$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

$$\frac{dA}{dt} = -k_1 A + k_2 B$$

$$\frac{dB}{dt} = k_1 A - k_2 B$$

REFORMULATE AS A TRANSITION MATRIX:

{MARKOV / STOCHASTIC}

PROB START AS A

PROB START AS B

$\begin{bmatrix} & \\ & \end{bmatrix}$ ← PROB END AS A AFTER Δt ← PROB END AS B AFTER Δt

COLUMN SUMS TO 1.0

IMAGINE ONE MOLECULE OF "A"

OVER Δt, IT CAN: STAY A <u>OR</u> BECOME B

$P(A \to B; \Delta t) = k_1 \Delta t$ ← CHOOSE <u>SMALL</u> Δt (OTHERWISE $p > 1$!) RULE OF THUMB 10X BELOW FASTEST RATE.

$P(A \to A; \Delta t) = (1 - P_{A\to B})$

$P(B \to A; \Delta t) = k_2 \Delta t$

$P(B \to B; \Delta t) = 1 - P_{B \to B}$

$$\begin{bmatrix} A(t+\Delta t) \\ B(t+\Delta t) \end{bmatrix} = \begin{bmatrix} P_{AA} & P_{BA} \\ P_{AB} & P_{BB} \end{bmatrix} \begin{bmatrix} A(t) \\ B(t) \end{bmatrix}$$

$$A(t+\Delta t) = A \cdot P_{AA} + B \cdot P_{BA}$$
$$B(t+\Delta t) = A \cdot P_{AB} + B \cdot P_{BB}$$

EXAMPLE WITH REAL NUMBERS:

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

$A(t=0) = 5$
$B(t=0) = 0$
$k_1 = 100\,s^{-1}$
$k_2 = 10\,s^{-1}$

$\Delta t = 0.001\,s$

$P_{AB} = 100 \times 0.001 = 0.1$
$P_{AA} = 1 - P_{AB} = 0.9$

$P_{BA} = 10 \times 0.001 = 0.01$
$P_{BB} = 1 - P_{BA} = 0.99$

$$\begin{array}{cc} A & B \end{array}$$
$$\begin{bmatrix} 0.9 & 0.01 \\ 0.1 & 0.99 \end{bmatrix}$$

$$\begin{bmatrix} 0.9 & 0.01 \\ 0.1 & 0.99 \end{bmatrix} \begin{bmatrix} 5 \\ 0 \end{bmatrix} \to \begin{matrix} 5(0.9) + 0(0.01) \\ 5(0.1) + 0(0.99) \end{matrix} \begin{matrix} = 4.5 \\ = 0.5 \\ \overline{5.0} \end{matrix}$$

5.0 ← CONSERVATION OF MASS!

$$\begin{bmatrix} 0.9 & 0.01 \\ 0.1 & 0.99 \end{bmatrix} \begin{bmatrix} 4.5 \\ 0.5 \end{bmatrix} \to \begin{matrix} 4.5(0.9) + 0.5(0.01) \\ 4.5(0.1) + 0.5(0.99) \end{matrix} = \begin{matrix} 4.055 \\ 0.945 \\ \overline{5.000} \end{matrix}$$

5.000 ✓

$$\begin{bmatrix} 0.9 & 0.01 \\ 0.1 & 0.99 \end{bmatrix} \begin{bmatrix} 4.055 \\ 0.945 \end{bmatrix} \rightarrow \begin{matrix} 4.055(0.9) + 0.945(0.01) \\ 4.055(0.1) + 0.945(0.99) \end{matrix} = \begin{matrix} 3.659 \\ \underline{1.341} \\ 5.000 \checkmark \end{matrix}$$

WHAT DOES THIS GO TO OVER LONG TIMES?

- WHAT VALUE FOR [B] YIELDS B_e WHEN FED INTO MARKOV MATRIX?

$$A \cdot P_{AA} + B \cdot P_{BA} = A_e$$
$$A \cdot P_{AB} + B \cdot P_{BB} = B_e$$

$$A \cdot P_{AB} = B_e - B \cdot P_{BB}$$

$$A = \frac{B_e}{P_{AB}} - \frac{B \cdot P_{BB}}{P_{AB}}$$

$$A \cdot P_{AA} + B \cdot P_{BA} = A_e$$

$$\left(\frac{B_e}{P_{AB}} - \frac{B \cdot P_{BB}}{P_{AB}}\right) P_{AA} + B \cdot P_{BA} = A_e$$

$$\frac{B_e P_{AA}}{P_{AB}} - \frac{B \cdot P_{BB}}{P_{AB}} P_{AA} + B \cdot P_{BA} = A_e$$

$$B \cdot P_{BA} - \frac{B \cdot P_{BB}}{P_{AB}} P_{AA} = A_e - \frac{B_e P_{AA}}{P_{AB}}$$

$$B\left(P_{BA} - \frac{P_{BB} \cdot P_{AA}}{P_{AB}}\right) = A_e - B_e (P_{AA}/P_{AB})$$

$$\boxed{B = \frac{A_e - B_e(P_{AA}/P_{AB})}{P_{BA} - \frac{P_{BB} \cdot P_{AA}}{P_{AB}}} = 4.5454 \Leftarrow B_e!}$$

FIND B_e ([B] AT EQUILIBRIUM).

$$A_e + B_e = 5 \; ; \; K_{eq} = B_e / A_e$$

$$\frac{B_e}{K_{eq}} + B_e = 5 \qquad A_e = B_e / K_{eq}$$

$$B_e\left(\frac{1}{K_{eq}} + 1\right) = 5$$

$$B_e = \frac{5}{\frac{1}{K_{eq}} + 1} \times \frac{K_{eq}}{K_{eq}}$$

$$= 5 \frac{K_{eq}}{1 + K_{eq}}$$

$$= 5 \cdot \frac{10}{10+1} = \boxed{4.5454 = B_e}$$

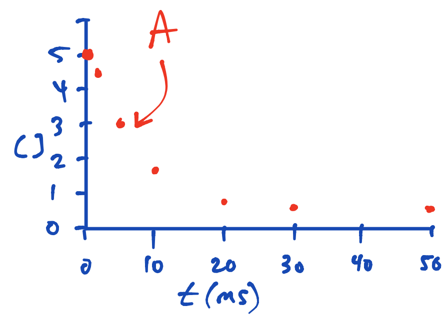
WHEN APPLIED MANY TIMES MATRIX CONVERGES ON A_e AND B_e!

<u>OTHER COOL FEATURE:</u>

$$V_1 = T \cdot V_0$$
$$V_2 = T \cdot V_1 = T \cdot (T \cdot V_0)$$
$$V_3 = T \cdot V_2 = T(T \cdot V_1) = T(T(T \cdot V_0))$$

$\boxed{V_n = T^n V_0}$ TO CALCULATE CONCENTRATION AT ANY TIME, RAISE TO $t/\Delta t$!

n	A	B
0 :	5.000	0.000
1 :	4.500	0.500
5 :	2.993	2.007
10 :	1.872	3.128
20 :	0.896	4.104
30 :	0.592	4.408
50 :	0.468	4.532



CAN MAKE ARBITRARILY COMPLICATED:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C$$

$$P_{AA} = (1 - P_{AB} - P_{AC})$$
$$P_{AB} = k_1 \Delta t$$
$$P_{AC} = \emptyset$$

$$\begin{bmatrix} P_{AA} & P_{BA} & \emptyset \\ P_{AB} & P_{BB} & P_{CB} \\ \emptyset & P_{BC} & P_{CC} \end{bmatrix}$$

$$P_{BB} = (1 - P_{BA} - P_{BC})$$
$$P_{BA} = k_1 \Delta t$$
$$P_{BC} = k_2 \Delta t$$

$$P_{CC} = (1 - P_{CB} - P_{CA})$$
$$P_{CB} = k_{-2} \Delta t$$
$$P_{CA} = \emptyset$$

KEY POINTS:

1. FORMULATE MATRIX OF TRANSITION PROBS (COLUMNS SUM TO 1)
2. WHEN APPLIED TO VECTOR OF CONCENTRATIONS
   - GIVES NEW CONC AFTER STEP Δt.
   - CONSERVES MASS
   - CAN BE EXTENDED TO ANY TIME BY RAISING T TO POWER $t/\Delta t$
   - TENDS TO EQUILIBRIUM AS $t \to \infty$