Stochastic chemical kinetics

The general Master Equation is given as follows.

$$\frac{d}{dt}p(x,t) = \sum_y \left[W_{yx}p(x,t) - W_{x,y}p(x,t) \right]$$

We represented the state of the chemical system with the vector $X(t) = [X_1(t), X_2(t), ..., X_n(t)]^T$ where $X_i(t)$ represents the number of molecules of substance i. We can do a random walk over a lattice, where each point is represented by an n-dimensional vector.

Michaelis-Menton

We can revisit Michaelis-Menton now with the Master Equation notation.

$$S_1 + S_2 \rightleftharpoons S_3 \rightarrow S_4 + S_2$$
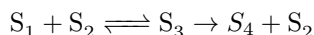
Here, S_1 is substrate, S_2 is enzyme, S_3 is substrate/enzyme complex, and S_4 is product.

1. $S_1 + S_2 \xrightarrow{C_1} S_3$
2. $S_3 \rightarrow C_2 S_1 + S_2$
3. $S_3 \rightarrow C_3 S_4 + S_2$

State vector: $S(t) = [S_1(t), S_2(t), S_3(t), S_4(t)]^t$.
With every part of the reaction (listed 1-3 above), we associate a stochiometric vector.

1. $V_1 = [-1, -1, 1, 0]^T$
2. $V_2 = [1, 1, -1, 0]^T$
3. $V_3 = [0, 1, -1, 1]^T$

Every time reaction j occurs, the state of the system changes from state $S(t)$ to $S(t) + V_j$
What are the transition probabilities? The probability for a V_j transition is given by $a_j(S(t))\Delta t$. How are the a_j's computed?

$$a_1 = c_1 s_1 s_2$$

$$a_3 = c_3 s_3$$

$$p(S, t + \Delta t) = p(s,t) \left[1 - \sum_{j=1}^{M} a_j(S(t))\Delta t \right] + \sum_{j=1}^{M} p(S - V_j, t)a_j(S(t))\Delta t$$

$$\frac{d}{dt}p(s,t) = \sum_{j=1}^{M} p(S - V_j, t)a_j(S(t)) - \sum_{j=1}^{M} p(s,t)a_j(S(t))$$

Question: how are kinetic rates related to the propensities a_j?

$$\frac{d}{dt}[S_3] = k_1[A][B]M\text{sec}^{-1}$$

Units: $k : M^{-1}\text{sec}^{-1}$, $a_j : \text{sec}^{-1}$, $c_j : (\# \text{ molecules})^{-2}\text{sec}^{-1}$

$$k_1 \sim M^{-1}\text{sec}^{-1} \sim \frac{L}{mole} \cdot \frac{1}{\text{sec}} \sim \frac{L}{N_A} \cdot \frac{1}{\text{sec}} \left(\frac{1}{L} \cdot \frac{1}{N_A} \right)$$

In general, $c_1 = \frac{k_1}{N_A \cdot \text{volume}}$