1. Some work toward an Analytic Solution

Consider the system of ordinary differential equations

(1) $$\frac{dx}{dt} = -k_1 z + k_2 xy - k_3 x$$

(2) $$\frac{dy}{dt} = -k_2 xy$$

(3) $$\frac{dz}{dt} = k_1 z - k_2 xy$$

where k_1, k_2, k_3 are positive parameters. Given the physical nature of the problem, we are searching for solutions that are non-negative on the closed interval $[0, t_f]$, where t_f denotes the time when the reaction is complete. Outside of this interval, however, nothing can be said about the behavior of the solution of the system. Since t is the only independent variable in the system, we will denote $\frac{dx}{dt}, \frac{dy}{dt}$, and $\frac{dz}{dt}$ by x', y', and z' respectively, from now and on.

First, let us notice that adding equations (1) and (3) yields that

$$x' + z' = -k_3 x$$

Second, equation (2) yields that

$$ln(y)' = -k_2 x$$

These two equations together imply that

$$ln(y)' = \frac{k_2}{k_3}(x+z)'$$

From this, we get that

(4) $$ln(y) = \frac{k_2}{k_3}(x+z) + C^*,$$

for some $C^* \in \mathbb{R}$. Thus, we get that

(5) $$y = Ce^{\frac{k_2}{k_3}(x+z)}$$

for some $C \in \mathbb{R}$.

On the other hand, $x' + z' = -k_3 x$ implies that

(6) $$z = -k_3 \int x - x$$

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. Thus, we have that

$$y = Ce^{-k_2(\int x)} \tag{7}$$

Thus, if we introduce a new variable v,

$$v \equiv \int x,$$

we get that (1) turns into the second order non-linear homogeneous equation:

$$v'' = -k_1(-k_3 v - v') + k_2 C v' e^{-k_2 v} - k_3 v' \tag{8}$$

Or,

$$v'' + (k_3 - k_1 - k_2 C e^{-k_2 v})v' - k_1 k_3 v = 0 \tag{9}$$

1.1. **Some special Cases.**

1.1.1. $k_2 = 0$. In this case, equation (9) turns into a second order linear homogeneous equation with constant coefficients. It can be checked, due to the positivity of the rate constants, that the solutions to the corresponding characteristic equation are real. If we call these roots λ_1 and λ_2, we have that v, thus x, can be written as a linear combination of $e^{\lambda_1 x}$ and $e^{\lambda_2 x}$, and, since $z = -k_3 \int x - x$, it follows that z is also some linear combination of $e^{\lambda_1 x}$ and $e^{\lambda_2 x}$. Moreover, $y' = 0$, so y is a constant function.

1.1.2. $k_1 = 0$. Although equation (9) is a "simplified" form of the system, we return to the original system to find the solutions for this case:

$$\frac{dx}{dt} = k_2 xy - k_3 x \tag{10}$$

$$\frac{dy}{dt} = -k_2 xy \tag{11}$$

$$\frac{dz}{dt} = -k_2 xy \tag{12}$$

It is clear that z and y differ only by a constant, so, we will focus only upon the first two equations in the simplified system. Make a preliminary change of variables:

$$u \equiv ln(x), w \equiv ln(y)$$

Then, we have that equations (10) and (11) turn into, respectively,

$$\frac{du}{dt} = k_2 e^w - k_3 \tag{13}$$

$$\frac{dw}{dt} = -k_2 e^u \tag{14}$$

If we divide the two equations, we get that

$$\frac{du}{dw} = \frac{k_2 e^w - k_3}{-k_2 e^u}$$

We now have a separable equation, which when solved yields

$$-k_2e^u = k_2e^w - k_3w + D, \tag{15}$$

for some constant D. If we now recall equation (14), we have that

$$\frac{dw}{dt} = k_2e^w - k_3w + D,$$

which is a separable equation. Unfortunately, the integral that shows up on the left hand side of this equation can only be numerically computed.

1.1.3. $k_3 = 0$. It is possible to turn equation (9) into a first order non-linear equation by observing that when $k_3 = 0$,

$$0 = v'' + (k_3 - k_1 - k_2Ce^{-k_2v})v' - k_1k_3v \tag{16}$$

$$= v'' + (-k_1 - k_2Ce^{-k_2v})v' \tag{17}$$

$$= v'' - k_1v' + C(e^{-k_2v})' \tag{18}$$

Thus,

$$E = v' - k_1v + Ce^{-k_2v}, \tag{19}$$

for some constant E. This is, again, a separable equation that involves an integral which cannot be analytically computed.

1.2. **A Taylor Series solution about the initial point $t = 0$.** From the original equations, we see that x,y, and z must be infinitely often differentiable. So, we assume that each of x,y, and z has a Taylor Series expansion around $t = 0$:

$$x = \sum_{j=0}^{\infty} a_jt^j \tag{20}$$

$$y = \sum_{j=0}^{\infty} b_jt^j \tag{21}$$

$$y = \sum_{j=0}^{\infty} c_jt^j \tag{22}$$

Recall that $x' + z' = -k_3x$. Thus, by (20) and (21), we have that

$$\sum_{j=0}^{\infty} (j+1)(a_{j+1} + c_{j+1})t^j = \sum_{j=0}^{\infty} -k_3a_jt^j$$

Thus, we get that for all $j \geq 0$,

$$(j+1)(a_{j+1} + c_{j+1}) = -k_3a_j, \tag{23}$$

so, we can write c_j in terms of a_j and a_{j-1} for each $j \geq 1$. Notice here, that we have no way of knowing c_0 from any a_j, which is expected since c_0 is an initial value. Using the same method, along with the relation

$$y' - z' = -k_1 z,$$

we get that for all $j \geq 1$,

$$b_j = \frac{1}{j}(-k_1 c_0 - k_1(\frac{k_3}{j} a_{j-1} - a_j) + k_3 a_{j-1} - k_3 a_{j-1}) \tag{24}$$

Finally, from equation (1), we get the recursive relation,

$$a_{k+1} = \frac{1}{k+1}(k_1 c_k - k_2 \sum_{i=0}^{j} a_i b_{j-i} - k_3 a_j) \tag{25}$$

which is valid for all $j \geq 0$. We note here that we have demonstrated a way of determining the derivatives of x,y, and z evaluated at 0 up to any order, in terms of k_1, k_2, and k_3.

1.3. **A method to Calculate the Rate Constants.** Consider the original system:

$$\frac{dx}{dt} = -k_1 z + k_2 xy - k_3 x \tag{26}$$

$$\frac{dy}{dt} = -k_2 xy \tag{27}$$

$$\frac{dz}{dt} = k_1 z - k_2 xy \tag{28}$$

Then, notice the following:

$$\frac{z' - y'}{z} = k_1 \tag{29}$$

$$\frac{y'}{-xy} = k_2 \tag{30}$$

$$\frac{x' + z'}{-x} = k_3 \tag{31}$$

Since these relations are true for all values of t, they are true, in particular, for the inital value t=0. Thus, if we can measure (to a good degree of certainty) the value of the rate of increase or decrease in the concentration of x,y, and z initially, we can determine k_1, k_2, and k_3.