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Math 231:Introduction to Ordinary Differential Equations
Mini-Project: Modeling Chemical Reaction Mechanisms

Chemical kinetics, a topic in several chemistry courses, illustrates the connection between mathematics and chemistry. Chemical kinetics deals with chemistry experiments and interprets them in terms of a mathematical model. The experiments are perfomed on chemical reactions as they proceed with time. The models are differential equations for the rates at which reactants are consumed and products are produced. By combining models with experiments, chemists are able to understand how chemical reactions take place at the molecular level.

A reaction mechanism is a collection of reactions showing how molecules react in steps to lead to the overall stoichiometric reaction. The set of reactions specifies the path (or paths) that reactant molecules take to finally arrive at the product molecules. Starting from reactant molecules intermediates may be formed and the intermediate molecules subsequently react to form products. All species in the reaction appear in at least one step and the sum of the steps gives the overall reaction. The mechanism leads directly to differential equations that govern the rate of the reaction.

Each species in the mechanism is consumed or formed at a rate with contributions from various steps in the mechanism. Steps that form a species contribute positive terms and those that consume the species contribute negative terms to the rate. Coefficients of species in the mechanism steps appear as powers in the terms of the rate equations. We say a step is bimolecular when two molecules come together before a reaction, unimolecular when one molecule reacts without colliding with another, termolecular if three must collide, etc.

Caveat - Disclaimer It is impossible to assign a mechanism with complete certainty to any real chemical reaction. The best that can be done is to find a mechanism that is consistent with the known data about the reaction. Sometimes more than one mechanism is consistent with the data; in such cases new experiments are needed to choose between mechanisms.

Instructions: For the following three problem settings you will need to: 1. Do a full phase plane analysis for the system of two equations that result after making the prescribed simplification instructed at the end of each setting. Find equillibria, comment on their apparent stability or instability, and explain your results in terms of the behavior of the physical problem described.

Problem Setting 1. **The Lotka-Volterra Model of Oscillating Chemical Reactions**

This is the earliest proposed explanation for why a reaction may oscillate. In 1920 Lotka proposed the following reaction mechanism (with corresponding rate equations). Each reaction step refers to the MOLECULAR mechanism by which the reactant molecules combine to produce intermediates or products. For example, in step 1 a molecule of species A combines with a molecule of species X to yield two molecules of species X. This step depletes molecules A (and adds molecules X) at a rate proportional to the product of the concentrations of A and X. **Molecular reaction step contributions to differential rate laws:**

1 $A + X \rightarrow 2X$ with reaction rate k_1

2 $X + Y \rightarrow 2Y$ with reaction rate k_2

3 $Y \rightarrow B$ with reaction rate k_3

The effective rate laws for the reactant A, the product B, and the intermediates X and Y are found by summing the contributions from each step:

1 $\frac{d[A]}{dt} = -k_1[A][X]$

2 $\frac{d[X]}{dt} = k_1[A][X] - k_2[X][Y]$

3 $\frac{d[Y]}{dt} = k_2[X][Y] - k_3[Y]$

4 $\frac{d[B]}{dt} = k_3[Y]$

Instructions: Assume that the concentration of the reactant A is actually held constant (it is fed into the system at a rate equivalent to it's removal by reaction). Note also that $\frac{d(A+X+Y+B)}{dt} = 0$, so that the sum $A + X + Y + B$ is always constant. In particular $A + B + X + Y = A_0 + X_0 + Y_0$, assuming there is no product B present initially. This tells us that we don't need to actually solve the ODE for $B = X_0 - X + Y_0 - Y$ if we know $X(t)$ and $Y(t)$. So, in this case, we can reduce the system to two ODE's for X and Y only. Use these two in your analysis.

Problem Setting 2. **Bimolecular decomposition**

Mechanism:

Step one: $2A \rightarrow A + A*$; with rate constant k_1.

Two molecules of A collide and one acquires energy leaving it in an excited state A*. This is a bimolecular step requiring that two molecules of A come together.

Step two: $A * + A \rightarrow 2A$; with rate constant k_1.

Step one is reversible. This is also bimolecular since A* must collide with A for deactivation to occur.

Step three: $A* \rightarrow B$; with rate constant k_2.

Excited molecule $A*$ can rearrange to form the product B. This is a unimolecular process since no molecular collisions are required. The overall reaction is found by adding steps one, two and three with multipliers so that the intermediate $A*$ cancels: $2(2A \rightarrow A + A*) + (A * + A \rightarrow 2A) + (A* \rightarrow B) = A \rightarrow B$.

Translation into Differential rate equations:

$$d[A]/dt = -k_1[A]^2 + k_1[A*][A]$$

;

Species A is consumed in step one and re-generated in step two. The products of concentrations reflects the increased frequency of bimolecular collisions as concentrations of colliders increases.

$$d[A*]/dt = k_1[A]^2 - k_1[A*][A] - k_2[A*]$$

;

Species A* is formed in the bimolecular collisions of step one. It is removed in the bimolecular collisions of step two and in the unimolecular step three.

$$d[B]/dt = k_2[A*]$$

;

The product species B is created in step three.

The mechanism has yielded three coupled differential equations that might be solved with a software tool.

Instructions: As in problem setting 1, B does not need to be solved for through its ODE, since $\frac{d(A+A*+B)}{dt} = 0$. Solve the system for A and $A*$ alone and deduce B from that solution.

Problem Setting 3. **Reaction between dinitrogen pentoxide and nitric oxide**

In this project you will write the rate equations for the following proposed mechanism for reaction between dinitrogen pentoxide and nitric oxide in the gas phase, and study the resulting system of equations.

- step one: $N_2O_5 \rightarrow NO_2 + NO_3$, rate constant k_1 (reactant N_2O_5 dissociates to two intermediates: NO_2 and NO_3)
- step two: $NO_2 + NO_3 \rightarrow N_2O_5$, rate constant k_2 (step one is reversible)
- step three: $NO + NO_3 \rightarrow 2NO_2$, rate constant k_3 (reactant NO combines with one of the dissociation intermediates of step 1)

NOTE: In addition to the above mentioned work, you must first develop the system of ODE's that represents the above reaction of N_2O_5 and NO. Here we will assume that the toxic end product of this reaction, nitrogen dioxide (NO_2) is kept at a constant level in the system (it is removed at the same rate it is created), and note that similar to the other two examples, $\frac{d([N_2O_5]+[NO_3]-[NO])}{dt} = 0$ so that $[NO]$ does not need to be solved for through its ODE, but can be expressed in terms of the other two concentrations. Thus a system can be obtain of two ODEs in terms $[N_2O_5]$ and $[NO_3]$ only. This is the system you will analyze.

Nitric oxide, or nitrogen oxide, also known as nitrogen monoxide, is a molecule with chemical formula NO. It is a free radical and is an important intermediate in the chemical industry. Nitric oxide is a by-product of combustion of substances in the air, as in automobile engines, fossil fuel power plants, and is produced naturally during the electrical discharges of lightning in thunderstorms. In mammals including humans, NO is an important cellular signaling molecule involved in many physiological and pathological processes. Low levels of nitric oxide production are important in protecting organs such as the liver from ischemic damage. Nitric oxide should not be confused with nitrous oxide (N_2O), an anaesthetic and greenhouse gas, or with nitrogen dioxide (NO_2), a brown toxic gas and a major air pollutant. However, nitric oxide is rapidly oxidised in air to nitrogen dioxide. Humphry Davy discovered this to his discomfort, when he inhaled the gas early in his career.

Dinitrogen pentoxide is the chemical compound with the formula N2O5. Also known as nitrogen pentoxide, N2O5 is one of the binary nitrogen oxides, a family of compounds that only contain nitrogen and oxygen. It is an unstable and potentially dangerous oxidizer that once was used as a reagent when dissolved in chloroform for nitrations but has largely been superseded by NO2BF4 (nitronium tetrafluoroborate). N2O5 is a rare example of a compound that adopts two structures depending on the conditions: most commonly it is a salt, but under some conditions it is a polar molecule.

Citation: http://www.idea.wsu.edu/ChemKinetics/mechanism.htm