

Math 521 Lecture #14

§2.5.1: The Law of Mass Action

We look at the rule that models the rate of chemical reactions based upon their concentrations.

This rule is not limited to chemical reactions as it applies to the interactions of predator and prey, infected and susceptible, seller and buyer, etc.

Example 2.22 (Unitary reaction). A single molecule decays into a daughter particle and releases energy.

This unimolecular reaction is denoted by



with a rate of reaction proportional to the amount present, $r = kX$.

We are using the letter X for both the molecule and its concentration.

The model for the decay of X is the exponential law

$$\frac{dX}{dt} = -kX.$$

Notational we write this as



Example 2.23 (Binary Reaction). A molecule of X and a molecule of Y (the reactants) combine to form a molecule of Z (the product):



The reaction rate presumably depends on the concentrations X and Y : what is the reaction rate $r(X, Y)$?

We expect that $r(0, Y) = 0$ for all Y and $r(X, 0) = 0$ for all X : both X and Y are needed to form Z .

Because the graph of $r(X, Y)$ is identically zero along the horizontal coordinate axes, the partial derivatives $r_X(0, Y), r_{XX}(0, Y), \dots$ and $r_Y(X, 0), r_{YY}(X, 0), \dots$ are identically zero.

By Taylor's Theorem we have that

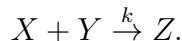
$$\begin{aligned} r(X, Y) &= r(0, 0) + r_X(0, 0)X + r_Y(0, 0)Y \\ &\quad + (1/2)r_{XX}(0, 0) + r_{XY}(0, 0)XY + (1/2)r_{YY}(0, 0)Y^2 + \text{h.o.t.} \\ &= r_{XY}(0, 0)XY + \text{h.o.t.} \end{aligned}$$

Assuming that the rate of the binary reaction is proportional to the product of the concentrations,

$$r(X, Y) = kXY$$

for a rate constant k , is known as the **law of mass action**.

Notational this is written



The rate constant k is not really constant because the rate of reaction also depends on the temperature as in

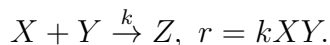
$$k = k_0 \exp(-E/RT)$$

where R is the gas constant, T is the temperature in degrees Kelvin, and E is the activation energy.

This form of k is known as the **Arrhenius rate**.

As a simplifying assumption we will ignore temperature dependence in the rate constant, i.e., we assume the reactions are **isothermal**.

Example 2.27. We show how to get differential equations from



With one molecule of X and one molecule of Y combining at a rate of $r = kXY$ to produce one molecule of Z , we have that the change in the concentrations of X , Y , and Z are determined by

$$\frac{dX}{dt} = -r, \quad \frac{dY}{dt} = -r, \quad \frac{dZ}{dt} = r.$$

By subtracting the second from the first we get

$$\frac{dX}{dt} - \frac{dY}{dt} = 0,$$

so that $X - Y$ is a constant determined by the initial concentrations of X and Y .

The expression $X(t) - Y(t) = X(0) - Y(0) = c$ is a **conservation law**.

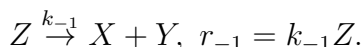
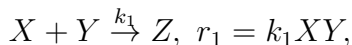
From it we can solve for $Y(t) = X(t) - c$ for all t , which gives the familiar looking logistic growth model for X ,

$$\frac{dX}{dt} = -r = -kXY = -kX(X - c) = kcX \left(1 - \frac{X}{c}\right).$$

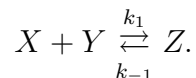
We can assume WLOG that $c = X(0) - Y(0) > 0$, so that $X(t) \rightarrow c$ (the stable equilibrium in the logistic equation) while $Y(t) \rightarrow 0$.

There is another conservation law, namely $X + Z$ is constants with $X(t) + Z(t) = X(0)$ for all t , so that $Z(t) \rightarrow X(0) - c = Y(0)$, i.e., all of Y is converted into Z .

Example 2.28 (Reversible Reactions). Sometimes a reaction is reversible, as in



Notational we write this reversible reaction as



The associated system of differential equations is

$$\frac{dX}{dt} = -r_1 + r_{-1}, \quad \frac{dY}{dt} = -r_1 + r_{-1}, \quad \frac{dZ}{dt} = r_1 - r_{-1}.$$

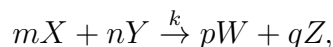
Two conservation laws are $X - Y = c_1$ and $X + Z = c_2$ which allows us to write a single equation

$$\frac{dX}{dt} = -k_1XY + k_{-1}Z = -k_1X(X - c_1) + k_{-1}(c_2 - X).$$

This can be analyzed by the geometric approach to obtain the phase line.

An equilibrium solution of this satisfies $k_1XY = k_{-1}Z$, or $XY/Z = k_{-1}/k_1 = K$ where K , the ratio of the backward to forward rates is called an **equilibrium constant**.

General Reactions and Conservation Laws. Consider the reaction



where m molecules of X react with n molecules of Y to produce p molecules of W and q molecules of Z .

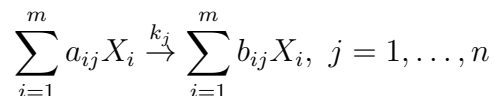
The law of mass action states that the rate of this reaction is $r = kX^mY^n$.

The system of differential equations for this reaction is

$$\frac{dX}{dt} = -mr, \quad \frac{dY}{dt} = -nr, \quad \frac{dW}{dt} = pr, \quad \frac{dZ}{dt} = qr.$$

Some conservation laws here are $nX - mY = c_1$ and $pX + mW = c_2$.

In the most general setting, consider m different chemical species X_i , $i = 1, \dots, m$ and n reactions of the form



where the **stoichiometric coefficients** a_{ij} and b_{ij} are nonnegative integers.

The reactions rates are

$$r_j = k_j \prod_{i=1}^m X_i^{a_{ij}}, \quad j = 1, \dots, n.$$

The system of differential equations for the reactions is

$$\frac{dX_i}{dt} = \sum_{j=1}^n (b_{ij} - a_{ij})r_j, \quad j = 1, \dots, n.$$

If we let S be the $m \times n$ matrix with entries $b_{ij} - a_{ij}$ (the **stoichiometric matrix**), $\vec{X} = [X_1, \dots, X_m]^T$, and $\vec{r} = [r_1, \dots, r_n]^T$, then the system of differential equations in matrix form is

$$\frac{d\vec{X}}{dt} = S\vec{r}.$$

A conservation law has the form

$$\frac{d}{dt} \sum_{i=1}^m c_i X_i = 0$$

for constants c_1, \dots, c_m (not all zero).

In terms of initial concentrations $\vec{X}(0) = [X_1(0), \dots, X_m(0)]^T$ and $\vec{c} = [c_1, \dots, c_m]^T$, we have

$$\vec{c}^T \vec{X} = \vec{c}^T \vec{X}(0).$$

Multiplying the system of differential equations through by \vec{c}^T we get

$$\vec{c}^T S \vec{r} = \vec{c}^T \frac{d\vec{X}}{dt} = \frac{d}{dt} (\vec{c}^T \vec{X}) = \frac{d}{dt} (\vec{c}^T \vec{X}(0)) = 0.$$

This holds for all values of \vec{r} , so that $\vec{c}^T S = 0$, or $S^T \vec{c} = 0$.

Thus the conservation laws are given by nonzero elements $\vec{c} \in \ker S^T$, where the number of linearly independent conservation laws is given by the dimension of the kernel of S^T .