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MAT 493

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Boom! Chemical Kinetics

Chemical reactions happen all around us every day. “There are reactions when you take medications, light a match, and take a breath” (Helmenstine). The oxygen that we breathe comes from a reaction that converts carbon dioxide into oxygen. Without chemical reactions, the high-tech society that we live in today would be very different. Thirty years ago, some of the electronic products that are so common today were not even possible.

When chemicals react, there must be a collision between the particles with enough energy for the reaction to take place. All chemical reactions occur at different rates. Some reactions are fast, some are slow. Chemical kinetics is a branch of physical chemistry that studies the rates of chemical reactions and the factors that influence the reaction rates (McKibben & Webster). These factors include ideas on how temperature effects the reaction, to how catalysts and inhibitors change the rates of the reaction.

Chemical reactions are made up of reactants. These reactants are transformed into products at a reaction rate, *k*. The rate, *k*, comes from the law of mass action (also called the rate law). The law of mass action, formulated by Guldberg and Waage, states “that the rate of any chemical reaction is proportional to the product of the masses of the reacting substances, with each mass raised to a power equal to the coefficient that occurs in the chemical equation” (“Law of Mass Action”). This definition is shown mathematically by the following reaction diagram:

The forward rate of reaction is and the backward rate of reaction is . The reaction rates are analyzed at equilibrium:

Chemical kinetics problems deal with finding out how the reaction rate is changed by factors of interest. Factors of interest include: Concentration, Temperature, Pressure, Surface Area, Catalysts, and Inhibitors (“Chemical Reactions and Catalysts”). Two models will be studied throughout this paper, the Two-step sequence first-order reaction model (2-SFOM) and the Two-step sequence first order reaction model with back reactions (2-SFOBM). These reactions are of first order because the concentrations of the reactants and the products are all raised to the power of one. The model diagram for (2-SFOM) and (2-SFOBM) are shown below:

(1)

(2)

The difference between models (1) and (2) is that in model (1), A is being transformed into B, but nothing is being transformed back into A. In model (2), when A is transformed into B, some of B may transform back into A. Applying the rate law to models (1) and (2) yields the following set of differential equations:

(1.1)

(2.1)

In (1.1) and (2.1), [A](0), [B](0), and [C](0) represents the concentrations of A, B, and C at time in moles per liter.

Models (1.1) and (2.1) can be rewritten into a compact vector form, with a coefficient matrix containing all of the reaction rates. This is known as a Homogeneous Cauchy Problem (HCP). HCP has the following form:

Rewriting (1.1) and (2.1) into HCP gives:

(1.3)

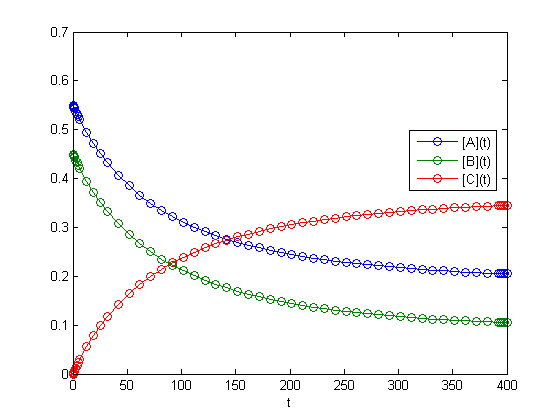
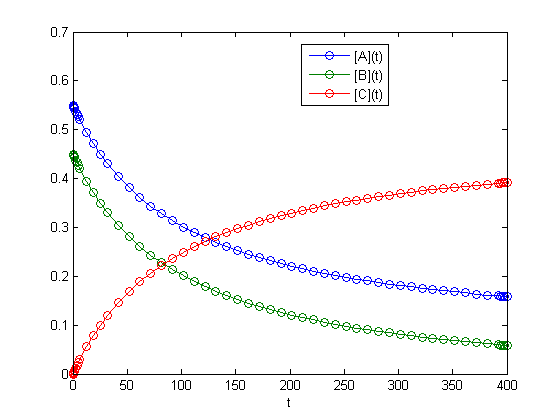
(2.3)

Rewriting these models in HCP has many benefits. If the model can be written in HCP form, then it must have a solution. Theorem 4.6.1 states that for every , HCP has a unique classical solution given by:

Clearly for (1.3) and (2.3), . With this condition satisfied, (1.3) and (1.4) have unique solutions of the form shown above, with . Chemical reaction models can consist of more than just two steps. In the two step model, reactant A transforms into B, which then transforms into product C. In an n-step reaction, A transforms into B, which will transform into other products n times until it reaches the final product. This n-step reaction will consist of an coefficient matrix, and a initial condition vector, which satisfies the requirement of . So, the n-step reaction model has a solution of the same form as the 2-step reaction.

The rate of reaction for these reaction models must all be calculated by humans. The rate law uses the concentration of the reactants and products to calculate the rate. This calculation relies heavily on measuring the concentrations of the reactants and products. We would like these perturbed models to behave just like the non-perturbed models, meaning that the solutions behave the same. In **EXPLORE!** (118-120), as long as the measurement errors are small, the perturbed (1.3) and (2.3) behave exactly like the unaltered versions. Therefore, (1.3) and (2.3) depend continuously on the initial data.

Chemical reaction models with and without back reactions are similar. Figure 1 show the MATLAB GUI printouts of two reaction models, one with back reactions and one without.

  
**Figure 1**. MATLAB\_Reactions GUI printouts. Model without back reactions (left) and with back reactions (right)

The MATLAB\_Reactions GUI assumes a reaction of the form:

For a model with [A](0) = 0.55, [B](0) = 0.45, and [C](0) = 0, the concentrations of the reactants and product are shown by the colored lines. The model had a forward rate of reaction of 0.02 and a backward rate of ration of 0.001. The concentrations were observed for 400 seconds. In both cases, the concentrations of A and B have decreased from their initial point, while the concentration of C increased. When back reactions are included, the concentrations of A and B decrease at a slower rate. This is due to when A and B transform into C, some of C might transform back into A and B. This also explains why the concentration of C in the model with back reactions is lower than the model without back reactions.

As mentioned earlier, the reaction rates can be affected by factors of interest. If the pressure were to increase, the particles in the reaction will be forced closer to each other, making a collision more likely. Likewise, “Catalysts are chemicals that speed up a reaction without actually entering into it” (Green). Models (1) and (2) can be modified to include these factors of interest:

(3)

(4)

In (3) and (4), X represents the catalyst. When the rate law is applied to (3) and (4), the following systems are created:

(3.1)

(4.1)

Models (3.1) and (4.1) are similar to their HCP counterparts. However, these models cannot be written in HCP form. The models can still be written in a compact vector form with a coefficient matrix, but now an additional term is added on to capture the effects of the catalyst in the model. This is known as a Non-homogeneous Cauchy Problem (Non-CP). Non-CP has the following form:

Rewriting (3.1) and (4.1) into Non-CP form gives:

(3.2)

(4.2)

Rewriting these models in Non-CP form has many advantages. One of these advantages is that a solution equation is easily found. Theorem 5.3.1 states that if , , be a continuous function, then Non-CP has a unique classical solution given by:

Clearly for (3.2) and (4.2), **A** is a matrix in and is in , and . With the conditions met, (3.2) and (4.2) have solutions of the form above with . Similar to the HCP case, reactions can consist of more than two steps. For the n-step reaction, the same conditions hold as HCP, except now a forcing term is added on. This reaction model will satisfy Theorem 5.3.1 and a solution of the form above exists.

When describing a model in Non-CP, there is an assumption that the exact nature of the forcing term is known for all time. This assumption is not realistic because of the imprecision of the measurement of the term. The ideal case is that these small errors in measurement do not change how the solution behaves. This is the same idea as the HCP case, except now the model has an extra term (the forcing term). As seen in **EXPLORE!** (145-147), as long as the measurement errors are sufficiently small, Non-CP will depend continuously on the initial data.

Chemical reactions are important in our daily lives. In fact, chemical reactions occur within all living things. However, most of these reactions occur too slowly to sustain life. As mentioned above, catalysts help speed up chemical reactions. “Enzymes are proteins that speed up chemical reactions in the cell” (McKinley & O’Loughlin). In enzyme models, the reactants are call substrates, and when they join, an enzyme-substrate complex is formed. This process creates a new product, and when the product is released, the enzyme goes to work again to repeat the process with another substrate.

The enzyme process was modeled by Leonor Michaelis and Maud Leonora Menten. “The model serves to explain how an enzyme can cause kinetic rate enhancement of a reaction and explains how reaction rates depend on the concentration of enzyme and substrate” (Le, Algaze, & Tan). A Michaelis-Menten Enzyme Kinetics model is shown below:

In the model, E represents the enzyme, S represent a substrate, ES and EZ are enzyme complexes, and Z and P are products. To make the analysis simpler, the overall model will be broken down into two smaller models: the first model being the two top lines, and the second being the bottom. Applying the rate law to these smaller models yields (with appropriate initial conditions):

These models make use of a few assumptions. The first assumption is that the total concentration of the enzyme catalyst remains constant, shown below as:

The second assumption is the quasi-steady-state assumption. This means that we are assuming that the reaction is in a steady-state, when realistically it is not. Mathematically, this represented as:

When these assumptions are applied to and , the following models are created:

Every model that we have seen so far was able to be written in a compact vector form, with a coefficient matrix. Some models included a forcing term. These two models cannot be written in HCP or Non-CP form. To analyze the solution to these two models, they must be written as a Semi-linear Cauchy Problem (Semi-CP). Semi-CP has the following form:

However, these models cannot be written in Semi-CP form. There is no way to identify the coefficient matrix for these two Michaelis-Menten models. Therefore, the model is not in semi-linear form, or in any form that can be analyzed using the tools learned in class.

Suppose that solutions of the form exist. A first and second order Taylor approximation for can be used to create two models that can be analyzed in Semi-CP form. Consider these two models:

(6)

(7)

where,

The assumptions made here are the same as the assumptions made for the Michaelis-Menten model. When is distributed through in each equation, it becomes easy to identify the parts of the model that make up Semi-CP:

(6.1)

(7.1)

Rewriting these models in Semi-CP form yields:

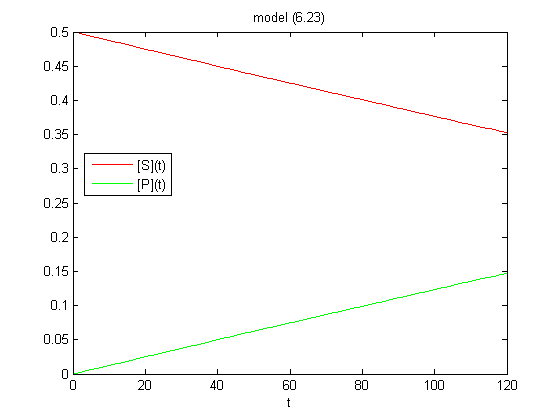
(6.2)

(7.2)

Writing these models in Semi-CP form has advantages. Theorem 7.6.1 states that if , , and be a continuous function, then Semi-CP has a unique mild solution given by:

for all real numbers .

For models (6.2) and (7.2), clearly and and . With the conditions met, (6.2) and (7.2) have unique mild solutions given by the form above with . The behavior of the solution of (6.2) and (7.2) will generally be the same. Model (7.2) will be more accurate than (6.2) because (7.2) has an additional Taylor approximation term. In general, the more Taylor approximation terms that are included in the model, the more accurate the model will be. In general, both models will behave similar to what is shown in Figure 2, which shows the behavior of [S] and [P] as time grows large.

  
**Figure 2**. MATLAB\_Reactions\_Semilinear GUI printout.

All of the reactions seen in this paper are of first order. Chemical reactions can be of second, third, or even fourth order. Generally, the higher the order of the reaction, the more complex the model. Combining kinetics with thermodynamics can create a deeper understand of how a chemical reaction works. “Thermodynamics tells us which direction a reaction will go … kinetics can tell us how quickly it will get there” (Krylov).

Some of these models could be improved. For example, in (1) and (2), the model just assumes a single reactant transforming into a single product. There are many other reactions that use a sum of two or three reactants in each step, and they might create more than one product. Also, there can be reactants of higher order included in the reaction with each other. For example, a reaction of the form:

This model is very different from (1) and (2), but is still analyzed in the same way.

In conclusion, chemical reactions are very important to how the world works. All of the objects around us are made up of chemicals. Some of the objects that we use in our everyday lives would not be possible without chemical reactions. Chemical reactions allow life to exist, and keep living things living. The kinetics behind all of the reactions allow us to understand how these reactions work, and how we can change them to create new objects.

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