Chemical Reaction Kinetics

Differential equations governing the rate of change of chemical concentrations is based on the law of mass action

$$mA + nB \xrightarrow{k} P$$

where m, n are integers; A and B are reactants and P is a product

Law of mass action

$$r = kA^m B^n = \text{reaction rate}$$

Here A, B are concentrations in some units; k is a rate constant

EXAMPLE $\quad A + 2B \underset{k_-}{\overset{k_+}{\rightleftharpoons}} C$

$$\frac{dA}{dt} = -k_+ AB^2 + k_- C$$

$$\frac{dB}{dt} = -2k_+ AB^2 + k_- C$$

$$\frac{dC}{dt} = +k_+ AB^2 - k_- C$$

Here the factor of 2 in $\frac{dB}{dt}$ comes from the fact that twice as many B molecules are lost in the $A + 2B$ reaction as A.

Enzyme Kinetics

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C \xrightarrow[k_3]{} P + B$$

where

A = reactant
B = enzyme
C = reactant/enzyme complex
P = product

The enzyme B is a catalyst to make a product P from A.

Dimensional Equations $\quad (\dot{\ }) = \frac{d}{dt}(\ )$

(1) $\dot{A} = -k_1 AB + k_2 C$

(2) $\dot{B} = -k_1 AB + k_2 C + k_3 C$

(3) $\dot{C} = k_1 AB - k_2 C - k_3 C$

(4) $\dot{P} = k_3 C$

with initial conditions

$$A(0) = A_0 \qquad B(0) = B_0 \qquad C(0) = P(0) = 0$$

The latter indicate initially there is no complex or product.

Adding eqns (2) and (3) we find

$$\frac{d}{dt}(B + C) = 0$$

says that the total amount of enzyme in its bound (complex) and unbound states is constant, i.e.,

$$(5) \qquad B + C = B_0$$

Suffices to examine and nondimensionalize

$$(6) \qquad \dot{A} = -k_1 A (B_0 - C) + k_2 C = F_1(A, C)$$

$$(7) \qquad \dot{C} = +k_1 A (B_0 - C) - (k_2 + k_3) C = F_2(A, C)$$

where

$$A(0) = A_0 \qquad C(0) = 0$$

If we can approximate $C(t)$ from this second order nonlinear system, the product concentration is found from integrating eqn (4):

$$P(t) = k_3 \int_0^t C(s)\, ds$$

Nondimensionalized model

$$a = \frac{A}{A^*} \qquad c = \frac{C_1}{C_1^*} \qquad \tau = \frac{t}{t^*}$$

The choice (see text)

$$A^* = A_0 \qquad \text{initial A conc.}$$

$$C^* = B_0 \qquad \text{initial B conc.}$$

$$t^* = \frac{1}{k_1 B}$$

yields

$$(1) \qquad \frac{da}{d\tau} = -a + (a+\lambda)c \quad , \quad a(0) = 1$$

$$(2) \qquad \varepsilon \frac{dc}{d\tau} = a - (a+\mu)c \quad , \quad c(0) = 0$$

where the three dimensionless parameters

$$\varepsilon = \frac{B_0}{A_0} \qquad \lambda = \frac{k_2}{A_0 k_1} \qquad \mu = \frac{k_2 + k_3}{A_0 k_1}$$

As a model of enzyme kinetics we expect

$$\varepsilon = \frac{B_0}{A_0} << 1 \qquad \text{(assumption)}$$

since 'few' enzyme molecules are needed to facilitate 'product production.

Outer solution $(\varepsilon = 0)$

Letting

$$a(\tau) = a_0(\tau) + o(1) \qquad c(\tau) = c_0(\tau) + o(1)$$

and setting $\varepsilon = 0$ we find, $(\ )' = \frac{d}{d\tau}(\ )$

$$(1') \qquad a_0' = -a_0 + (a_0 + \lambda) c_0$$

$$(2') \qquad 0 = a_0 - (a_0 + \mu) c_0$$

From which (2') implies

$$(3) \qquad c_0 = \frac{a_0}{a_0 + \mu}$$

* Note that even if $a_0(0) = 1$, c_0 does not satisfy the initial condition $c_0(0) = 0$. This implies $c(\tau)$ has an initial layer

Using (3) in (1') we find

$$(4) \qquad \boxed{\frac{da_0}{d\tau} = -\frac{(\mu - \lambda) a_0}{\mu + a_0}}$$

This is the so called Michaelis-Menten reaction rate for enzyme kinetics.

Solving (4) for $a_0(\tau)$ one finds the long term evolution of c_0 from (3) above.

Since there must be a layer at $t=0$, we do not yet know appropriate initial conditions for $a_0(\tau)$.

Nevertheless, eqn (4) is separable

$$\frac{da_0}{d\tau} = -\frac{a_0}{(\mu + a_0)}(\mu - \lambda)$$

$$\left(1 + \frac{\mu}{a_0}\right) da_0 = -(\mu - \lambda)\, dt$$

integrating,

$$\boxed{a_0 + \mu \log a_0 = -(\mu - \lambda)\tau + K}$$

Defines $a_0(\tau)$ in outer region implicitly up to an unknown constant K.

K to be found using matching.

Inner Problem

$$a(\tau) = A(t) \qquad c(\tau) = C(t) \qquad t = \frac{\tau}{\varepsilon}$$

Here the layer width $\delta(\varepsilon) = \varepsilon$.

$$\frac{dA}{dt} = \varepsilon\left(-A + (A+\lambda)C\right) \qquad A(0) = 1$$

$$\frac{dC}{dt} = A - (A+\mu)C \qquad C(0) = 0$$

Inner layer A, C <u>must</u> satisfy I.C.

The leading solution of these equations are

$$A_0(t) = 1$$

$$C_0(t) = \frac{1}{(\mu+1)}\left(1 - e^{-(\mu+1)t}\right)$$

The former follows from $A_0' = 0$, $A_0(0) = 1$. Hence $A_0(t) = 1$ in the leading eqn for C_0, i.e.

$$C_0' = 1 - (1+\mu)C_0 \qquad C_0(0) = 0$$

Here C_0 rises quickly while A_0 changes little.

Matching

$$(\mathrm{I})\quad M_a = \lim_{\tau \to 0^+} a_0(\tau) = \lim_{t \to \infty} A_0(t) = 1$$

$$(\mathrm{II})\quad M_c = \lim_{\tau \to 0^+} c_0(\tau) = \lim_{t \to \infty} C_0(t) = \frac{1}{\mu + 1}$$

The former determines K in the implicitly defined a_0. Recall

$$a_0 + \mu \log a_0 = -(\mu - \lambda)\tau + K$$

as $\tau \to 0^+$, $a_0 \to 1$ for first matching cond $\Rightarrow$

$$1 + \mu \log 1 = 0 + K$$

hence $K = 1$ and a_0 defined implicitly by

$$a_0 + \mu \log a_0 = -(\mu - \lambda)\tau + 1$$

Lastly, (II) is satisfied automatically since

$$\lim_{\tau \to 0^+} C_0 = \lim_{\tau \to 0^+} \frac{a_0}{a_0 + \mu} = \frac{1}{1 + \mu}$$

$$\lim_{t \to \infty} C_0 = \frac{1}{1 + \mu}$$

(See text for uniform solns)