

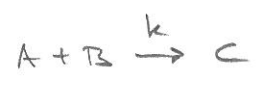
12. NOISE AND STOCHASTIC CHEMICAL KINETICS

12.1. FOUNDATIONS

Assumption: system is well-mixed, i.e.

- (1) Prob. that a given pair of molecules reacts is independent of time
- (2) A given molecule is equally likely to interact with every other molecule in the system.

Consider a system with two molecules A, B that react to form C:



$k dt$: Prob. for reaction in $[t, t+dt)$

$f(t)$: Probability density for time of reaction if $t_0 = 0$

$F(t) = \int_0^t dt' f(t')$: cumulative prob. for reaction to occur at $T < t$.

$G(t) = 1 - F(t) = P(T > t)$: Prob. that reaction occurs at $T > t$

For well-mixed system (Markov assumption):

$P(T > t + \tau | T > \tau) = P(T > t)$: Memoryless!

(Def. of cond. prob. $P(A|B) = P(A \cap B) / P(B) \Rightarrow P(A \cap B) = P(A|B) P(B)$)

$$P(T > t + \tau \text{ AND } T > \tau) = P(T > t + \tau) = \frac{P(T > t + \tau | T > \tau) \cdot P(T > \tau)}{P(T > \tau)}$$

$$\Rightarrow P(T > t + \tau) = P(T > t) P(T > \tau)$$

$$\Rightarrow G(t + \tau) = G(t) G(\tau)$$

$$\Rightarrow G(t) = e^{-\alpha t}, \quad F(t) = 1 - e^{-\alpha t}$$

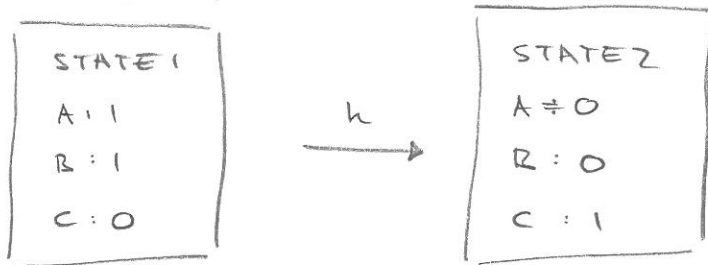
$$F(dt) = 1 - e^{-\alpha dt} \approx 1 - (1 - \alpha dt) = \alpha dt \stackrel{!}{=} k dt$$

$$f(t) = \frac{d}{dt} F(t) = k e^{-kt}$$

12.2 CHEMICAL MASTER EQUATION

A, B, C SYSTEM: discrete state, continuous time Markov process

Two states:



Probs. for states:

$$P_1(t) = e^{-kt} \quad (= G(t))$$

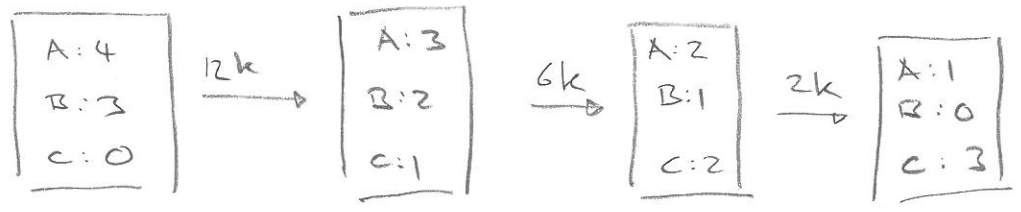
$$P_2(t) = 1 - e^{-kt} \quad (= F(t))$$

$$\dot{P}_1 = -k e^{-kt} = -k P_1(t)$$

$$\dot{P}_2 = +k e^{-kt} = +k P_2(t)$$

$$\dot{\vec{P}} = \begin{pmatrix} \dot{P}_1 \\ \dot{P}_2 \end{pmatrix} = \begin{pmatrix} -k & 0 \\ +k & 0 \end{pmatrix} \vec{P} \quad \text{"chemical master equation"}$$

EXAMPLE 1: $A + B \xrightarrow{k} C$, $4A$, $3B$



$$\begin{pmatrix} \dot{P}_0 \\ \dot{P}_1 \\ \dot{P}_2 \\ \dot{P}_3 \end{pmatrix} = \begin{pmatrix} -12k & 0 & 0 & 0 \\ 12k & 6k & 0 & 0 \\ 0 & -6k & -2k & 0 \\ 0 & 0 & 2k & 0 \end{pmatrix} \begin{pmatrix} P_0 \\ P_1 \\ P_2 \\ P_3 \end{pmatrix}$$

$$P_i(t=0) = 1 \quad P_i(t) = e^{-12kt}$$

$$P_1(t) = 2e^{-12kt} (e^{6kt} - 1)$$

$$\vdots$$

$$\langle C \rangle = \sum_i i P_i = 3 - \frac{1}{5} e^{-12t} - e^{-6t} - \frac{2}{5} e^{-2t} \quad \text{mean}$$

$$\langle C^2 \rangle = \sum_i i^2 P_i = 9 - e^{-12t} - e^{-6t} - 9e^{-2t}$$

EXAMPLE 2: $\xrightarrow{k_1} m \xrightarrow{k_2} \phi$

STATES $m=0, 1, 2, \dots$

$$\dot{P}_0 = -k_1 P_0 + k_2 P_1$$

$$\dot{P}_1 = +k_1 P_0 - (k_1 + k_2) P_1 + 2k_2 P_2$$

$$\dot{P}_2 = k_1 P_1 - (k_1 + 2k_2) P_2 + 3k_2 P_3$$

$$\vdots$$

STEADY STATE:

$$P_1^* = \frac{k_1}{k_2} P_0$$

Adding the first two equations:

$$0 = -k_1 P_1^* + 2k_2 P_2^* \Rightarrow P_2^* = \frac{k_1}{2k_2} P_1^* = \frac{k_1^2}{2k_2^2} P_0^*$$

Adding the first n equations:

$$P_n^* = \frac{\alpha^n}{n!} P_0^* \quad \alpha = k_1/k_2$$

What is P_0

$$\sum_{n=0}^{\infty} P_n^* = \sum_{n=0}^{\infty} \frac{\alpha^n}{n!} P_0 = 1$$

$$\Rightarrow P_0^{-1} = \sum_{n=0}^{\infty} \frac{\alpha^n}{n!} = e^{\alpha}$$

$$\Rightarrow P_0 = e^{-\alpha}, \quad P_n^* = \frac{\alpha^n}{n!} e^{-\alpha}$$

$$\langle m \rangle = \sum_{n=0}^{\infty} n P_n = \alpha = \frac{k_1}{k_2}$$

$$\langle m^2 \rangle = \sum_{n=0}^{\infty} n^2 P_n^* = \alpha + \alpha^2$$

$$\text{STANDARD DEV: } \sqrt{\langle m^2 \rangle - \langle m \rangle^2} = \sqrt{\alpha} = \sqrt{k_1/k_2}$$