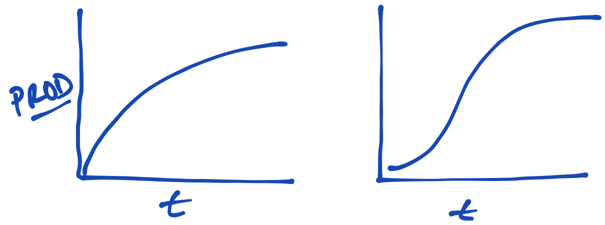
KINETICS I:

THERMODYNAMICS DESCRIBES DIRECTION OF REACTION. KINETICS DESCRIBES TIME-DEPENDENCE.

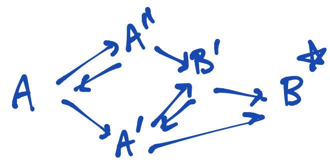


VOCAB:

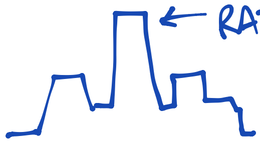
ORDER OF REACTION:

ZEROTH: RATE $\sim k$
FIRST: RATE $\sim k[A]$
SECOND: RATE $\sim k\cdot[A][B]$

BULK VS MICROSCOPIC



BULK $A \rightarrow B^*$



← RATE LIMITING STEP CONTROLS RATE.

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.

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

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

$$-\frac{dA}{dt} = \frac{dB}{dt}$$

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

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

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

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

REARRANGE/SUBSTITUTE:

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

$$= k_+[A] - k_-A_e - k_-K_eA_e + k_-A$$

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\frac{d}{dt}\begin{bmatrix} A \\ B \end{bmatrix} = \underbrace{\begin{bmatrix} -k_+ & k_- \\ k_+ & -k_- \end{bmatrix}}_{T} \underbrace{\begin{bmatrix} A \\ B \end{bmatrix}}_{\vec{x}} \longrightarrow \begin{aligned} \frac{dA}{dt} &= A(-k_+) + Bk_- \\ \frac{dB}{dt} &= Ak_+ - Bk_- \end{aligned}$$

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