Plan for 9/22

→ plotting example in MATLAB
  ⊕ clarifying the difference between decay probability and decay rate

→ Overview of main results for chemical kinetics

→ Quiz [15min]

Decay probability vs Decay rate

$$N(t+dt) = N(t)(1-\delta)$$

decay probability

$$\Downarrow$$

$$\frac{N(t+dt)-N(t)}{dt} = -\frac{\delta}{dt}N$$

$$\Downarrow$$ when is this true?

$$\frac{dN}{dt} = -\frac{\delta N}{dt} \sim -\tilde{\delta} N$$

decay rate

It is tempting to write

$$\tilde{\delta} = \frac{\delta}{dt}$$

so if you have $\{\delta_1, dt\}$ and $\{\delta_M, M\times dt\}$

$$\Rightarrow \quad \frac{\delta_1}{dt} = \tilde{\delta} = \frac{\delta_M}{M dt} \Rightarrow \delta_M = M\delta_1$$

But this is not generally true!

Recall: $\delta_M = 1-(1-\delta_1)^M \simeq M\delta_1$ only if δ_1 is small !?

Chemical kinetics

In class, you showed how

$$2H_2 + O_2 \underset{\beta}{\overset{\alpha}{\rightleftharpoons}} 2H_2O$$

Can be modelled by the ODEs:

$$\frac{d}{dt}[H_2] = -2\alpha[H_2]^2[O_2] + 2\beta[H_2O]^2$$

$$\frac{d}{dt}[O_2] = \alpha[H_2]^2[O_2] + \beta[H_2O]^2$$

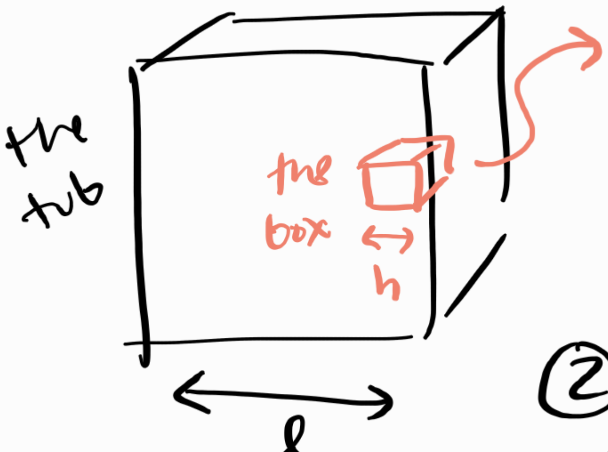
$$\frac{d}{dt}[H_2O] = +2\alpha[H_2]^2[O_2] - 2\beta[H_2O]^2$$

How did we get here? Let's review:

key assumptions

h: $O(\mu m)$

l: $O(m)$



① h is large enough s.t. many atoms fit in h^3

⇒ for independence

② h is small enough s.t. there are not actually many atoms in the box

⇒ so Binomial Distribution ~ first order terms

③ h is small enough s.t. $h^3 << l^3$

⇒ so we can make a mean-field approx

④ dt is large enough so atoms bounce around a lot

$dt: O(\mu s)$

⇒ for independence

⑤ dt is small enough so concentrations do not change much from $t \to t + dt$

⇒ for continuity

⑥ tub is "well mixed"

⇒ for indepence

⑦ many molecules $N >> 1$

⇒ so actual # of molecules reflects estimated probabilities

⑧ reactions only happen when molecules are close together

Deriving probability of a reaction

For each reagent: (over a timestep)

$\Rightarrow$ probability of k molecules of N being in the box:

k molecules are independent

$$P(k|N) = \binom{N}{k} \cdot \delta^k \cdot (1-\delta)^{N-k}$$

binomial coefficient

$$\binom{N}{k} = \frac{N!}{(N-k)!\,k!}$$

δ: probability a molecule is in the box

probability the rest of the molecules are not in the box

$\Rightarrow$ assume that h is small enough, so δ is small s.t.

$$P(0|N) \gg P(1|N) \gg P(2|N) \gg \ldots$$

$$\Rightarrow P(k|N) \approx \frac{N^k}{k!}\delta^k = \frac{(N\delta)^k}{k!}$$

$$\Rightarrow \text{Let } \delta = \frac{1}{\#\text{ boxes}} = \frac{\text{boxsize}}{\text{tubsize}} = \frac{h^3}{l^3}$$

$$\Rightarrow N\delta = \frac{N}{l^3} \cdot h^2 = [A] \cdot h^3$$

concentration

$\Rightarrow$: $P(k|N) \approx \frac{1}{k!}([A])^k h^{3k}$

Now, assume $5A + B \leftrightarrow 2C$

$$P(5A \,\&\, 1B) = P(5A) \cdot P(1B)$$

$$= \frac{1}{5!}[A]^5 [B] h^{3\cdot 6}$$

Everytime 5A & 1 B molecules are close, $\exists$ some probability $\tilde{\alpha}$ of a reaction:

$$P(5A + B \rightarrow 2C) = \frac{h^{3\cdot 6}\tilde{\alpha}}{5!}[A]^5[B]$$

Probablity 5 A molecules & 1 B molecule are in the box and react to form 2C

Similarly, for the reverse reaction:

$$P(2C \rightarrow 5A + B) = \frac{h^{3\cdot 2}\tilde{\beta}}{2!}[C]^2$$

Probability 2C molecules are in the box and the reverse reaction occurs to form 5A and 1B molecule

Difference equation

N: number of C molecules

$$N(t+dt) = N(t) + \sum_{\text{boxes}} \underbrace{\#\text{ produced}} - \sum_{\text{boxes}} \#\text{ removed}$$

2 produced per box with

probability $\dfrac{h^{3\cdot 6}\tilde{\alpha}}{5!}[A]^5[B]$

2 removed per box with

probability $\dfrac{h^{3\cdot 2}\tilde{\beta}}{2!}[C]^2$

$$\Rightarrow N(t+dt)+dt =$$

$$N(t) + \sum_{\text{boxes}} \left(2\frac{h^{3\cdot 6}\tilde{\alpha}}{5!}[A]^5[B] - 2\frac{h^{3\cdot 2}\tilde{\beta}}{2!}[C]^2 \right)$$

$$= N(t) + [\#\text{ boxes}] \cdot \text{〃} \qquad \text{〃}$$

$$\ell^3/h^3$$

Divide both sides by ℓ^3, so we have a difference equation for concentration

$$\Downarrow$$

$$[C](t+dt) = [C](t) + 2\frac{h^{3\circ 5}\tilde{\alpha}}{5!}[A]^5[B] - 2\frac{h^3\tilde{\beta}}{2!}[C]^2$$

now let us get the ODE

$$\Downarrow$$

$$\frac{[C](t+dt)-[C](t)}{dt} = 2\,\frac{h^{3\circ 5}\tilde{\alpha}}{5!\,dt}[A]^5[B] - 2\,\frac{h^3\tilde{\beta}}{2!\,dt}[C]^2$$

α β

assume continuity

$$\frac{d[C]}{dt} = 2\alpha[A]^5[B] - 2\beta[C]^2$$

reaction rate (forward)

reaction rate (backward)

Example: Find the ODEs for

$$2A \xrightarrow{\alpha} C$$

$$1A + 3B \xrightarrow{\beta} D$$

$$\frac{d[A]}{dt} = -2\alpha[A]^2 - 1\beta[A]^1[B]^3$$

$$\frac{d[B]}{dt} = -3\beta[A]^1[B]^3$$

$$\frac{d[C]}{dt} = +\alpha[A]^2$$

$$\frac{d[D]}{dt} = +\beta[A]^1[B]^3$$

$\boxed{Q}$: What will happen in this system over long time, if you start with high concentrations of A and B?

Example: Find the ODE for $[X]$

when $\begin{cases} A + X \xrightarrow{\alpha} 2X \quad (*) \\ 2A + X \xrightarrow{\beta} B \end{cases}$

$$\frac{d[X]}{dt} = \underline{\underline{+1\alpha[A][X]}} - 1\beta[A]^2[X]$$

In $(*)$, you produce 2 X molecules with probability $\propto [A][X]$ but you lose 1 X molecule with probability $\propto [A][X]$.

So, overall gain is $\oplus 1$

Example: Lotka-Volterra model

$$\begin{cases} \text{Prey: rabbits} \longrightarrow R \\ \text{predator: foxes} \longrightarrow F \end{cases}$$

rabbit food

$$A + R \xrightarrow{k_1} 2R \quad \text{rabbit growth}$$

$$R + F \xrightarrow{k_2} 2F \quad \text{fox eats rabbit}$$

$$F \xrightarrow{k_3} B \quad \text{fox death}$$

assume constant ☆

$$\begin{cases} \dfrac{d[R]}{dt} = +k_1 [A][R] - k_2 [R][F] \\ \dfrac{d[Y]}{dt} = +k_2 [R][F] - k_3 [F] \end{cases}$$

$\boxed{Q}$ What are some assumptions of this model?

① $\exists$ enough [A] food at all times ☆

② foxes only eat rabbits

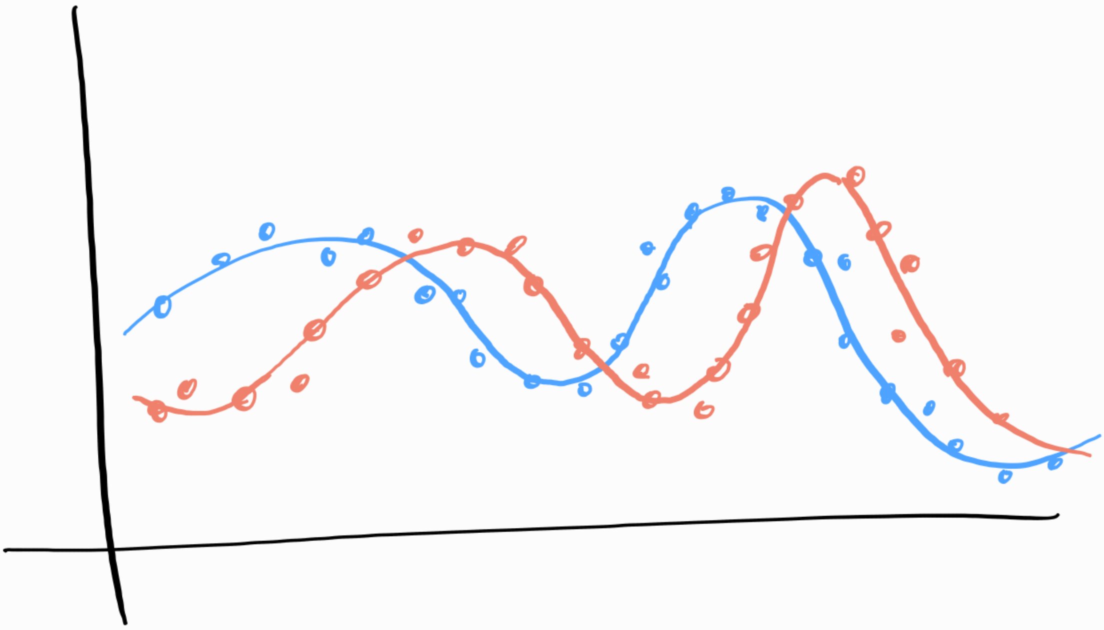
(3) all rabbits & foxes are alike within their respective species (no genetic variations)

(4) foxes have limitless appetite

(5) no spatial distributions or spatial interactions affect the dynamics (e.g. rabbits do not cluster)

Example: Estimating rates

Let's consider the Lotka-Volterra model for rabbits and foxes. Suppose you are given data of the # of rabbits and # of foxes in 5 acres of farmland over time:



Let's just consider the equation for rabbits:

$$\frac{d[R]}{dt} = \alpha [R] - \beta [R][F]$$

Can you find α & β? How?

E.g., estimate $\frac{d[R]}{dt}$ at each time t_i so that you have

$$\sim \frac{d[R]}{dt}(t_i) \approx \alpha [R](t_i) - \beta [R](t_i)[F](t_i)$$

$\Rightarrow$ perform multivariate regression (i.e., like finding a best fit line, except you have <u>two</u> unknowns)

$y_i = m x_i$, m unknown

Quiz

1. Suppose you have a box of radioactive material. At 9:00am, you have 2500 atoms. You come back after an hour and count 2460 atoms.

   (a) What is the probability an atom decays over 1 hr?

   (b) Write down the difference equation describing this system

   (c) Write down the ODE that models this system (approximately)

   (d) Using your answer in (b) or (c), how many atoms do you expect to have at 5:00pm?

2. Imagine that you had a well-mixed reaction with reagents A, B, and C.

   Let's imagine the reaction takes the form

$$2A + B \xrightarrow{\alpha} 2C$$

but the reverse reaction takes the form

$$2C + A \xrightarrow{\beta} 3A + B$$

In other words, A acts as a catalyst for the reverse reaction.

What might the kinetic equations be?

Answers

$\boxed{1}$

ⓐ $N(t+\delta t) = 2460 = 2500 \cdot (1-\delta)$

$\Longrightarrow \delta = 0.016$

ⓑ $N(t+\delta t) = N(t)(1-0.016) = 0.984 \times N(t)$

ⓒ $\dfrac{dN}{\delta t} = -\left[\dfrac{\delta}{\delta t}\right] N(t) = -0.016 \,/_{hr}\, N(t)$

ⓓ Using difference eqn:

$N(8\,hrs) = 2500(1-\delta)^8 \approx 2197$ atoms

Using the ODE:

$\Rightarrow N(t) = 2500 \exp(-0.016t)$

$N(8\,hrs) = 2500 \cdot \exp(-0.16 \times 8) \approx 2199$ atoms

$\boxed{2}$

$$\begin{cases} \dfrac{dA}{\delta t} = -2\alpha A^2 B + 2\beta A C^2 \\[2ex] \dfrac{dB}{\delta t} = -\alpha A^2 B + \beta A C^2 \\[2ex] \dfrac{dC}{\delta t} = +2\alpha A^2 B - 2\beta A C^2 \end{cases}$$