. We cannot see the two lines separately as the are on top of each other. This is a good indicator the time-integration program works.

3.2. Non-linearity

We continue to look at the slightly more difficult example of the dissolution of calcite

$$\mathrm{CaCO_3 + H^+ \underset{-}{\overset{+}{\rightleftharpoons}} Ca^{2+} + HCO_3{}^-} \tag{3.7}$$

As this reaction includes acidity we have to include acidity term of Arrhenius equation 2.10.

$$k_+ = A_{CaCO_3} \cdot e^{\frac{-E_a^{CaCO_3}}{RT}} + A_{H^+} \cdot e^{\frac{-E_a^{H^+}}{RT}} \cdot a_{H^+}{}^{1.6} \tag{3.8}$$

The subscript, $CaCO_3$, of the Arrhenius constant here is to signify that it is for the dissolution reaction of Calcite, the neutral term. And H^+ for the fact that the acid term depends on the activity of H^+. Because there is an extra Arrhenius term that depends on one of the species' activity we cannot reuse equation 3.2. It has now become a system of non linear differential equations. These are not easily solved analytically, so we must now rely on our time-integration program.

Just like before we have to derive a system of differential equations. We still neglect the reactions of H^+ and HCO_3^-. we still assume that the activity of Ca^{2+} and HCO_3^- are equal and abbreviated to the variable a. Calcite is a solid so its activity is equal to 1. We now get the following system of equations.

$$\begin{cases} \frac{da}{dt} = k_+ a_{H^+} - k_- a^2 \\ \frac{da_{H^+}}{dt} = k_- a^2 - k_+ a_{H^+} \\ a(t_0) = a_0 \\ a_{H^+}(t_0) = 10^{-pH} \end{cases} . \tag{3.9}$$

It is important to note here that both k_+ and k_- depend on the variable a. In figure 3.2 we have the same starting activity of Ca^{2+} and HCO_3^-, but we use two different starting pH values. It is interesting to see that the pH in both cases goes towards a pH around 7.8, but the activity of Ca^{2+} and HCO_3^- increases on the left and decreases on the right.

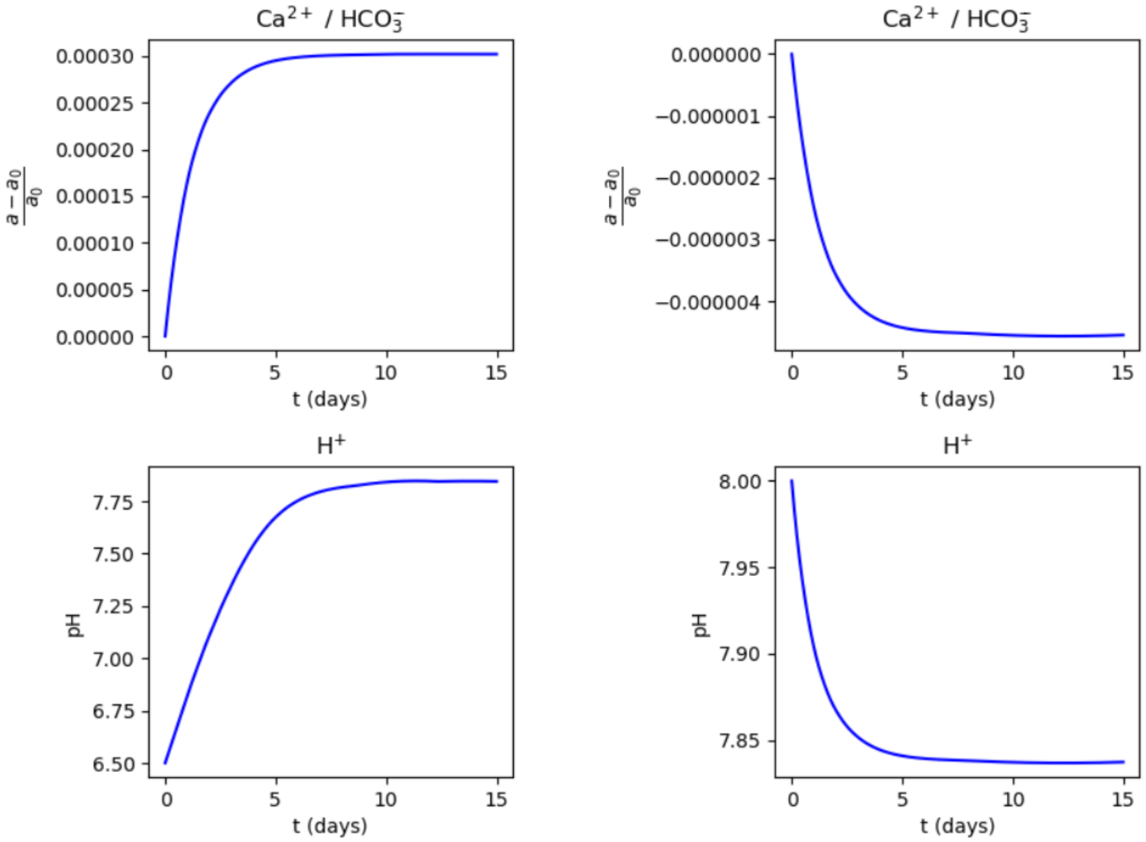

Figure 3.2: Activity of Ca^{2+} / HCO_3^- and pH values. Left figures start with pH=6.5, right figures start with pH=8.0. Both left and right plots use the same starting activity of 0.001 for Ca^{2+} and HCO_3^-. y-axis of activity is scaled by subtracting and dividing by the starting activity $\frac{a-a_0}{a_0}$

We now return to the example given in section 2.3 with the five reactions. All necessary parameters are found in Palandri et al.[9] or in the rates library of the PHREEQC program [11].

$$\begin{cases} \text{Calcite} \quad \mathrm{Ca^{2+} + HCO_3{}^-} & \xrightleftharpoons[k_-^1]{k_+^1} \mathrm{CaCO_3 + H^+} \\ \text{Dolomite} \quad \mathrm{Ca^{2+} + Mg^{2+} + 2\,HCO_3{}^-} & \xrightleftharpoons[k_-^2]{k_+^2} \mathrm{CaMg(CO_3)_2 + 2\,H^+} \\ \text{Goethite} \quad \mathrm{Fe^{3+} + H_2O} & \xrightleftharpoons[k_-^3]{k_+^3} \mathrm{FeOOH + 3\,H^+} \\ \text{Magnetite} \quad \mathrm{2\,Fe^{3+} + 4\,H_2O + Fe^{2+}} & \xrightleftharpoons[k_-^4]{k_+^4} \mathrm{Fe_3O_4 + 8\,H^+} \\ \text{Hematite} \quad \mathrm{3\,H_2O + 3\,Fe^{3+}} & \xrightleftharpoons[k_-^5]{k_+^5} \mathrm{Fe_2O_3 + 6\,H^+} \end{cases} \tag{3.10}$$

We run the program without inflow at 20°C. As starting activities we take the mineral composition of Bar-le-Duc water [1]. For iron we use a different source.[2]. The source found an average amount of iron in deep ground water. It does not say which type of iron so we divide the amount by two for both the isotopes Fe^{3+} and Fe^{2+}. In figure 3.3 we see the activity of the six species over the course of 1 day. The y-axes have been scaled again to show the relative difference from the starting activity. It can be seen that the activities of most species and particularly Fe^{2+} and Mg^{2+} change very little. The pH does change quite significantly.

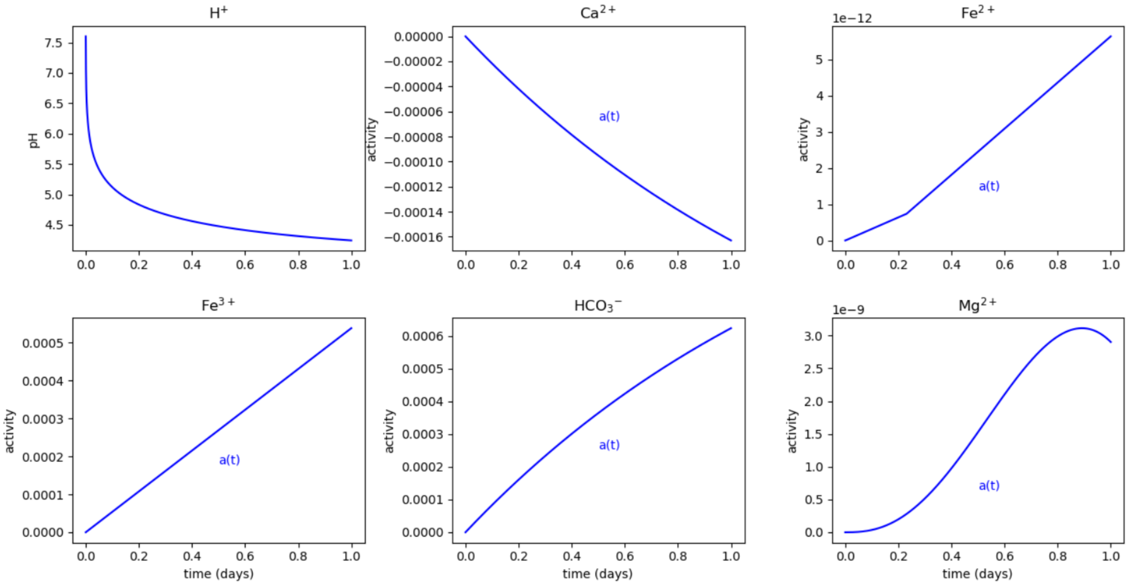

Figure 3.3: 5 reactions, 6 species at 20°C for 1 day. y-axis is scaled to relative activity from starting activity as $\frac{a-a_0}{a_0}$. Starting activities in order are pH 7.6, 47, 0.68, 0.68, 170, 3.4 mg/liter.

4

Testing the time-integration program

In this chapter we aim to test the time-integration program that we made. We shall test two aspects of the program. The first aspect is numerical stability. The systems of equations that we calculate are most likely to be stiff. It is important to know the step size limit of integration in order to prevent error in the calculation. This is done by running the program several times with the same input, but each time increase the size of time steps. The second aspect is the influence of residence time = $\frac{V}{\phi}$. By varying the value of the inflow ϕ we alter the residence time of species in the tank.

It is possible to run the time-integration program until equilibrium is reached for all species. But some species take a very long time to reach their equilibrium. The third section in this chapter is to use non-linear algebraic solvers to find the equilibrium solutions. The solutions of a non-linear algebraic solver are very dependent on the initial guess. The idea is to start by using the time-integration program to integrate an amount of time, then using the activities at that point in time as initial guess in a non-linear algebraic solver.

4.1. Stability of the numerical time-integration

In order to test the numerical stability of the programs time integration of a set of differential equations, the same simulation will be run with increasingly larger time steps. In the following figures the starting and inflow activity will remain the same and ϕ is 0.01 $m^3 s^{-1}$. The y-axis is scaled such that the starting activity is 0 and inflow activity is 1, the volume is 1 m^3. A system of 6 reactions is tested consisting of the 5 reactions from equation 3.10 combined with 3.2. We add the halite reaction as it is much faster than any of the reactions from equation 3.10. We see that it is faster by comparing the time scales of figures 3.1 and 3.3. The halite species reach equilibrium in 30 seconds and the 6 other species do not reach equilibrium after a day. This difference can result in instability for large time steps.

In figure 4.1 the size of a time step is 0.2 seconds. In this figure there is no instability to be seen, so we take this to be the benchmark.

In figure 4.2 the step size increased to 0.25 seconds. We see some instability in the plots of Cl^- and Na^+. There is a jump in the activity. When even further increasing the step size to 0.33 seconds in figure 4.3. We see much instability. The conclusion may be that for this instance of the simulation the turning point for instability is between step sizes of 0.20 and 0.25 seconds.

As the dissolution of halite is a very fast reaction, especially compared to the other reactions, we shall take it out of the simulation to see if we can further increase the step size. before we see instability again.

In figure 4.4 we take a big jump to a step size of 10 seconds. In this figure there is no instability. In the following figure 4.5 the step size is doubled to 20 seconds and there is still no instability.

In figure 4.6 the step size is doubled again to 40 seconds. Because we run the program for 1000 seconds there are only 25 time steps left. Two things now differ from the previous figure. The graph of H^+ is no longer smooth, there is a sharp corner before the pH increases again. The same goes for Fe^{3+}, but also the maximum value of its graph is higher than before.

The largest time step possible before crashing the program is 143 seconds. In figure 4.7 the curves resemble those in the previous figures, but the instability shows in the y-axis of H^+ and Fe^{3+}. The pH now drops to pH=

5.7 instead of the previous pH=5.2 and the peak value of Fe^{3+} is now 70 instead of 1.6. The conclusion is that for this set of 5 reactions 3.10, the tipping point between stability and instability lies between step sizes of 20 and 40 seconds.

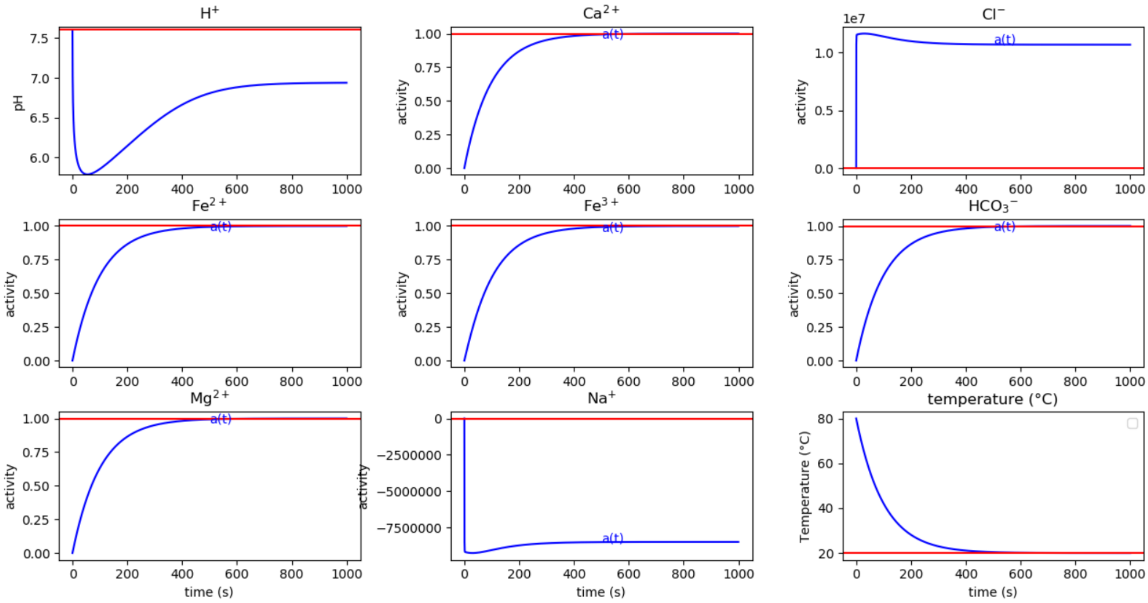

Figure 4.1: Plot of 8 species and temperature for the system of 6 reactions (3.2+3.10). The blue line is the activity or temperature through time, the red line is the inflow activity or temperature. The y-axis is scaled such that 0 corresponds to the starting activity and 1 corresponds to the inflow activity. Time step is 0.2 seconds.

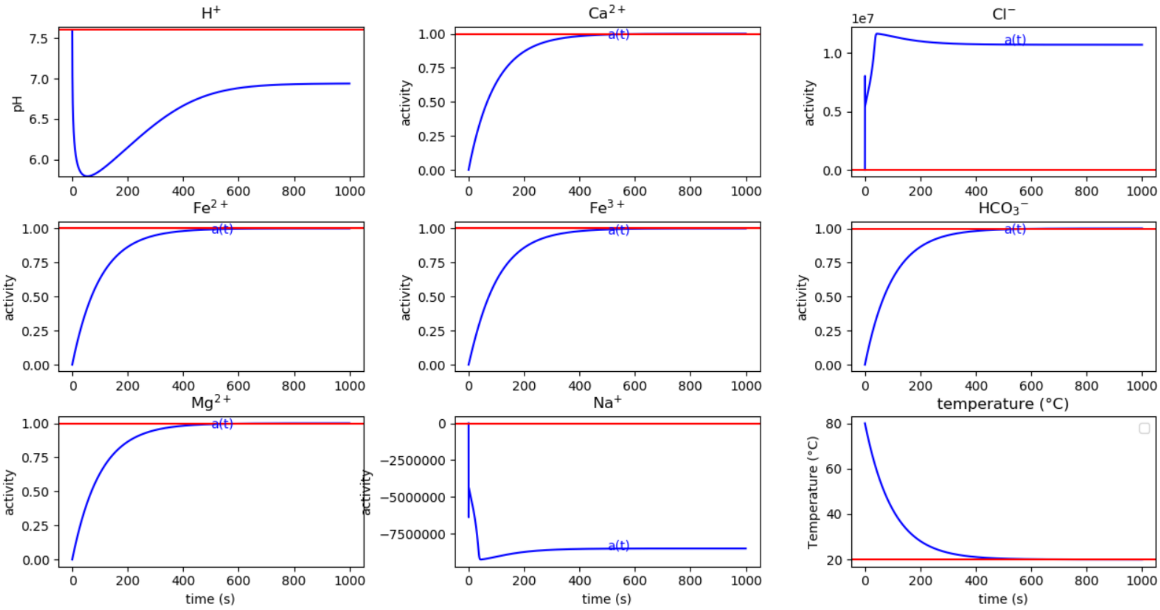

Figure 4.2: Plot of 8 species and temperature for the system of 6 reactions (3.2+3.10). The blue line is the activity or temperature through time, the red line is the inflow activity or temperature. The y-axis is scaled such that 0 corresponds to the starting activity and 1 corresponds to the inflow activity. Time step is 0.25 seconds.

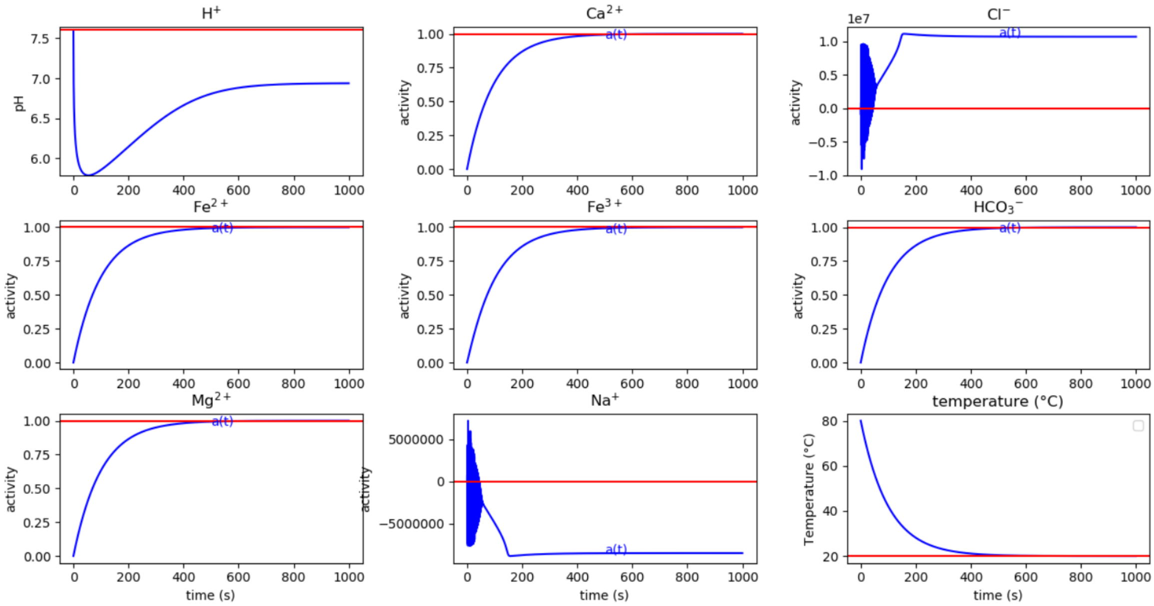

Figure 4.3: Plot of 8 species and temperature for the system of 6 reactions (3.2+3.10). The blue line is the activity or temperature through time, the red line is the inflow activity or temperature. The y-axis is scaled such that 0 corresponds to the starting activity and 1 corresponds to the inflow activity. Time step is 0.33 seconds.

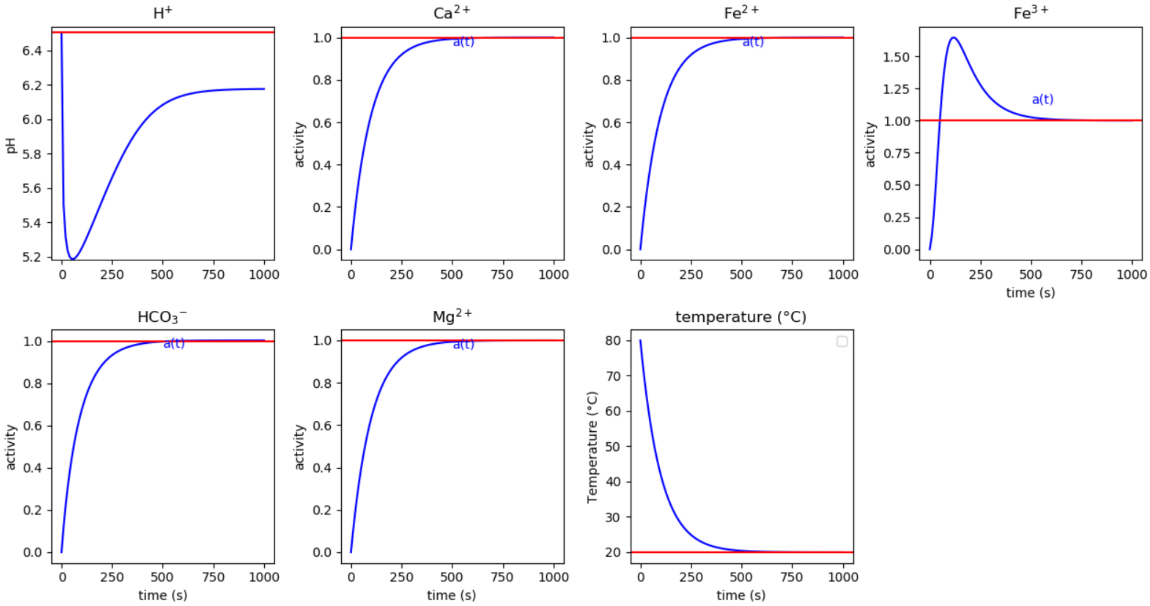

Figure 4.4: Plot of 6 species and temperature for the system of 5 reactions (3.10). The blue line is the activity or temperature through time, the red line is the inflow activity or temperature. The y-axis is scaled such that 0 corresponds to the starting activity and 1 corresponds to the inflow activity. Time step is 10 second.

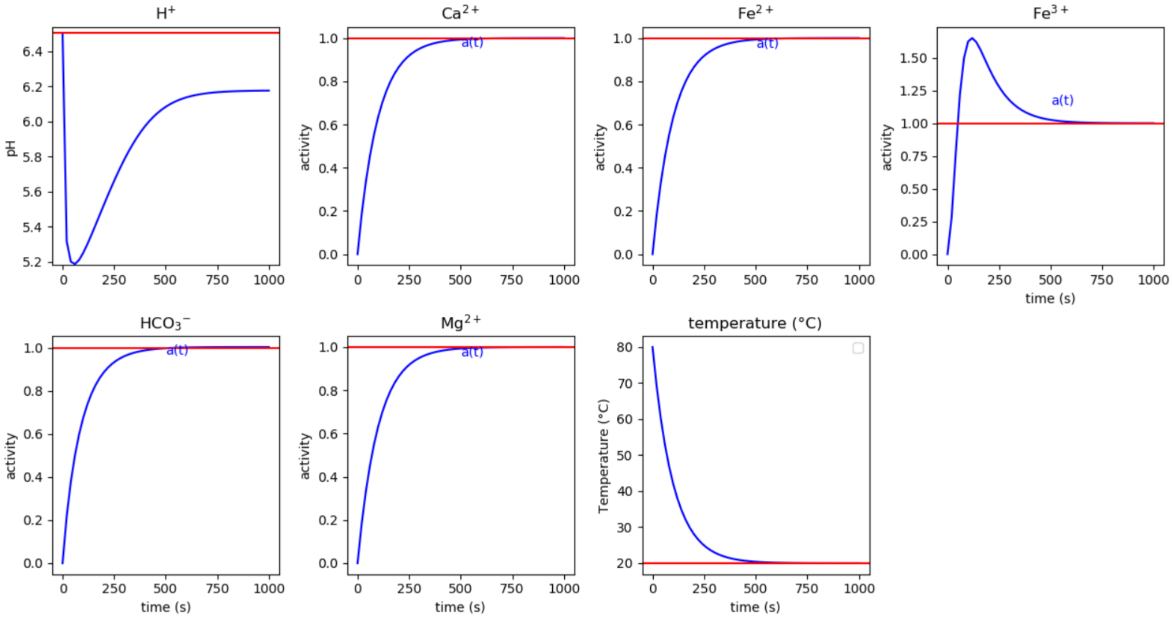

Figure 4.5: Plot of 6 species and temperature for the system of 5 reactions (3.10). The blue line is the activity or temperature through time, the red line is the inflow activity or temperature. The y-axis is scaled such that 0 corresponds to the starting activity and 1 corresponds to the inflow activity. Time step is 20 seconds.

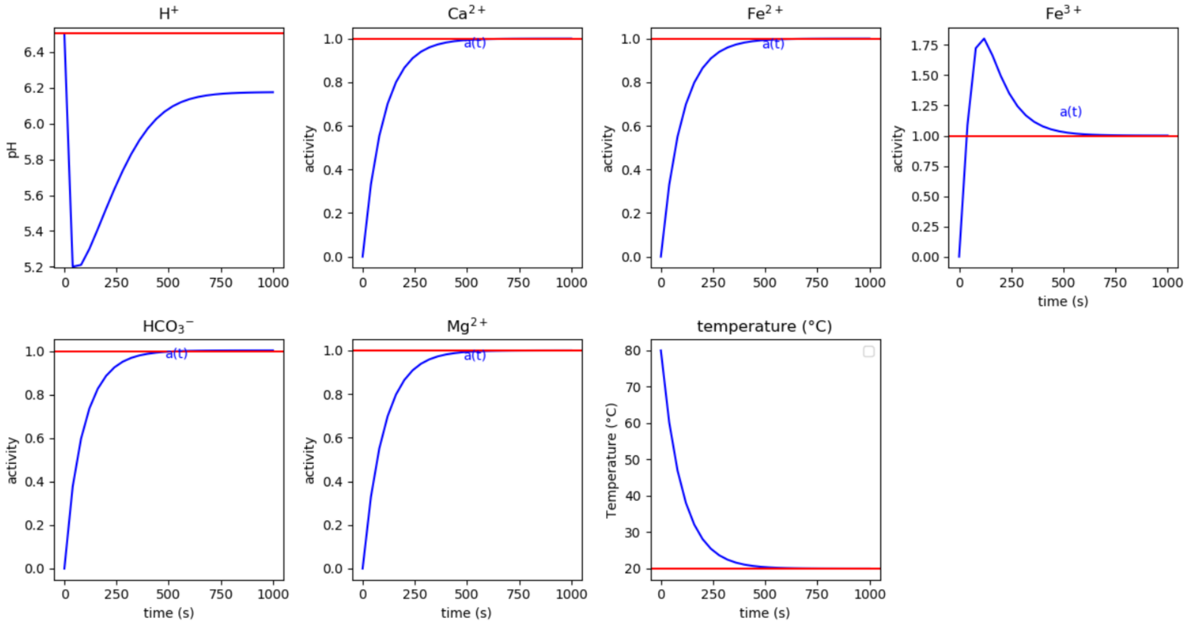

Figure 4.6: Plot of 8 species and temperature for the system of 5 reactions (3.10). The blue line is the activity or temperature through time, the red line is the inflow activity or temperature. The y-axis is scaled such that 0 corresponds to the starting activity and 1 corresponds to the inflow activity. Time step is 40 seconds.

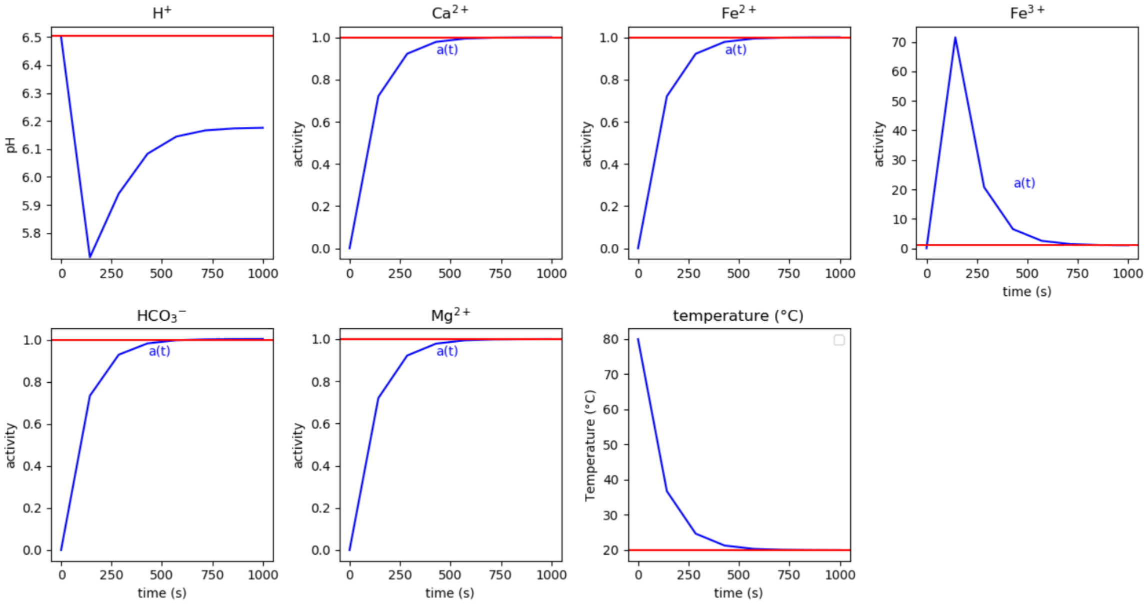

Figure 4.7: Plot of 8 species and temperature for the system of 5 reactions (3.10). The blue line is the activity or temperature through time, the red line is the inflow activity or temperature. The y-axis is scaled such that 0 corresponds to the starting activity and 1 corresponds to the inflow activity. Time step is 143 seconds.

4.2. The influence of residence time on species concentration evolution

To examine the function of the residence time of the tank we graph plots with varying values of $\tau = \frac{V}{\phi}$ in seconds. The volume of the tank is always V= 1 m^3. In the coming plots the blue lines represent the activity through time, except for the first and the last plot, which respectively are the pH value and the temperature. The red line is the inflow activity per species or temperature. So for example the inflowing water has a pH of approximately 6.5 and has a temperature of 20°C.

The x-axis is time in seconds. The y-axis of all species except for H^+ are scaled such that 0 corresponds to the starting activity of that specie, and 1 corresponds to the activity of that specie in the inflowing water called the inflow activity. The inflow activity is between 1% more or less than the starting activity. In these graphs the inflow activity of H^+ is 0.9% less than the starting activity.

In figure 4.8 $\tau = 10^6 s$. As the inflow is very small, none of the species activity converges to the inflow activity. The temperature has hardly changed. Since the y-axes are scaled such that 1 corresponds to the inflow we can see that the kinetics of Fe^{3+} play a much larger role in determining its activity. Its activity is 10^8 times the inflow activity. In the next figures as τ decreases that number drops to 1. The activity of Mg^{2+} becomes negative due to the scaling. This means that the activity is diverging from the inflow value. In this particular case the inflow activity is lower than the starting activity. So the graph becoming negative means that the activity is increasing.

In figure 4.9 and 4.10 $\tau = 10^5 s$ and $10^4 s$ respectively. We see that most activities start converging to the inflow activities. Fe^{2+} is no longer 0; Fe^{3+} has dropped one order of magnitude. The graph of Mg^{2+} went from negative to positive. This signifies that the kinetics part of the ODE for Mg^{2+} is no longer outweighs the inflow/outflow part. For this specie with these parameters the equilibrium τ where the inflow/outflow and the kinetics are equal is somewhere between 10^5 and $10^4 m^3 s^{-1}$

In figure 4.11 $\tau = 10^3 s$. At this point τ is small enough that the inflow/outflow part outweighs the kinetics part of the ODE for all species. In the graphs of H^+, Fe^{3+} and HCO_3^- even show a reversal of direction. This is due to the change in temperature. As the temperature decreases, generally, the reactions are slower, so the inflow/outflow part of the ODE become dominant.

In figure 4.12 $\tau = 10^2 s$. The inflow has become large enough to quickly reach equilibrium. H^+ is the only specie where this equilibrium is not the inflow activity itself.

In figure 4.13 $\tau = 10\ s$. By now the inflow is so large that equilibrium is reached almost instantaneously. The next figure,4.14, will zoom in to the first 100 seconds.

In figure 4.15 $\tau = 1 s$. The time scale now ends at 5 seconds. Again the equilibrium is quickly reached and the equilibrium pH becomes closer to the inflow pH.

The last figure is figure 4.16 where $\tau = 0.2$. The time scale is just 1 second as we would expect from so short a residence time. H^+ remains the only specie that first diverges from the equilibrium activity. It seems that at the higher temperature the reactions that produce H^+ are so fast that at first they can still outpace the inflow.

These simulations were all done using a small enough time step size for each time scale. This was done so there would be no instability.

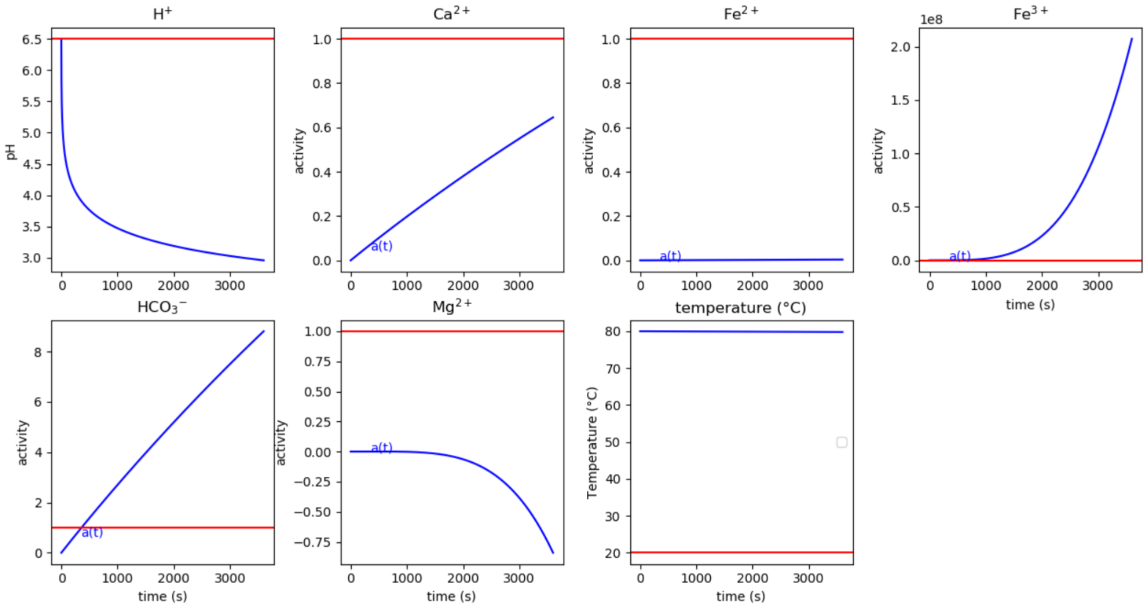

Figure 4.8: 6 plots of species activity and temperature for the system of 5 reactions (3.10) and $\tau = \frac{V}{\phi} = 10^6$s. The blue line represents activity of a species through time, scaled such that 0 correspond to starting activity and 1 to the inflow activity. The red line is the inflow activity or temperature. The activity of H^+ is on the pH scale and temperature is in Celcius. The time scale is 1 hour in seconds.

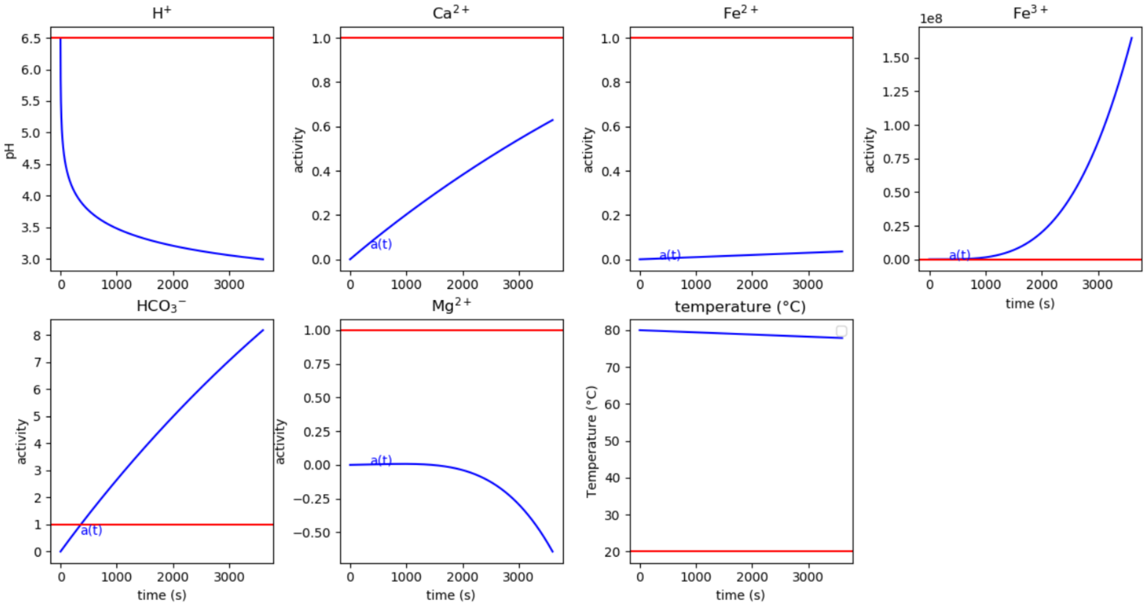

Figure 4.9: 6 plots of species activity and temperature for the system of 5 reactions (3.10) and $\tau = \frac{V}{\phi} = 10^5$s. The blue line represents activity of a species through time, scaled such that 0 correspond to starting activity and 1 to the inflow activity. The red line is the inflow activity or temperature. The activity of H^+ is on the pH scale and temperature is in Celcius. The time scale is 1 hour in seconds.

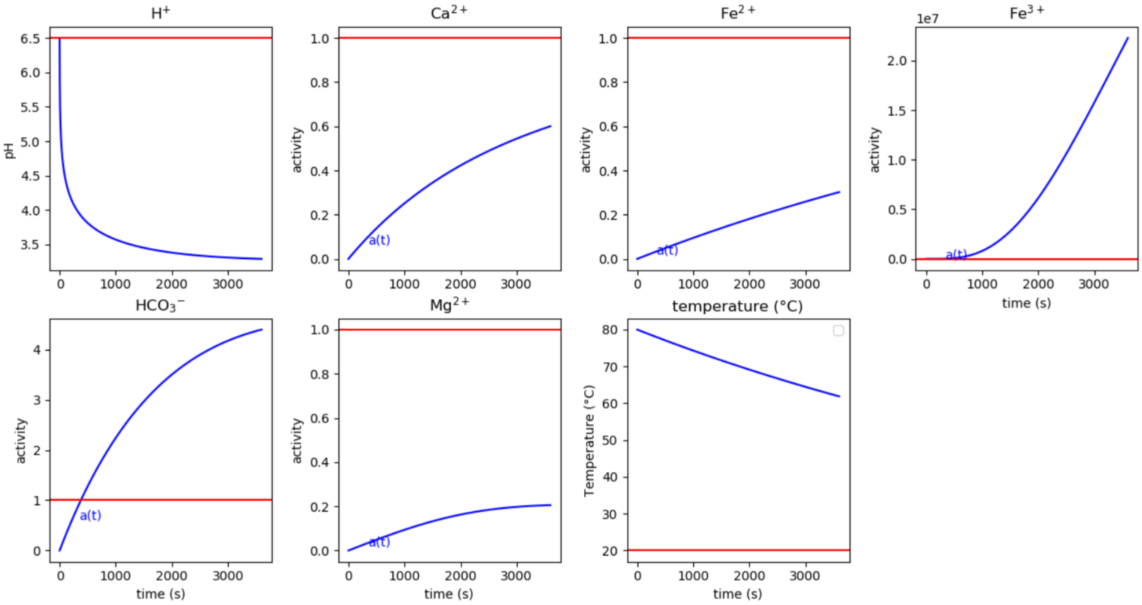

Figure 4.10: 6 plots of species activity and temperature for the system of 5 reactions (3.10) and $\tau = \frac{V}{\phi} = 10^4$s. The blue line represents activity of a species through time, scaled such that 0 correspond to starting activity and 1 to the inflow activity. The red line is the inflow activity or temperature. The activity of H^+ is on the pH scale and temperature is in Celcius. The time scale is 1 hour in seconds.

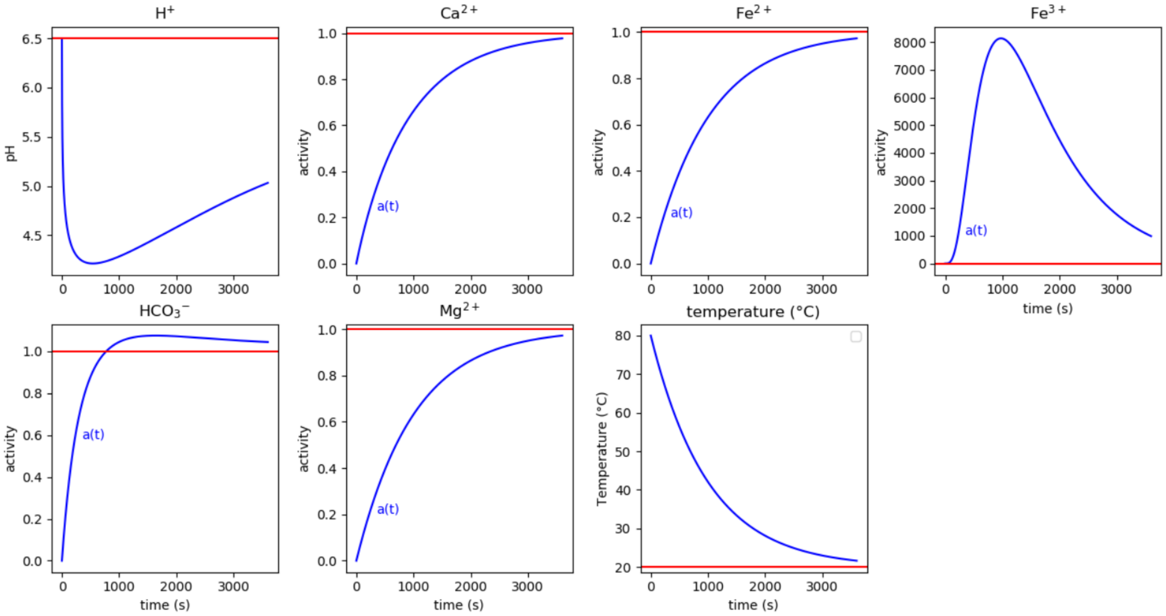

Figure 4.11: 6 plots of species activity and temperature for the system of 5 reactions (3.10) and $\tau = \frac{V}{\phi} = 10^3$s. The blue line represents activity of a species through time, scaled such that 0 correspond to starting activity and 1 to the inflow activity. The red line is the inflow activity or temperature. The activity of H^+ is on the pH scale and temperature is in Celcius. The time scale is 1 hour in seconds.

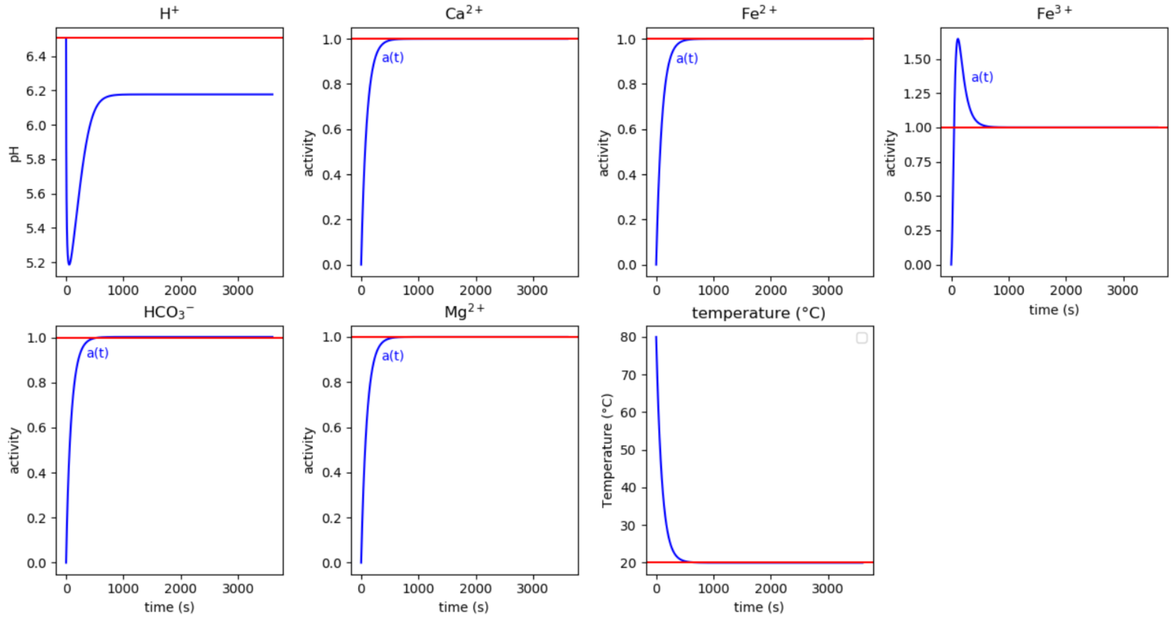

Figure 4.12: 6 plots of species activity and temperature for the system of 5 reactions (3.10) and $\tau = \frac{V}{\phi} = 10^2$s. The blue line represents activity of a species through time, scaled such that 0 correspond to starting activity and 1 to the inflow activity. The red line is the inflow activity or temperature. The activity of H^+ is on the pH scale and temperature is in Celcius. The time scale is 1 hour in seconds.

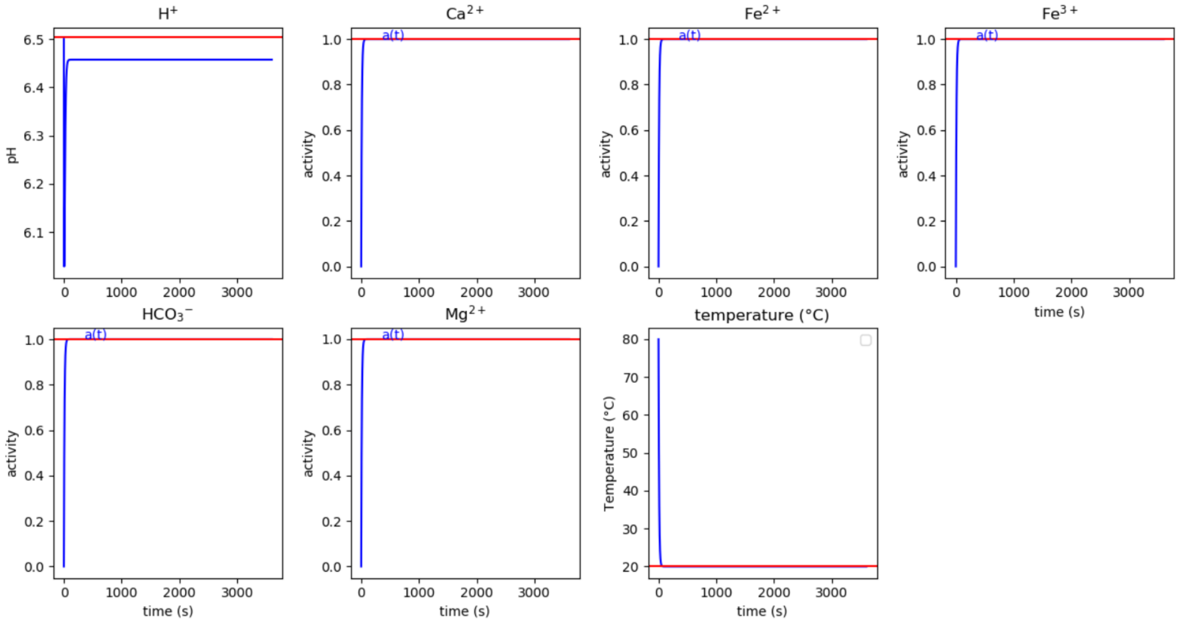

Figure 4.13: 6 plots of species activity and temperature for the system of 5 reactions (3.10) and $\tau = \frac{V}{\phi} = 10$s. The blue line represents activity of a species through time, scaled such that 0 correspond to starting activity and 1 to the inflow activity. The red line is the inflow activity or temperature. The activity of H^+ is on the pH scale and temperature is in Celcius. The time scale is 1 hour in seconds.

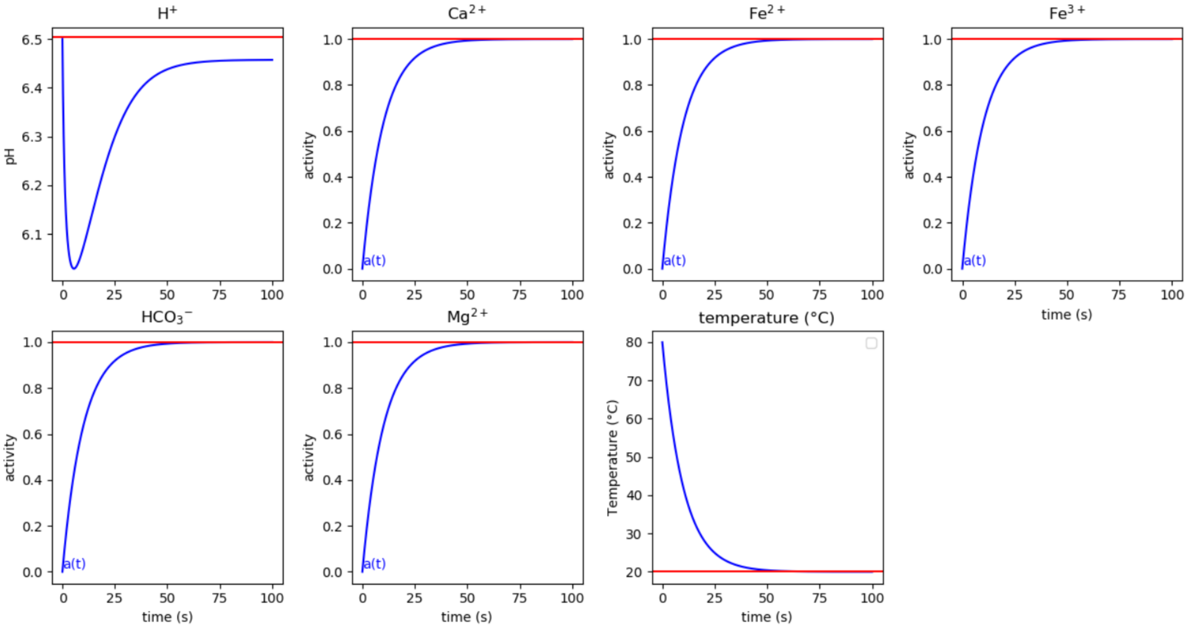

Figure 4.14: 6 plots of species activity and temperature for the system of 5 reactions (3.10) and $\tau = \frac{V}{\phi} = 10$s. The blue line represents activity of a species through time, scaled such that 0 correspond to starting activity and 1 to the inflow activity. The red line is the inflow activity or temperature. The activity of H^+ is on the pH scale and temperature is in Celcius. The time scale is 100 seconds.

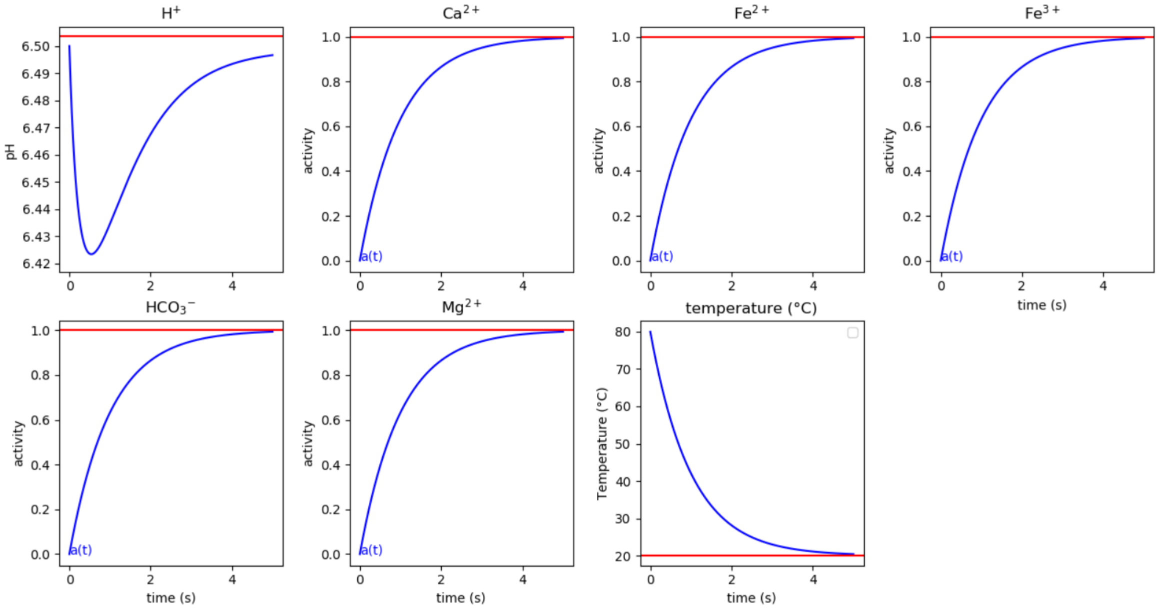

Figure 4.15: 6 plots of species activity and temperature for the system of 5 reactions (3.10) and $\tau = \frac{V}{\phi} = 1$s. The blue line represents activity of a species through time, scaled such that 0 correspond to starting activity and 1 to the inflow activity. The red line is the inflow activity or temperature. The activity of H^+ is on the pH scale and temperature is in Celcius. The time scale is 5 seconds.

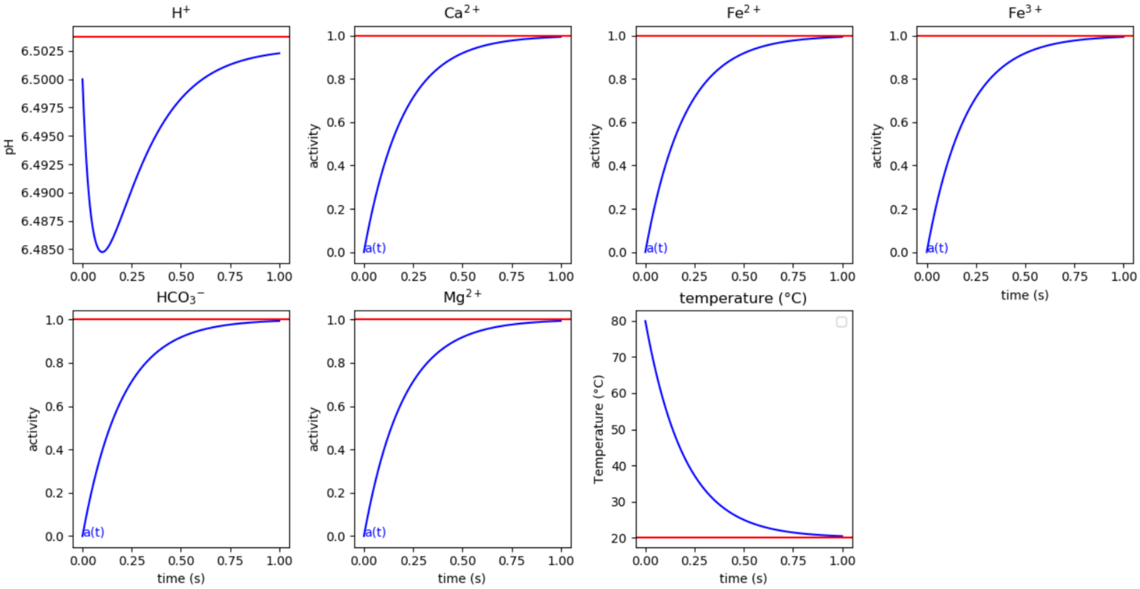

Figure 4.16: 6 plots of species activity and temperature for the system of 5 reactions (3.10) and $\tau = \frac{V}{\phi} = 0.2$s. The blue line represents activity of a species through time, scaled such that 0 correspond to starting activity and 1 to the inflow activity. The red line is the inflow activity or temperature. The activity of H^+ is on the pH scale and temperature is in Celcius. The time scale is 1 second.

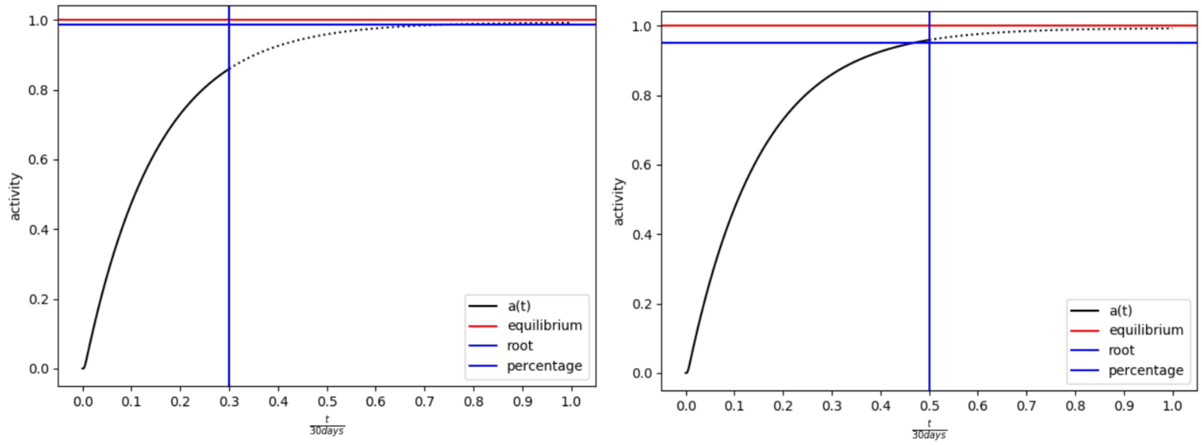

Figure 4.18: Two plot illustrating where the solver gets its x0 and how the root found relates to the actual equilibrium. The left figure starts at 30% and the right figure at 50%. the y-axis is scaled such that a(0)=0 and the equilibrium activity equals 1. the x-axis is scaled such that it represents a percentage of 30 days.

4.3. Using non-linear algebraic solvers to find equilibrium solutions

To find the equilibrium activities of all species it is possible to run the time-integration program until all species reach their equilibrium. This however can take a very long time. To decrease this computation time we could search for the equilibrium activities by solving the algebraic equilibrium equation, that is setting the the left hand side of equation 2.15 to 0, since equilibrium happens when $\frac{dA}{dt} = 0$, and then using algebraic equation solvers. We now have system of algebraic equations, which can be solved using a solving method like Newton-Raphson. The solution is then called a root. To be more precise we shall use the solver 'root' from the SciPy optimize library. scipy.optimize.root has many sub-methods it can use to find the roots of a system of algebraic equations. The default method is the 'hybrid' method which comes from the MINPACK library, which in turn is a modification of Powell's Method [5]. The solver is, as the name suggests, a hybrid of Newtons method.

When using algebraic solvers to find the roots of a system of non-linear algebraic equations the initial guess is very important. If the initial guess is too far away from the actual root, a solver could overshoot and find a different root. An example of this is explained in appendix A.3.

To make sure we have a good initial guess we run our time-integration program for an amount of time. Then we use the activities at that time as initial guess for the algebraic solver. We do this for various amounts of time expressed as a percentage of some total time. For the long-term equilibrium activities, we run the time-integration program until all reactions are in equilibrium. This took a long time as expected.

To look at the error between the algebraic solvers' answer and the long-term equilibrium we turn off the inflow and let the time-integration program simulate 30 days and 9 years at 80 degrees Celsius. We do two different time scales as some reactions reach equilibrium before 30 days, and some much later. We take as initial guess for the algebraic solver the activity at a percentage of time of the 30 days and 9 years. In figure 4.18 an illustration is given of this process. In the left figure we took x0 at 30% of the 30 days. The full curve represents the activity before 30% and the dotted curve represents what would happen if we continued to use the time-integration program to find the equilibrium. The red line is the equilibrium activity and the blue line is the equilibrium activity according to the algebraic solver. The figure on the right takes x0 at 50%. As we can see the equilibrium found by the algebraic solver is further away from the true equilibrium even though x0 was closer this time.

The algebraic solver gives us an array with the algebraic equilibrium . We define the error between the algebraic equilibrium (AE) and the long-term equilibrium (LTE) by the following equation $error = \frac{AE-LTE}{LTE}$. We want to compare this error to the initial guess. Therefore we define the difference between the initial guess and the equilibrium with the same equation $difference = \frac{x_0-LTE}{LTE}$. The error and difference are still arrays, which are hard to compare, so we take the l_2-norm, which is the square root of the sum of squared numbers. $l_2 = \sqrt{d_1^2 + d_2^2 + ...}$

% of 30 days	l_2 norm of difference	l_2 norm of error
0	1.73	1.78
0.5	1.41	1.21
1	1.39	0.00864
2	1.34	0.041
5	1.24	0.0268
10	1.12	0.100
50	0.966	0.0328
100	0.932	0.00590

% of 9 years	l_2 norm of difference	l_2 norm of error
1	0.927	0.0206
2	0.859	0.00716
5	0.684	0.00571
10	0.468	0.00385
50	0.0219	0.00710
100	$1.21 \cdot 10^{-9}$	0.00186

Table 4.1: l_2 norm of the difference between initial guess and long-term equilibrium and l_2 norm of the error between the calculated algebraic equilibrium and the long-term equilibrium. Left table is for the simulation of 30 days. The right table is for the simulation of 9 years

In table 4.1 we see the results of using an algebraic solver. The left table takes percentages of the 30 days run and the table on the right uses the 9 years run. It is important to note that three of the species reach 99% of their equilibrium value after 0.009% of the 30 days, the fourth at 70% and the fifth at 97% of the 9 years. The second column of both the tables is the l_2 norm of the difference and the third column is the l_2 norm of the error.

The difference decreases with each increment in time, this is not always to be expected. In figure 4.16 we see that the pH first decreases and then increases again. At 0% of 30 days, before the program has done anything, we see that the initial guess for the algebraic solver is so bad that it gets us further away from the correct answer than we started with. Also note that 1% of 9 years is 33 days, which is close to 30 days. However the error has increased by a factor of 4. This further shows that the algebraic solver is extremely sensitive to the initial guess.

The table shows that even when the initial guess is very close to the equilibrium, the algebraic solver still gives a root that is not as close as the initial guess. It is clear that using a algebraic solver always gives error. But if we accept the fact that the error is small enough for our purposes, then the table also gives good news. The right table shows that an initial guess that was far away gives roots that have about the same amount of error. This means that in this case it is possible to use a algebraic solver to find the equilibrium with minimal use of the time-integration program.

5

Discussion

We set out to make a program that models what happens when cooled water that went through a heat exchanger that changed the temperature of the water from 80°C into 20°C is pumped back into the hot ground. To do this we used some simple assumptions.

The subterranean earth was reduced to a zero dimensional tank with only one inflow and one outflow. The actual minerals that are in suspension, which we want to track, we do not take into account in the kinetics of the water flowing. In the zero dimensional tank we used a simplified chemistry model of 6 minerals and 6 reversible dissolution reactions.

The time-integration program as is works smoothly. It is stable enough for the step sizes required for most simulations. There were some problems with one of the six reactions, namely the halite reaction, because it was incredibly fast. When excluding this very fast reaction, the program could run 20.000 integration steps for the remaining five reactions in around 5 seconds. The inflow parameter did not cause any additional instability in the numerical procedure. For realistic systems the inflow would be within the orders of magnitude that were tested.

The main reason the program is incomplete at the moment is because there are many reactions missing that regulate the pH. At the moment pH of normal mineral water, the Bar-le-Duc example of figure 3.3, drops to 4. This is not what we would expect normal water under normal circumstances to do. The reason for this is normally the HCO_3^- bicarbonate would react with H^+ to form H_2CO_3 which would then turn into just water and carbon dioxide gas. This reaction and other important reactions are missing to make the program more accurate.

When looking at figure 3.3 we can say that within one day only the pH has changed significantly. Ca^{2+}, Fe^{3+} and HCO_3^- change only 1 part in 10.000. The activities of Fe^{2+} and Mg^{2+} change extremely little in parts per billion or trillion.

6

Conclusion

In this section we draw conclusion from the work in this report and summarize what can be done to improve the time-integration program and model.

To model chemical reaction in the underground water we simplified the underground porous soil to a Continuously Stirred Tank Reactor, where there is an inflow of water containing a concentration of species, and where chemical reactions happen between those species. A time-integration program was written using the Python computer language. A separate file is used to put in the chemical reactions and their parameters. The time-integration program itself works properly and can predict the activities of species as a function of time. The code is very flexible when it comes to adding or deleting reactions by typing the relevant information in the .txt file. When the time-integration program has calculated the activities of the species it automatically plots them in a compact form.

Improvements:
Speed: For now the time-integration program is very fast, as we are only using 5 reactions. When adding many more it could become too slow. It could be usefull to categorize reaction by whether they are slow or fast and then integrate them with separate step sizes.

Accuracy: The time-integration program is incomplete and needs some more features to actually simulate the real world.
- we need to add more reactions that happen even when there are no dissolvable minerals.
- Since the activity of a mineral was always 1, the time-integration program does not know how much of the undissolved mineral there is. There needs to be a part that know how much of a mineral is produced, or how much is dissolved.
-To support this the time-integration program could have some conservation rules that make sure that the amount of atoms stays the same during the chemical reactions.

In addition to just asking whether something is dissolved or not. We could look at the clumping of material when it comes out of solution. We could also introduce the transport equations which would add spacial dimensions to the model.

In the future more things can be added to go back from a CSTR to the real underground. A first thought would be CSTR's set in series and parallel to mimic the 'capillary' structures underground.

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A

Appendix

A.1. The derivation of equation 3.3

In this appendix we follow the same steps taken by Atis [4] in order to derive the solution to equation 3.3

$$\frac{da}{dt} = k_+ - k_- a^2 = k_-(a_{eq}^2 - a^2) = k_-(a_{eq} - a)(a_{eq} + a)$$

Where we use the definition of the equilibrium constant, equation 3.4

$$\frac{da}{k_-(a_{eq} - a)(a_{eq} + a)} = dt$$

$$(\frac{\frac{1}{2a_{eq}}}{a_{eq} - a} + \frac{\frac{1}{2a_{eq}}}{a_{eq} + a})\frac{da}{k_-} = dt$$

$$(\frac{\frac{1}{2a_{eq}}}{a_{eq} - a} + \frac{\frac{1}{2a_{eq}}}{a_{eq} + a})\frac{da}{k_-} = dt$$

formalize the integral with bounds and dummy variables

$$\int_{t_0}^{t} \tilde{t} d\tilde{t} = \frac{1}{2a_{eq}k_-}\int_{a_0}^{a} (\frac{1}{a_{eq} - s} + \frac{1}{a_{eq} + s})ds$$

$$t - t_0 = \frac{1}{2a_{eq}k_-}\Big[-ln(|a_{eq} - s|) + ln(a_{eq} + s)\Big]_{a_0}^{a}$$

$$t - t_0 = \frac{1}{2a_{eq}k_-}\Big[ln(\frac{a_{eq} + a}{|a_{eq} - a|}) - ln(\frac{a_{eq} + a_0}{|a_{eq} - a_0|})\Big]$$

$$ln(\frac{a_{eq} + a}{a_{eq} - a}) = ln(\frac{a_{eq} + a_0}{a_{eq} - a_0}) + (t - t_0)2a_{eq}k_-$$

$$\frac{a_{eq} + a}{|a_{eq} - a|} = \frac{a_{eq} + a_0}{|a_{eq} - a_0|}e^{(t-t_0)2a_{eq}k_-}$$

$$a_{eq} + a = a_{eq}\frac{a_{eq} + a_0}{|a_{eq} - a_0|}e^{(t-t_0)2a_{eq}k_-} - a\frac{a_{eq} + a_0}{|a_{eq} - a_0|}e^{(t-t_0)2a_{eq}k_-}$$

$$a\left(1 + \frac{a_{eq} + a_0}{|a_{eq} - a_0|}e^{(t-t_0)2a_{eq}k_-}\right) = a_{eq}\left(\frac{a_{eq} + a_0}{|a_{eq} - a_0|}e^{(t-t_0)2a_{eq}k_-} - 1\right)$$

$$a = a_{eq}\frac{\frac{a_{eq}+a_0}{|a_{eq}-a_0|}e^{(t-t_0)2a_{eq}k_-} - 1}{1 + \frac{a_{eq}+a_0}{|a_{eq}-a_0|}e^{(t-t_0)2a_{eq}k_-}}$$

now this looks familiar tanh(x)= $\frac{e^{2x}-1}{e^{2x}+1}$. Depending on whether $a_{eq} > a_0$ or not depends if the absolute value changes sign.

$$e^{2x} = \frac{a_{eq}+a_0}{|a_{eq}-a_0|} e^{(t-t_0)2a_{eq}k_-}$$

$$x = \frac{1}{2} ln\Big(\frac{a_{eq}+a_0}{|a_{eq}-a_0|}\Big) + (t-t_0)a_{eq}k_-$$

So we arive at the answer

$$a(t) = \begin{cases} a_{eq}\tanh(\sqrt{k_-k_+}(t+C)) & \text{if } a_{eq} > a_0 \\ a_{eq}\frac{1}{\tanh(\sqrt{k_-k_+}(t+C))} & \text{if } a_{eq} < a_0 \end{cases}.$$

with

$$C = \frac{1}{2\sqrt{k_-k_+}} \ln(\frac{a_{eq}+a_0}{|a_{eq}-a_0|}) - t_0$$

A.2. A mistake on the way

When writing the code for this project I started thinking too simple. I started with the kinetics part, the big matrix M and how we get the $\frac{da}{dt}$. After this is made the simple step to include the inflow and outflow $(a-a_{in})\frac{\phi}{V}$. The mistake I made was not combining it with $\frac{da}{dt}$. What I did was first calculating the kinetics part, putting it through the fourth order Runge-Kutta (RK4) scheme and then separately add the inflow after that. In effect the inflow/outflow was a forward Euler scheme. This caused great instability. Where the example without halite in section 4.1 is stable all the way to time steps between the size of 20 to 40 seconds, figure A.1 was already unstable at time steps of 5 seconds. I have included this figure because it show how important it is we use the RK4 scheme, even when it is just a part of the ODE.

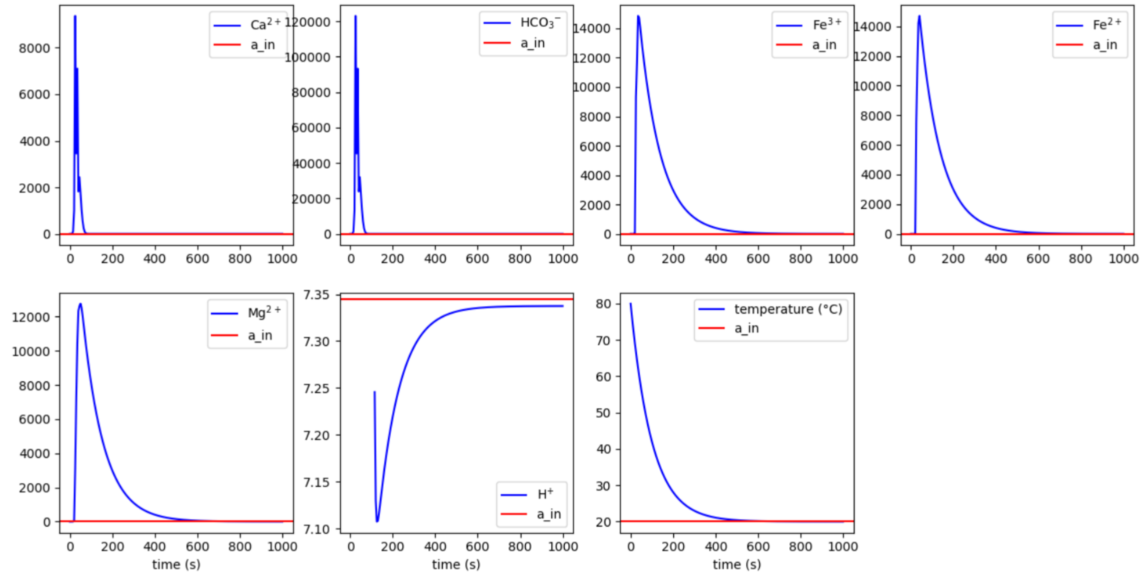

Figure A.1: Plot of a simulation of 6 species and temperature where the blue line is the species activity of temperature and the red line the inflow activity. Time steps of 5 seconds. y-axis is scaled such that 0 is the starting activity and 1 the final activity. This figure was made using old code where inflow/outflow was not included in the RK4 scheme

A.3. Newton’s method with large steps

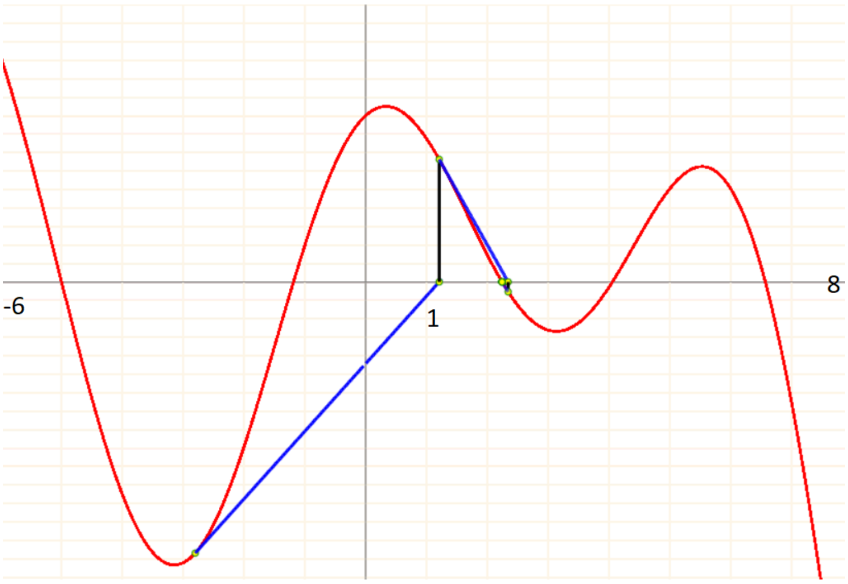

Figure A.2: A plot of $f(x) = 9cos(x) - 0.1x^3 + 3x$ [3] with an initial guess, x0, that leads to a different root

Ìn figure A.2 we see an example of Newton’s method that does not find the nearest root. This time x0 was around -3 and resulted in finding a root at around 2. If x0 was closer to -2 then Newton’s method would have found -1.2 as answer. In this case both roots would be a legitimate answer to the question at what x is f(x) equal to zero. But when when dealing with chemical reactions this is not the case. From any starting point there is only one true answer. And when integrating a set of ODE’s it is possible to obtain the wrong answer by take too large integrating steps.