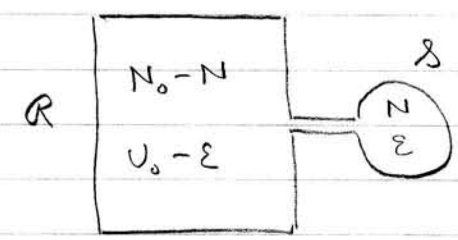
Lecture 12

In canonical ensemble, system S is in thermal contact with reservoir R. R maintains temperature T.
We considered N to be fixed

Now consider "grand canonical ensemble". R supplies both heat (to maintain T) and particles to system S.
So N is not fixed



Total system $R+S$ is isolated
so: $U_0 = U_R + \mathcal{E}$
$N_0 = N_R + N$ fixed

$$U_R = U_0 - \mathcal{E} \qquad N_R = N_0 - N$$

What are properties of the grand canonical ensemble?
Follow same approach as in Lecture 5

Suppose S is in a single quantum state i with $\mathcal{E}_i$, N_i
The probability of being in that state is:

$$p(N_i, \mathcal{E}_i) = \frac{\Omega_{R+S}(N_i, \mathcal{E}_i)}{\sum_{\text{All } \mathcal{E}, N} \Omega_{R+S}(N, \mathcal{E})}$$

$$\Omega_{R+S} = \Omega_R(N_0 - N_i, U_0 - \mathcal{E}_i) \underbrace{\Omega_S(N_i, \mathcal{E}_i)}_{1}$$

since it's a single quantum state

Look at ratio of two probabilities for 2 states 1, 2

$$\frac{p(N_1, \varepsilon_1)}{p(N_2, \varepsilon_2)} = \frac{\Omega_R(N_0-N_1, U_0-\varepsilon_1)}{\Omega_R(N_0-N_2, U_0-\varepsilon_2)} = \frac{e^{S_R(N_0-N_1, U_0-\varepsilon_1)/k_B}}{e^{S_R(N_0-N_2, U_0-\varepsilon_2)/k_B}}$$

$$= \exp\left[S_R(N_0-N_1, U_0-\varepsilon_1) - S_R(N_0-N_2, U_0-\varepsilon_2)\right]/k_B$$

For R U_R, N_R $\gg$ ε_i, N_i so we can expand this in a Taylor series

$$S_R(N_0-N_i, U_0-\varepsilon_i) \approx S_R(N_0, U_0) - N_i\left(\frac{\partial S_R}{\partial N}\right)_{U_0} - \varepsilon_i\left(\frac{\partial S_R}{\partial U}\right)_{N_0}$$

$$= S_R(N_0, U_0) + N_i \frac{\mu}{T} - \varepsilon_i \frac{1}{T} \quad *$$

$$\therefore \frac{p(N_1, \varepsilon_1)}{p(N_2, \varepsilon_2)} = \frac{e^{(\mu N_1 - \varepsilon_1)/k_B T}}{e^{(\mu N_2 - \varepsilon_2)/k_B T}}$$

(* At equilibrium μ, T are the same for R and S)

So $p(N_i, \varepsilon_i) \propto e^{-\beta(\varepsilon_i - \mu N_i)} = C(\mu, T)\, e^{-\beta(\varepsilon_i - \mu N_i)}$

Get $C(\mu, T)$ from normalization

$$1 = \sum_{N_i=0}^{\infty} \sum_{\varepsilon_i(N_i)} p(N_i, \varepsilon_i) = C \sum_{N_i}\sum_{\varepsilon_i} e^{-\beta(\varepsilon_i - \mu N_i)}$$

$$\therefore p(N, \varepsilon) = \frac{e^{-\beta(\varepsilon-\mu N)}}{\sum_N \sum_\varepsilon e^{-\beta(\varepsilon - \mu N)}} \quad \begin{array}{l} \leftarrow \text{"Gibbs factor"} \\ \leftarrow \text{"Gibbs" or "grand sum"} \end{array}$$

$$\boxed{\mathcal{Z}(\mu, T) = \sum_N \sum_\varepsilon e^{-\beta(\varepsilon - \mu N)}}$$

The Gibbs (or Grand) sum

We can relate $\mathcal{Z}$ to partition function Z

$$\mathcal{Z} = \sum_N \sum_{\varepsilon(N)} e^{-\beta(\varepsilon - \mu N)} = \sum_N e^{\beta\mu N} \underbrace{\sum_{\varepsilon(N)} e^{-\beta\varepsilon(N)}}_{Z(N,T)}$$

$$= \sum_N \lambda^N Z(N,T)$$

where $\lambda \equiv e^{\beta\mu}$ "absolute activity"

$Z(N,T)$ is the usual partition function for a system with N particles

Since N is <u>no longer fixed</u>, we have to sum over all possible N, weighted by the absolute activity $\lambda = e^{\beta\mu}$.

Have to determine $\langle N \rangle$ instead:

$$\langle N \rangle = \sum_N \sum_{\varepsilon(N)} \frac{N e^{-\beta(\varepsilon - \mu N)}}{\mathcal{Z}} = \sum_N \sum_{\varepsilon(N)} \frac{N \lambda^N e^{-\beta\varepsilon}}{\mathcal{Z}}$$

$$= k_B T \frac{\partial}{\partial\mu} \ln \mathcal{Z} \qquad \text{or} \qquad \lambda \frac{\partial}{\partial\lambda} \ln \mathcal{Z}$$

$$\langle \varepsilon \rangle = \sum_N \sum_{\varepsilon(N)} \frac{\varepsilon e^{-\beta(\varepsilon - \mu N)}}{\mathcal{Z}}$$

Look at $-\frac{\partial}{\partial\beta} \ln \mathcal{Z} = \frac{1}{\mathcal{Z}} \sum_N \sum_{\varepsilon(N)} (\varepsilon - \mu N) e^{-\beta(\varepsilon - \mu N)}$

$$= \langle \varepsilon \rangle - \mu \langle N \rangle$$

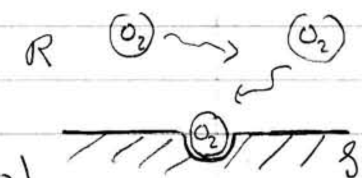
$$\therefore U = \langle \varepsilon \rangle = \mu \langle N \rangle - \frac{\partial}{\partial\beta} \ln \mathcal{Z}$$

$$= \frac{\mu}{\beta} \frac{\partial}{\partial\mu} \ln \mathcal{Z} - \frac{\partial}{\partial\beta} \ln \mathcal{Z}$$

Ex: myoglobin

Myoglobin (Mb) is a protein in our muscles that binds O_2

$$Mb + O_2 \longleftrightarrow MbO_2$$



Mb is $\mathcal{S}$ in contact with R of O_2.

of O_2 on Mb can be 0 (with energy 0)

or 1 (with binding energy $\varepsilon < 0$)

$$\therefore \quad \mathcal{Z} = \sum_N \sum_{\varepsilon(N)} e^{-\beta(\varepsilon - \mu N)}$$

$$= \underbrace{e^{-\beta(0 - \mu \cdot 0)}}_{\text{No } O_2} + \underbrace{e^{-\beta(\varepsilon - \mu \cdot 1)}}_{1\ O_2 \text{ bound}}$$

$$= 1 + e^{-\beta(\varepsilon - \mu)}$$

Find fraction of Mb that are bound to O_2

f = probability to be in occupied state, i.e.:

$$f = \frac{e^{-\beta(\varepsilon-\mu)}}{1 + e^{-\beta(\varepsilon-\mu)}} = \frac{1}{1 + e^{\beta(\varepsilon-\mu)}} = \frac{1}{1 + \lambda^{-1} e^{\varepsilon/k_BT}}$$

Treat O_2 as ideal gas. O_2 is in equilibrium with MbO_2

so $\mu(MbO_2) = \mu(O_2) = k_BT \ln\left(\frac{n_{O_2}}{n_Q}\right)$ $\qquad n_{O_2}$ = density of O_2

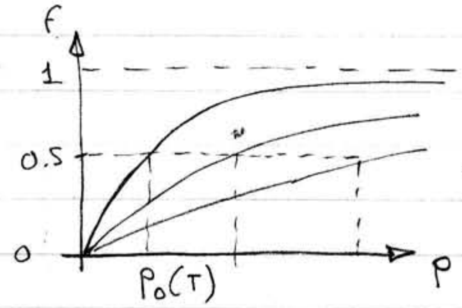
$$\therefore \quad \lambda^{-1} = e^{-\beta\mu} = \frac{n_Q}{n_{O_2}}$$

$$\therefore \quad f = \frac{n_{O_2}}{n_{O_2} + n_Q e^{\varepsilon/k_BT}}$$

can also write this in terms of partial pressure of O_2

$$p = n_{O_2} k_B T$$

$$\therefore \quad f = \frac{p}{p + n_Q k_B T e^{+\varepsilon/k_B T}} = \frac{p}{p + p_0} \qquad p_0 \equiv n_Q k_B T e^{+\varepsilon/k_B T}$$



Langmuir adsorption isotherm

p_0 = pressure at which 1/2 of Mb are occupied

Put in some numbers (from Schroeder):

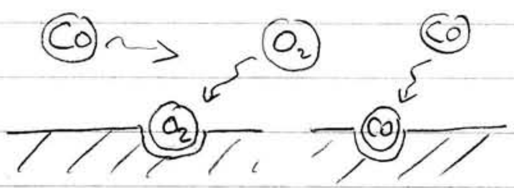
$\varepsilon = -0.7\,\text{eV}$ $\qquad p(O_2)$ near lungs $= 0.2$ atm

$\qquad \mu(O_2) = -0.6\,\text{eV}$

$\Rightarrow$ $f = 98\%$ almost all Mb are occupied

Ex: CO poisoning

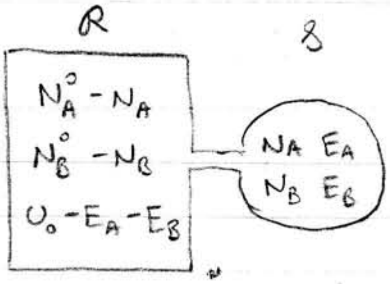
Now consider Mb in equilibrium with 2 species O_2 and CO



Binding energy with O_2 $= \varepsilon_{O_2}$

with CO $= \varepsilon_{CO}$

How do we deal with multiple species?
Same line of reasoning as before, now with multiple chemical potentials $\mu_A, \mu_B \cdots$



$$p(E_A, N_A, E_B, N_B) \propto \Omega_{\mathcal{R}}\left(U_0 - E_A - E_B,\ N_A^0 - N_A,\ N_B^0 - N_B\right)$$

$$\frac{P_1}{P_2} = \frac{\Omega_{\mathcal{R}}\left(U_0 - E_{A_1} - E_{B_1},\ N_A^0 - N_{A_1},\ N_B^0 - N_{B_1}\right)}{\Omega_{\mathcal{R}}\left(U_0 - E_{A_2} - E_{B_2},\ N_A^0 - N_{A_2},\ N_B^0 - N_{B_2}\right)} = \exp \frac{\Delta S_{\mathcal{R}}}{k_B}$$

$$\Delta S_{\mathcal{R}} \cong -(N_{A_1} - N_{A_2}) \underbrace{\frac{\partial S}{\partial N_A}}_{-\frac{\mu_A}{T}} - (N_{B_1} - N_{B_2}) \underbrace{\frac{\partial S}{\partial N_B}}_{-\frac{\mu_B}{T}} - \left[(E_{A_1} + E_{B_1}) + (E_{A_2} + E_{B_2})\right] \underbrace{\frac{\partial S}{\partial U}}_{\frac{1}{T}}$$

etc...

So $$\mathcal{Z} = \sum_{N_A, N_B \cdots} e^{\beta(\mu_A N_A + \mu_B N_B \cdots)} \sum_{\mathcal{E}(N_A, N_B \cdots)} e^{-\beta \mathcal{E}(N_A, N_B \cdots)}$$

where $\mathcal{E}(N_A, N_B) = E_A + E_B + \cdots$

Coming back to CO vs. O_2 problem, need μ_{CO}, μ_{O_2}

$$\mathcal{Z} = \underbrace{e^{\beta(\mu_{CO} \cdot 0 + \mu_{O_2} \cdot 0)} e^{-\beta(0+0)}}_{\text{No } O_2 \text{ or CO}} + \underbrace{e^{\beta(\mu_{CO} \cdot 0 + \mu_{O_2} \cdot 1)} e^{-\beta(0 + \mathcal{E}_{O_2})}}_{1\ O_2 \text{ bound}}$$

$$+ \underbrace{e^{\beta(\mu_{CO} \cdot 1 + \mu_{O_2} \cdot 0)} e^{-\beta(\mathcal{E}_{CO} + 0)}}_{1 \text{ CO bound}}$$

$$= 1 + e^{\beta(\mu_{O_2} - \mathcal{E}_{O_2})} + \underbrace{e^{\beta(\mu_{CO} - \mathcal{E}_{CO})}}_{\text{Extra term from CO}}$$

Now f = probability to be in O_2-bound state

$$f = \frac{e^{\beta(\mu_{O_2} - \varepsilon_{O_2})}}{1 + e^{\beta(\mu_{O_2} - \varepsilon_{O_2})} + e^{\beta(\mu_{CO} - \varepsilon_{CO})}}$$

$$\mu_{O_2} = k_B T \ln \frac{n_{O_2}}{n_Q(O_2)}$$

$$\mu_{CO} = k_B T \ln \frac{n_{CO}}{n_Q(CO)}$$

$$\therefore f = \frac{n_{O_2}}{n_{O_2} + n_Q(O_2) e^{\beta \varepsilon_{O_2}} \left(1 + \frac{n_{CO}}{n_Q(CO)} e^{-\beta \varepsilon_{CO}}\right)}$$

$$= \frac{p}{p + p_0 \left(1 + p_{CO}/p_0'\right)} < \frac{p}{p + p_0}$$

So $f(O_2 \text{ with } CO) < f(O_2, \text{ without } CO)$

CO competes with O_2, leads to less O_2 bound $\Rightarrow$ asphyxiation

Put in some numbers (from Schroeder):

$\varepsilon_{CO} \approx -0.85\,eV$ more tightly bound than O_2 $(\varepsilon_{O_2} \approx -0.7\,eV)$

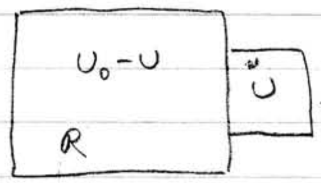
but p_{CO} is 100 x less than for O_2 $\mu_{CO} = -0.72\,eV$

$(\mu_{O_2} \approx -0.6\,eV)$

$f = 25\%$ (drops from 98% !)

Comparison of canonical vs. grand canonical ensembles

Canonical



Fixed in $\mathcal{S}$: N, T

Not fixed : $U = \langle \varepsilon \rangle$

$$p(\varepsilon_i) = \frac{e^{-\beta \varepsilon_i}}{Z}$$

Boltzmann factor

Partition function :

$$Z(T) = \sum_{\varepsilon_i} e^{-\beta \varepsilon_i}$$

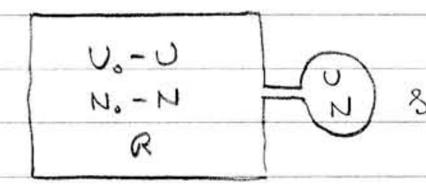
Mean values :

$$U = \langle \varepsilon \rangle = -\frac{\partial}{\partial \beta} \ln Z$$

Helmholtz free energy :

$$F \equiv U - TS$$
$$= -k_B T \ln Z$$

Grand Canonical



Fixed in $\mathcal{S}$: T, μ

Not fixed : $U = \langle \varepsilon \rangle$, $\langle N \rangle$

$$p(\varepsilon_i, N_i) = \frac{e^{-\beta(\varepsilon_i - \mu N_i)}}{\mathcal{Z}}$$

Gibbs factor

Grand or Gibbs sum :

$$\mathcal{Z}(\mu, T) = \sum_{N_i} \sum_{\varepsilon_i(N_i)} e^{-\beta(\varepsilon_i - \mu N_i)}$$
$$= \sum_{N_i} \lambda^{N_i} Z(N_i, T)$$

Mean values

$$U = \langle \varepsilon \rangle = \left(\frac{\mu}{\beta} \frac{\partial}{\partial \mu} - \frac{\partial}{\partial \beta} \right) \ln \mathcal{Z}$$

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z}$$

Grand free energy :

$$\Phi \equiv U - TS - \mu \langle N \rangle$$
$$= -k_B T \ln \mathcal{Z}$$