Ideal Gas

$$Z = \frac{1}{N!}\left(\frac{V\, Z_{int}}{v_Q}\right)^N \qquad v_Q = \left(\frac{h}{\sqrt{2\pi m}}\right)\beta^{3/2}$$

Z_{int} accounts for "internal" degrees of freedom (rotational, vibrational)

$Z_{int} = 1$ for point particles

$$F = -kT \ln Z$$

$$F = -kT\left[-(N\ln N - N) + N\ln V + N\ln Z_{int} - N\ln v_Q\right]$$

$\ln N + \frac{N}{N} - 1$

$$\mu = \frac{\partial F}{\partial N} = -kT\left[-\ln N + \ln V + \ln Z_{int} - \ln v_Q\right]$$

$$= kT \ln \frac{N\, v_Q}{V\, Z_{int}}$$

$v_Q = \text{stuff} \times \beta^{3/2}$

$$U = -\frac{\partial}{\partial\beta}\ln Z = -\frac{\partial}{\partial\beta}\left[-N\ln N + N + N\ln V + N\ln Z_{int} - N\ln v_Q\right]$$

$$U = -N\frac{\partial}{\partial\beta}\ln Z_{int} + \frac{\partial}{\partial\beta}\ln\beta^{3/2}$$

$$= N U_{int,1} + \underbrace{N\frac{\partial}{\partial\beta}\frac{3}{2}\ln\beta}$$

$$\frac{3}{2}\frac{N}{\beta} = \frac{3}{2}NkT$$

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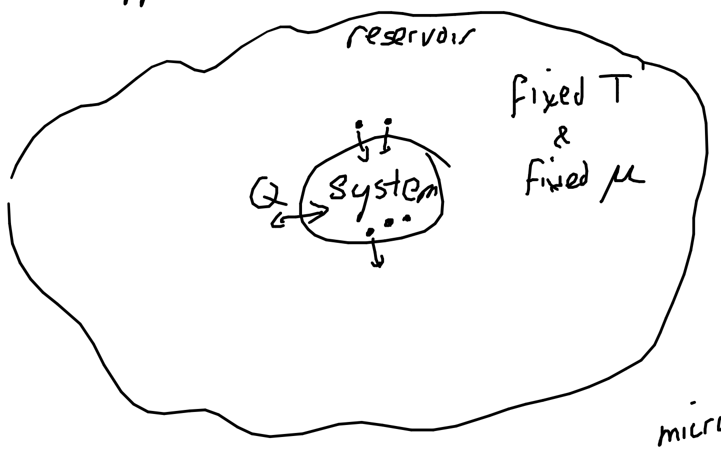
Suppose reservoir can exchange energy & particles



Probability that system is in microstate s_1

$$P(s_1) \propto \cancel{\Omega_{sys}(s_1)}^{\,1}\; \Omega_R(s_1)$$

$$\frac{P(s_1)}{P(s_2)} = \frac{\Omega_R(s_1)}{\Omega_R(s_2)} = e^{[S_R(s_1) - S_R(s_2)]/k}$$

$$dS_R = \frac{1}{T}\left[dU_R - \mu\, dN_R\right] = \frac{1}{T}\left[-dU_{sys} + \mu\, dN_{sys}\right]$$

$$\frac{P(s_1)}{P(s_2)} = e^{[-(U_s(s_1) - U_s(s_2)) + \mu(N_s(s_1) - N_s(s_2))]/kT}$$

$$\frac{P(s_1)}{P(s_2)} = \frac{e^{[-U(s_1) + \mu N(s_1)]/kT}}{e^{[-U(s_2) + \mu N(s_2)]/kT}}$$

$$\rightarrow P(s) = \frac{1}{\mathcal{Z}} \underbrace{e^{-\beta(E_s - \mu N_s)}}_{\text{Gibbs factor}}$$

$\mathcal{Z}$

Grand partition function

$$\mathcal{Z} = \sum_s e^{-\beta(E_s - \mu N_s)}$$

if there are multiple types of particles

$$e^{-\beta E_s}\, e^{\beta \mu_1 N_1}\, e^{\beta \mu_2 N_2} \cdots$$

μ usually negative e.g. $\mu = kT \frac{N v_Q}{V}$

$e^{\beta \mu N}$ ~~usually~~ decreases with N if $\mu < 0$ $\mu < 0$ if $N v_Q < V$

Gibbs statistics favors lower N & lower E.

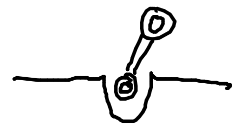
Hemoglobin has 4 sites that can attach oxygen

blood: $T = 310K?$

$\beta = 37.4/eV$

is the reservoir

$\mu_{O_2} = -0.6eV$



$N_{O_2} = 0$

$E = 0$

$N_{O_2} = 1$

$E = -0.7eV$

$e^{-\beta E_s} e^{\beta \mu N_s}$

$e^0 e^0 = 1$

$e^{-(37.4)(-0.7)} e^{(37.4)(-0.6)(1)}$

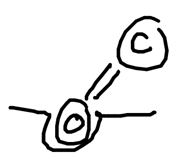
$= 40$

$\mathcal{Z} = 41$

$P_{empty} = \frac{1}{41} = 2\%$

$P_{occupied} = \frac{40}{41} = 98\%$

If carbon monoxide in the blood.



$E_{CO} = -0.85eV$

$e^{-\beta E} e^{\beta \mu_{O_2} N_{O_2}} e^{\beta \mu_{CO} N_{CO}}$ ($N_{O_2} = 0$, $N_{CO} = 1$)

Suppose 1% as much CO as O_2

$\mu = kT \ln \frac{N v_Q}{V} = kT \ln \frac{N}{V} + kT \ln v_Q$

μ is roughly $kT \ln 100 = 0.12eV$ smaller

$\mu_{CO} = -0.6eV - 0.12eV = -0.72eV$

$e^{-(37.4)(-0.85)} e^{(37.4)(-0.72)(1)} = 120.$

$\mathcal{Z} = 1 + 40 + 120 = 161$

$P_{CO} = \frac{120}{161} = 75\%$

$P_{O_2} = \frac{40}{161} = 25\%$