The chemical potential, μ

only for chemists?

- Ch. 2.6, pp 79-83: entropy of mixing
- Ch. 3.5, pp 115-121: diffusive equilibrium and the chemical potential
- Ch. 5.1, $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = \left(\frac{\partial F}{\partial N}\right)_{T,V}, \quad \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_i}$
- Ch. 5.2,
  - $G = \sum_i N_i \mu_i$
  - ideal gas: $\mu(T,P) = \mu^0(T) + kTln\left(\frac{P}{P_0}\right)$
  - ideal mixture: $\mu(T,P,x) = \mu^0(T,P) + kTln(x)$
  - Grand potential
- Ch. 6.7, $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kTln\left(\frac{VZ_{int}}{Nv_Q}\right), \quad G = N\mu$
- Thursday: Ch 7.1, open systems & the Gibbs factor
- Next week: Ch 7.2-7.6, quantum statistics, semi-conductors...

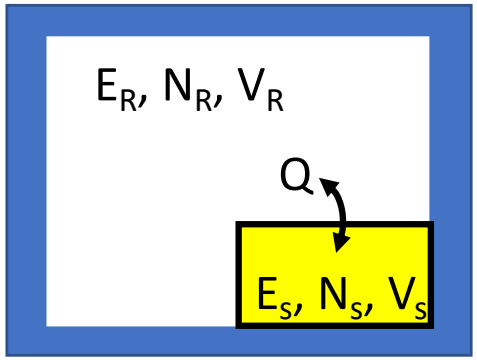
Ensembles

- An ensemble is the set of possible microstates corresponding to the macroscopic variables that are fixed
  - NVE: Microcanonical
  - NVT: Canonical
  - μVT: Grand canonical

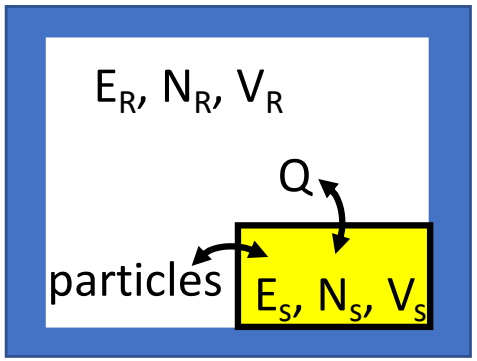
Ensembles

Microcanonical, (NVE) kept constant

Number of microstates: Multiplicity Ω
Probability of a microstate: $\mathrm{P} = 1/\Omega$
Entropy: $\mathrm{S} = \mathrm{k}\ln\Omega$

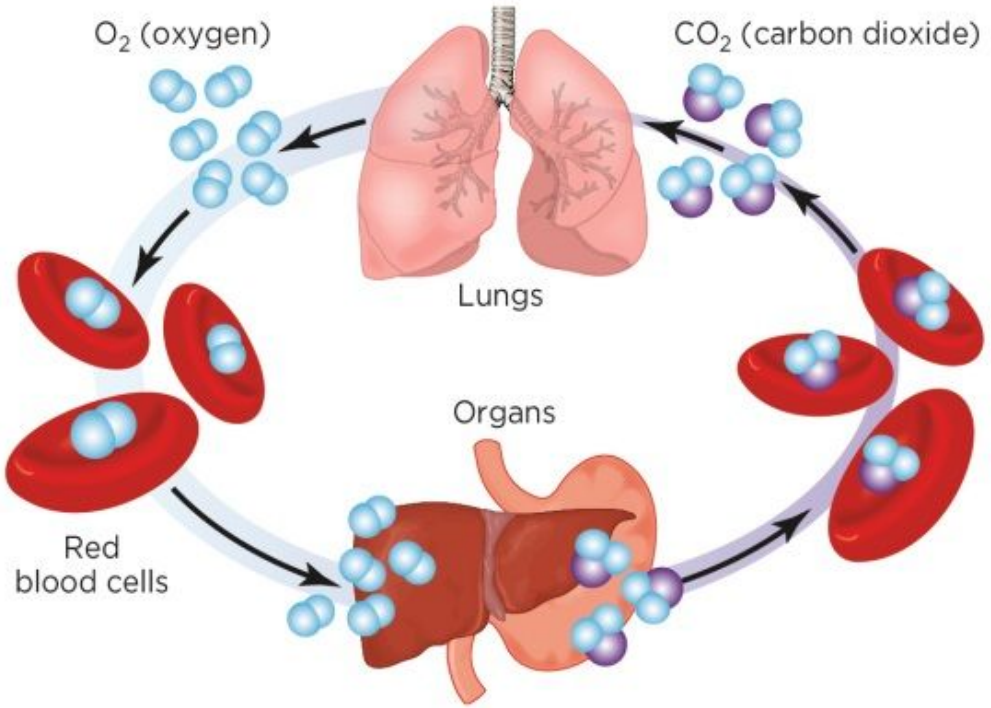


Canonical, (NVT) kept constant
Exchanges Q with (NVE) reservoir to keep T constant
Boltzmann factor: $e^{-\beta\varepsilon_i}$
Partition function: sum over all possible microstates: $Z = \sum_i e^{-\beta\varepsilon_i}$
Probability of a microstate: $P_i = {e^{-\beta\varepsilon_i}}/{Z}$
Free energy: Helmholtz, $F = -kT\ln Z$

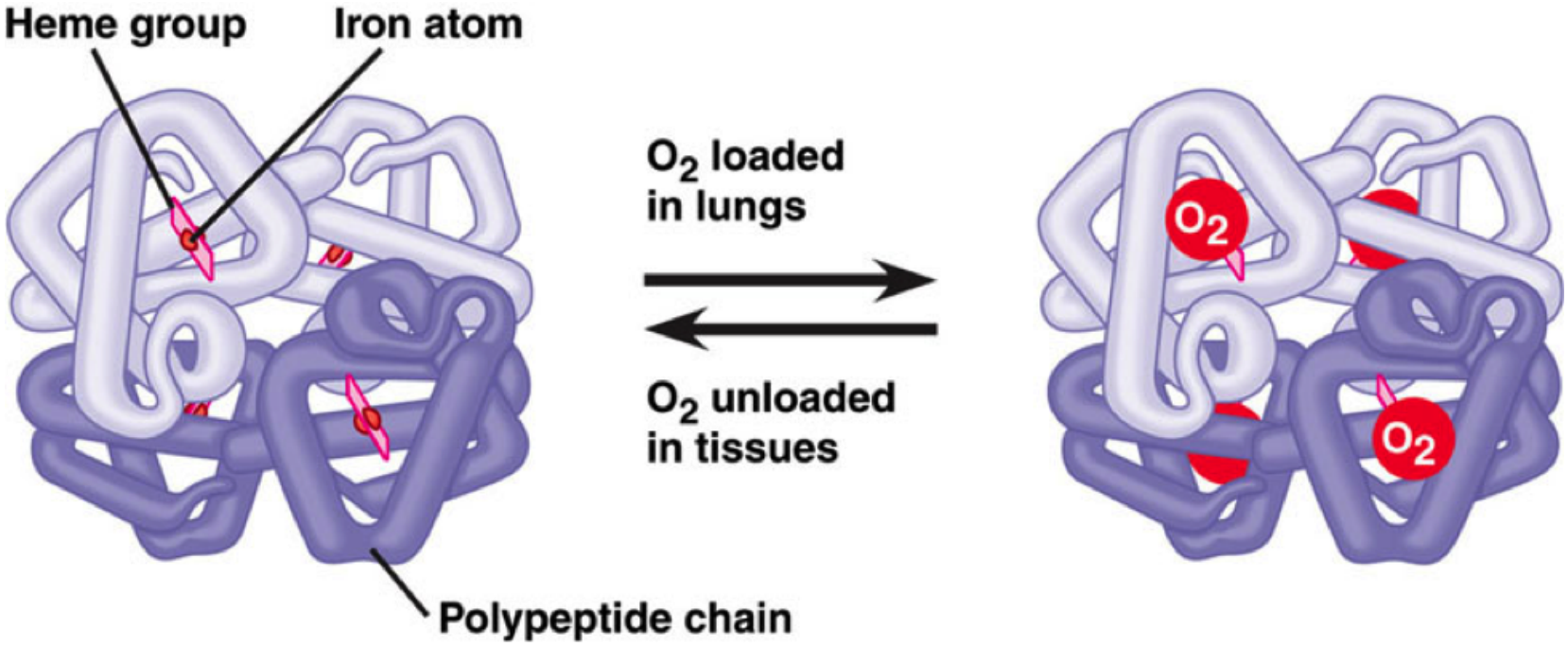


Grand canonical, (μVT) kept constant
Exchanges Q & particles with (NVE) reservoir to keep T & μ constant
Gibbs factor: $e^{-\beta(\varepsilon_i-\mu N_i)}$
Gibbs sum: sum over all possible microstates: $Z_G = \sum_i e^{-\beta(\varepsilon_i-\mu N_i)}$
Probability of a microstate: $P_i = {e^{-\beta(\varepsilon_i-\mu N_i)}}/{Z_G}$
Free energy: Grand potential, $\Phi = -kT\ln Z_G = U - TS - \mu N$

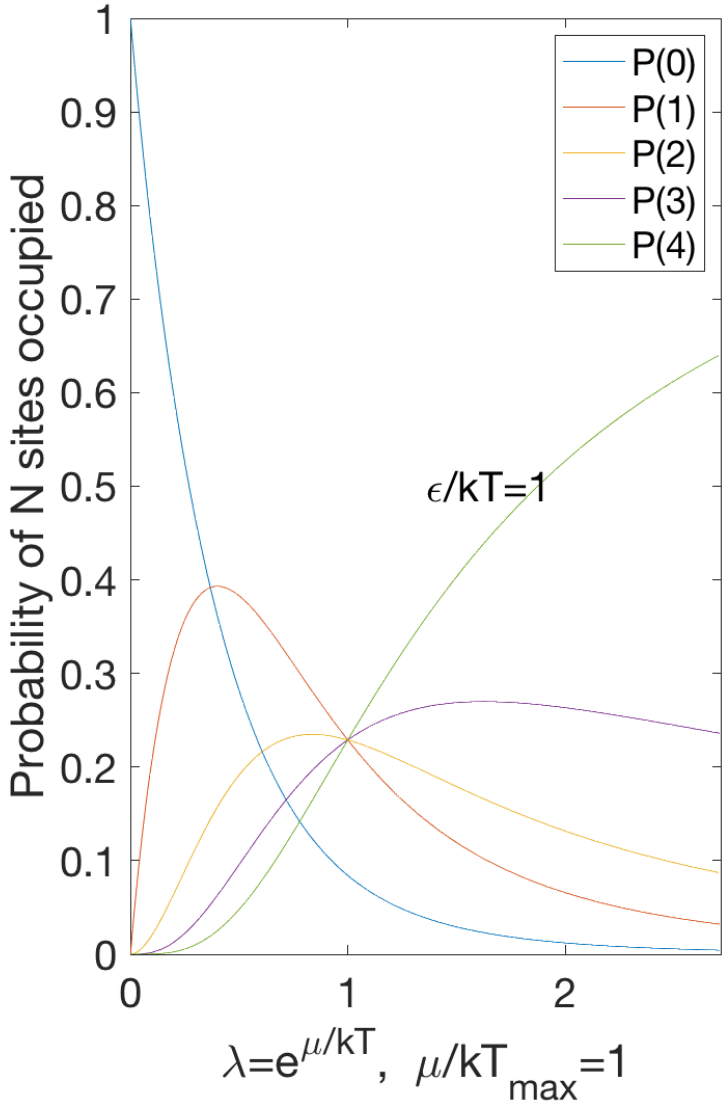
Fig 1. **Gas exchange in humans**

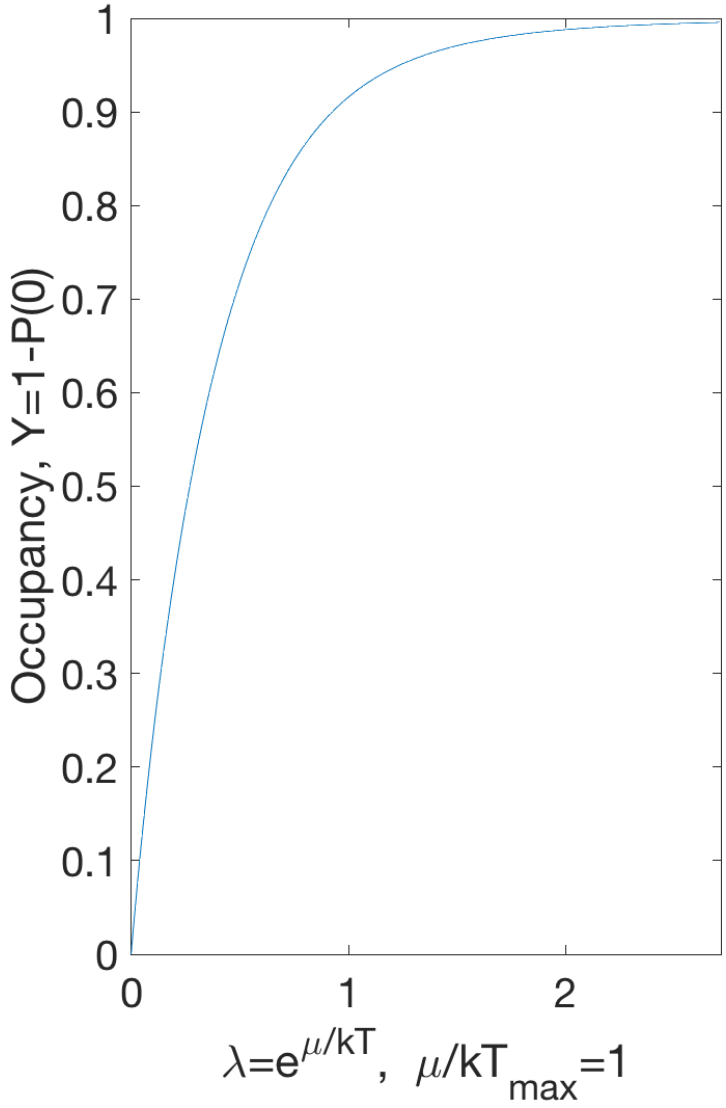


Hemoglobin O_2 uptake

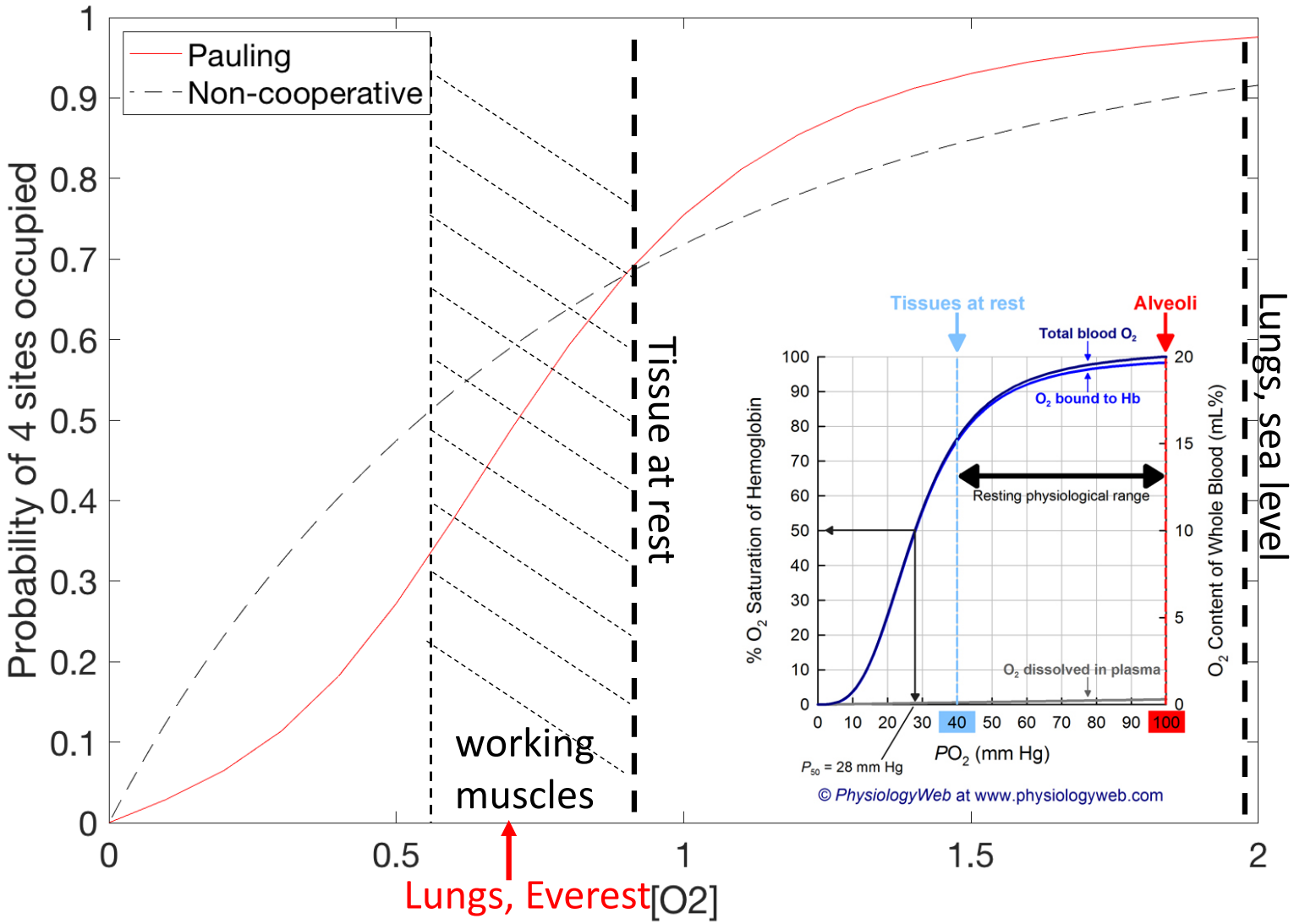


Non-cooperative model





O_2 saturation of hemoglobin



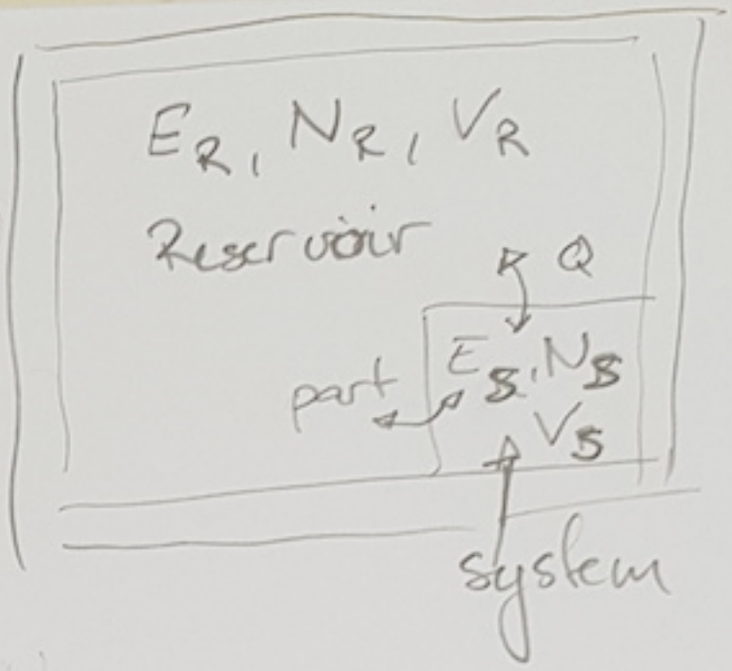
Simple Matlab script to calculate the curves

```
%% Noninteracting binding sites
kT=1;
eps=1;
a=exp(eps/kT);
mu=1;
lam=exp(mu/kT);
l=0:0.01:lam;
Zg=1+a*l+a*l.^2+a*l.^3+a*l.^4;
P0=1./Zg;
P1=a*l./Zg;
P2=a*l.^2./Zg;
P3=a*l.^3./Zg;
P4=a*l.^4./Zg;
Y=P1+P2+P3+P4;
```

```
%% Pauling
J=1;
eJ=exp(J/kT);
lam=0.5;
Pp0=1;
G0=1;
G1=a*l;
G2=a^2*l.^2*eJ;
G3=a^3*l.^3*eJ.^3;
G4=a^4*l.^4*eJ.^6;
Zp=G0+G1+G2+G3+G4;
Pp0=G0./Zp;
Pp1=G1./Zp;
Pp2=G2./Zp;
Pp3=G3./Zp;
Pp4=G4./Zp;
Yp=Pp1+Pp2+Pp3+Pp4;
```

① The Grand canonical ensemble

- The reservoir (R) + system (S) is closed & isolated = microcanonical



- We seek the probability of one particular microstate "S_1" in the system S with energy $\mathcal{E}_1$ and N_1. $\Omega_S(\mathcal{E}_1, N_1) = 1$
- Many states in R are compatible with state "S_1" in S. Multiplicity $\Omega_R(S_1)$ | $E_R = E - \mathcal{E}_1$, $N_R = N - N_1$
- The deviations are small $\frac{\mathcal{E}_1}{E} \ll 1$ $\frac{N_1}{N} \ll 1$

- Taylor expand entropy of reservoir around N, E

$$S_R = k \ln \Omega_R \simeq S_R(N,E) - N_1 \left(\frac{\partial S_R}{\partial N_R}\right)_{E,V} - \mathcal{E}_1 \left(\frac{\partial S_R}{\partial E_R}\right)_{N,V}$$

$$\left(\frac{\partial S_R}{\partial N_R}\right)_{E_R, V_R} = -\frac{\mu_R}{T_R}, \quad \left(\frac{\partial S_R}{\partial E_R}\right)_{N_R, V_R} = \frac{1}{T_R}$$

$$\Rightarrow k \ln \Omega_R \simeq S_R(N,E) + \frac{N_1 \mu_R}{T_R} - \frac{\mathcal{E}_1}{T_R}$$

$$\Rightarrow \Omega_R = C \cdot e^{(N_1 \mu_R - \mathcal{E}_1)/T_R} \qquad C - \text{const.}$$

- Probability $P(N_1, \mathcal{E}_1) = \frac{\Omega_R \Omega_S}{\sum \Omega_R \Omega_S} = C' e^{(N_1 \mu_R - \mathcal{E}_1)/T_R}$
- equilibrium $\mu_R = \mu_S = \mu$, $T_R = T_S = T \Rightarrow P = C' e^{(N_1 \mu - \mathcal{E})/T_R}$
- Normalization $\sum P = 1 = \sum_{N_1} \sum_{\mathcal{E}_1} C' e^{(N_1 \mu - \mathcal{E}_1)/kT}$

$$P(N,\varepsilon) = \frac{1}{Z_G} e^{(N\mu-\varepsilon)/kT}$$

Gibbs sum $\quad Z_G(\mu,V,T) = \sum_N \sum_\varepsilon e^{(N\mu-\varepsilon)/kT}$

Gibbs factor $\quad e^{(N\mu-\varepsilon)/kT}$

Averages :

$$\langle X \rangle = \sum_i X(N_i,\varepsilon_i) P(N_i,\varepsilon_i)$$

$$\langle N \rangle = \frac{1}{Z_G} \sum_i N_i e^{(N_i\mu-\varepsilon_i)/kT}$$

derivative trick : $\quad N e^{(N\mu-\varepsilon)/kT} = \frac{\partial}{\partial\mu} e^{(N\mu-\varepsilon)/kT}$

$$\Rightarrow \quad \langle N \rangle = \frac{kT}{Z_G} \frac{\partial Z_G}{\partial \mu} = kT \frac{\partial \ln Z_G}{\partial \mu}$$

(3) Hemoglobin has 4 sites that can bind O_2

Non-cooperative model. Each site binding energy $\varepsilon_0 < 0$

N	0	1	2	3	4	
$\mathcal{E}$	0	ε_0	$2\varepsilon_0$	$3\varepsilon_0$	$4\varepsilon_0$	independent
multiplicity	1	1	1	1	1	indistinguishable sites

$$Z_G = 1 + e^{\frac{\mu-\varepsilon_0}{kT}} + e^{2\left(\frac{\mu-\varepsilon_0}{kT}\right)} + e^{3\left(\frac{\mu-\varepsilon_0}{kT}\right)} + e^{4\left(\frac{\mu-\varepsilon_0}{kT}\right)}$$

$$= 1 + x + x^2 + x^3 + x^4, \quad x = e^{\frac{\mu-\varepsilon_0}{kT}}$$

$$P(i) = \frac{x^i}{Z_G}$$

$\mu = \mu_{O_2}$ is the chemical potential of O_2 in air / muscle in equilibrium with Hemoglobin

$$\mu_{O_2} = \mu_{O_2}^{\circ} + kT \ln \frac{C_{O_2}}{C_0} = \mu_{O_2}^{\circ} + kT \ln \frac{P_{O_2}}{P_0}$$

$$\Rightarrow e^{\mu_{O_2}/kT} = K \cdot C_{O_2} = K' P_{O_2}$$

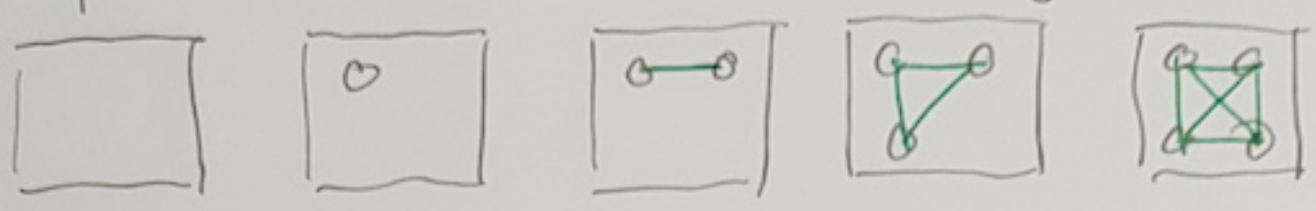
K: const; P_{O_2}: partial pressure O_2

Remember $P_{O_2}(z \approx 8\,km) \approx \frac{1}{3} P_{O_2}(z=0)$

Everest

(9) Hemoglobin

Cooperative model, Pauling



pairwise interactions

0	0	1	3	6	J

$\mathcal{E}$ 0 $\mathcal{E}_0$ $2\mathcal{E}_0+J$ $3\mathcal{E}_0+3J$ $4\mathcal{E}_0+6J$

$x = e^{\frac{\mu-\mathcal{E}_0}{kT}}$ $\quad y = e^{-J/kT}$

$$Z_G = 1 + x + x^2y + x^3y^3 + x^4y^6$$

From figure: observe that the cooperative model

x has inflection point

x is steeper in the region of CO_2 of tissue

rest -> working

Steep => More O_2 can be unloaded

x additional effects in muscles of CO_2 -> [pH] ....

(5) Gibbs sum for several species

Several gases in air : O_2, N_2, CO_2, CO

System + reservoir : $(T, V, N_1, N_2, \dots N_k)$

chemical potential of species i $\quad \mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j\neq i}}$

probability $\quad P(\varepsilon, N_1 \dots N_k) = \frac{1}{Z_G} e^{(\sum_i N_i \mu_i - \varepsilon)/kT}$

Gibbs sum $\quad Z_G(T, V, N_1 \dots N_k) = \sum_{N_1 \dots N_k} e^{(\sum_i N_i \mu_i - \varepsilon)/kT}$

Binding energies of N_2, CO_2 $\quad \varepsilon_i \ll \varepsilon_{O_2}$

$CO \quad \varepsilon_{CO} = -0,85\,eV$

$O_2 \quad \varepsilon_{O_2} = -0,7\,eV$

=> CO binds better to hemoglobin than O_2

What is the effect?

At $p_{O_2} = 0,2$ atm, $T = 310\,K$ $\quad \mu_{O_2} \simeq -0,6\,eV$ $\quad \Rightarrow e^{-(\varepsilon_{O_2} - \mu_{O_2})/kT} \simeq e^{\frac{0,1\,eV}{kT}} \simeq 40$

Assume $p_{CO} = 0,002$ atm $= p_{O_2}/100$ $\quad \Rightarrow \mu_{CO} = \mu_{O_2} - kT \ln 100 \simeq -0,72\,eV$

$\Rightarrow e^{-(\varepsilon_{CO} - \mu_{CO})/kT} \simeq e^{\frac{0,13\,eV}{kT}} \simeq 200$

non-cooperative model :

$$Z_G = \sum_{i=0}^{4} \left(x_{O_2}^{i} + x_{CO}^{i} \right) = \sum_{i=0}^{4} \left(40^i + 120^i \right)$$

1 site model : $\quad P(O_2) = \frac{40}{1 + 40 + 120} = 0,25$

$$Y = \frac{\sum_{i=1}^{4} 40^i}{Z_G} = 0,012$$

1% O_2 occupancy