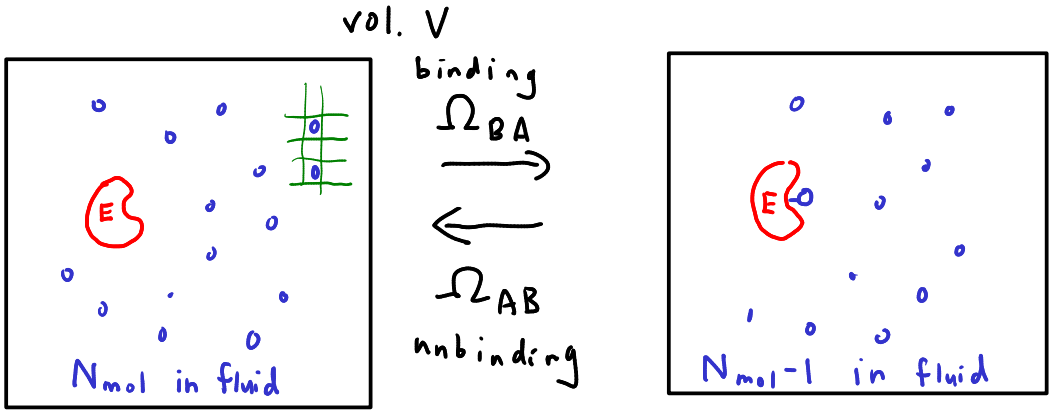
$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta\left(H_n - H_m - k_B T \ln \frac{\sigma_n}{\sigma_m} - W_{nm}\right)}$$

example:



macrostate A (includes many configs of mol in box)

macros. B

binding / unbinding

$$\frac{\Omega_{BA}}{\Omega_{AB}} = e^{-\beta\left(\underbrace{H_B - H_A}_{\text{typically } <0 \text{ b/c bond formed when binding}} - k_B T \ln \frac{\sigma_B}{\sigma_A}\right)}$$

$W_{BA} = 0$ (no other work)

σ_A = # configurations of N_{mol} molecules in a box of volume V (ignore enzyme volume $\ll V$)

divide up box into small volumes V_{mol} big enough to fit 1 molecule each

$$\# \text{ boxes} = N_{pos} = \frac{V}{V_{mol}}$$

$$\sigma_A = \binom{N_{pos}}{N_{mol}} = \frac{N_{pos}!}{N_{mol}!\,(N_{pos} - N_{mol})!}$$

$$\Omega_B = \binom{N_{pos}}{N_{mol}-1} = \frac{N_{pos}!}{(N_{mol}-1)!\,(N_{pos}-N_{mol}+1)!}$$

$$\frac{\Omega_B}{\Omega_A} = \frac{N_{mol}}{N_{pos}-N_{mol}+1} \approx \frac{N_{mol}}{N_{pos}} \quad \text{when } N_{pos} \gg N_{mol} \text{ (dilute sol'n)}$$

$$k_B T \ln \frac{\Omega_B}{\Omega_A} \approx k_B T \ln \frac{N_{mol}}{N_{pos}} \qquad N_{pos} = \frac{V}{V_{mol}}$$

$$= k_B T \ln c V_{mol} \qquad C = \frac{N_{mol}}{V} = \text{conc. of molecules}$$

$$= \underbrace{k_B T \ln V_{mol}}_{\equiv \mu_0 = \text{const.} = \text{"standard" chem. pot.}} + k_B T \ln c$$

Chemical potential $\mu = k_B T \ln \frac{\Omega_B}{\Omega_A} = \mu_0 + k_B T \ln c$

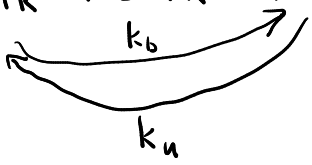
$$\Rightarrow \quad \frac{\text{binding}}{\text{unbinding}} \quad \frac{\Omega_{BA}}{\Omega_{AB}} = e^{-\beta(H_B - H_A - \mu)} \qquad (1)$$

when $N_{pos} >> N_{mol} \Rightarrow \mu < 0$

increase $c \Rightarrow \mu$ less negative

$\Rightarrow$ make Ω_{BA} larger relative to Ω_{AB}

(2) from early lecture (FAR NEAR BOUND)

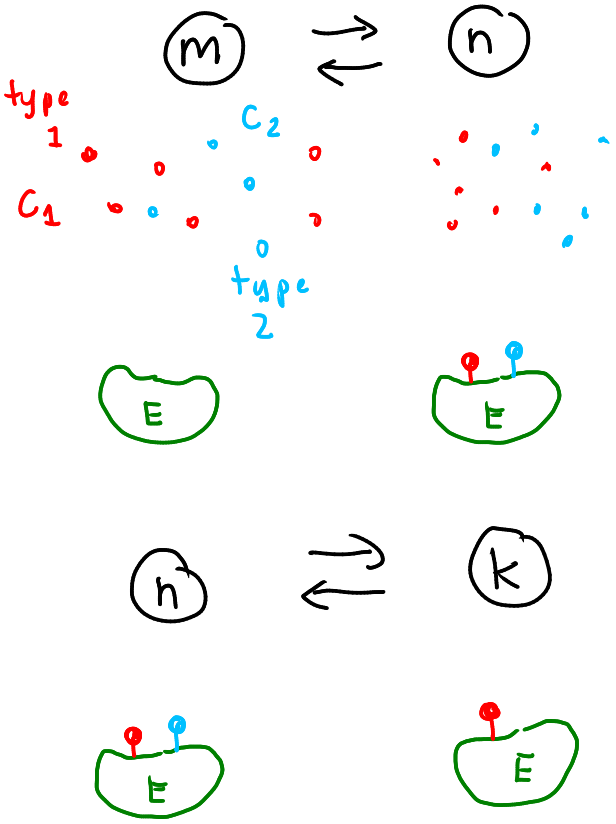


$$\frac{k_b}{k_u} = \frac{\alpha_b K_s c}{k_u} \qquad 0 \le \alpha_b < 1$$

Generalize: many types of molecules in fluid around system

type j: $\mu_j = \mu_0^j + k_B T \ln c_j$

c_j ↓ conc. of jth molec.



binding

$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta(H_n - H_m - \mu_1 - \mu_2)}$$

unbinding

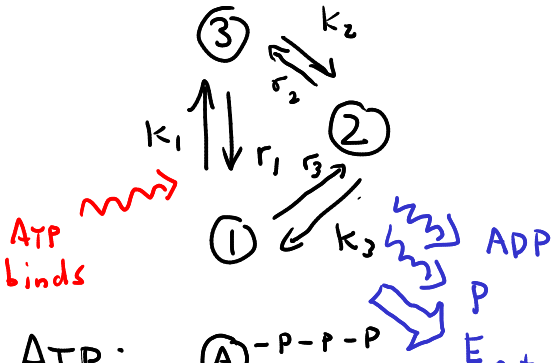
for every molec. that binds we get a $-\mu_j$

unbinding

$$\frac{\Omega_{kn}}{\Omega_{nk}} = e^{-\beta(H_k - H_n + \mu_2)}$$

binding

for every unbinding we get $+\mu_j$



ATP: A-P-P-P

ADP: A-P-P

$t \to \infty$ stationary state

$J_{31}, J_{23}, J_{12} \to J$ const.

$$J = \frac{k_1 k_2 k_3}{D}\left(1 - \frac{r_1 r_2 r_3}{k_1 k_2 k_3}\right)$$

↳ func. > 0

$$\mu_{ATP} = \mu^{\circ}_{ATP} + k_B T \ln c_{ATP}$$

. . .

$$\frac{k_1}{r_1} = e^{-\beta(H_3 - H_1 - \underbrace{\mu_{ATP}}_{E_{in} \text{ for photon}})}$$

$$\frac{k_2}{r_2} = e^{-\beta(H_2 - H_3)}$$

$$\frac{k_3}{r_3} = e^{-\beta(H_1 - H_2 + \underbrace{\mu_{ADP} + \mu_P + E_{out}}_{E_{out} \text{ for photon}})}$$

$$J = \frac{k_1 k_2 k_3}{D}\left(1 - e^{-\beta(\underbrace{\mu_{ATP} - \mu_{ADP} - \mu_P}_{\Delta\mu} - E_{out})}\right)$$

$\equiv$ chem. potential of ATP hydrolysis reaction

$$\Delta\mu = \overbrace{\mu_0^{ATP} - \mu_0^{ADP} - \mu_0^{P}}^{12\ k_B T} + k_B T \ln \frac{c_{ATP}}{c_{ADP}\, c_P}$$

$\approx 21 - 29\ k_B T$ in cells across all modern life

if $\Delta\mu > E_{out} \Rightarrow J > 0$ NESS

compare (1) & (2): both are prop. to c

$\Rightarrow$ consistent picture