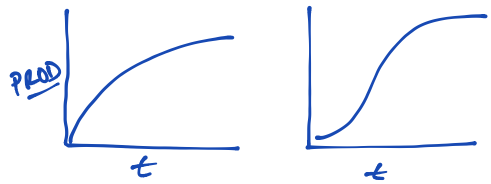
KINETICS I:

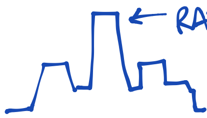
THERMODYNAMICS DESCRIBES <u>DIRECTION</u> OF REACTION. KINETICS DESCRIBES TIME-DEPENDENCE.



VOCAB:

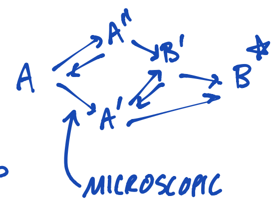
ORDER OF REACTION:

ZEROTH: RATE ~ K
FIRST: RATE ~ K[A]
SECOND: RATE ~ K·[A][B]



← RATE LIMITING STEP CONTROLS RATE.

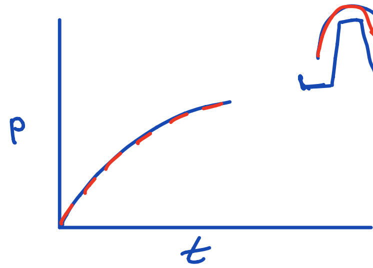
BULK VS MICROSCOPIC

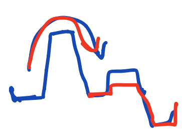


BULK A → B*

KEY IDEAS:

1. YOU CAN (USUALLY) ONLY SEE BULK RATES, NOT MICROSCOPIC RATES.
2. YOU CAN'T SEE STEPS AFTER RATE-LIMITING STEP.





RATE DETERMINED BY HIGHEST ENERGY STEP.

3. YOU HAVE TO BE CAREFUL INFERRING MICROSCOPIC MECHANISTIC INFORMATION FROM MACROSCOPIC RATES.

RATE LAWS:

SCHEME: $A \rightarrow B$

RATE LAW: $\frac{dA}{dt} = -k \cdot [A]$

$$\frac{dA}{[A]} = -k\,dt$$

$$\int \frac{dA}{[A]} = \int -k\,dt$$

$$\ln(A) = -kt + c \qquad \text{AT } t = \emptyset,\ A = A_0$$

$$\ln(A_0) = \emptyset + c$$

$$\ln(A) = -kt + \ln(A_0)$$

$$\ln(A) - \ln(A_0) = -kt$$

$$\ln(A/A_0) = -kt$$

$$A/A_0 = e^{-kt}$$

$$A = A_0 e^{-kt}$$

LET'S ADD A BACK REACTION:
WILL THIS CHANGE THE ORDER? NO.

$$A \underset{k_-}{\overset{k_+}{\rightleftharpoons}} B \qquad \frac{dA}{dt} = -k_+[A] + k_-[B]$$

$$\frac{dB}{dt} = k_+[A] - k_-[B] \qquad -\frac{dA}{dt} = \frac{dB}{dt}$$

① AT EQUILIBRIUM, $dA/dt = \emptyset$

$$\emptyset = k_+[A]_e - k_-[B]_e$$

$$k_-[B]_e = k_+[A]_e$$

$$\frac{[B]_e}{[A]_e} = \frac{k_+}{k_-} = K_{eq}$$

② CONSERVATION OF MASS

$$[A]_0 + [B]_0 = [A]_t + [B]_t = [A]_e + [B]_e$$

$$[B] = [A]_e + [B]_e - [A]_t$$

$$[B] = [A]_e + K_{eq}[A]_e - [A]_t$$

REARRANGE/SUBSTITUTE:

$$\frac{dB}{dt} = k_+[A] - k_-(A_e + K_{eq} A_e - A)$$

$$= k_+(A) - k_-A_e - k_- K_e A_e + k_-A$$

$$= k_+ A - k_- A_e - \cancel{k_-}\frac{k_+}{\cancel{k_-}} A_e + k_- A$$

$$= k_+ A - k_+ A_e - k_- A_e + k_- A$$

$$= k_+(A - A_e) - k_-(A - A_e)$$

$$\frac{dB}{dt} = (A - A_e)(k_+ - k_-)$$

$$-\frac{dA}{dt} = (A - A_e)(k_+ - k_-)$$

$$\frac{dA}{(A - A_e)} = -(k_+ - k_-)dt$$

$$\int \frac{dA}{(A - A_e)} = -\int (k_+ - k_-)dt$$

$$\ln(A - A_e) = -(k_+ - k_-)t + c$$

$$@\, t = 0,\quad A = A_0$$

$$\ln(A_0 - A_e) = c$$

$$\ln\left(\frac{A - A_e}{A_0 - A_e}\right) = -(k_+ - k_-)t$$

$$\frac{A - A_e}{A_0 - A_e} = e^{-(k_+ - k_-)t}$$

$$A = (A_0 - A_e)e^{-(k_+ - k_-)t} + A_e$$

NOTE: THIS RATE IS DIFFERENCE IN FORWARD AND REVERSE RATES → A <u>MACROSCOPIC</u> RATE NOT A <u>MICROSCOPIC</u> RATE.

YOU CAN ALSO WRITE AS RATE MATRIX:

$$\frac{d}{dt}\begin{pmatrix} A \\ B \end{pmatrix} = \underset{\uparrow \atop T}{\begin{bmatrix} -k_+ & k_- \\ k_+ & -k_- \end{bmatrix}} \underset{\uparrow \atop \vec{x}}{\begin{bmatrix} A \\ B \end{bmatrix}} \longrightarrow \begin{array}{l} \frac{dA}{dt} = A(-k_+) + Bk_- \\ \frac{dB}{dt} = Ak_+ - Bk_- \end{array}$$

$$\begin{bmatrix} A(t) \\ B(t) \end{bmatrix} = \begin{bmatrix} A_0 \\ B_0 \end{bmatrix} e^{\vec{\lambda} t}$$