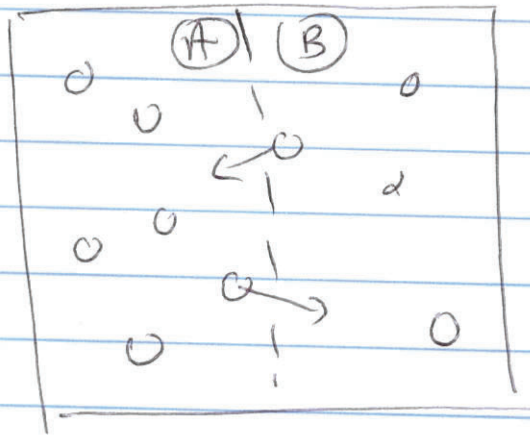
Chap. 9. Variable Number Particles



Particles pass through membrane from A to B

Total N conserved. $N_A + N_B = \text{const}$

$$dN_A = -dN_B$$

I. Gas Mixture

$$S = S_A + S_B$$

$$dS = \frac{\partial S_A}{\partial N_A} dN_A + \frac{\partial S_B}{\partial N_B} dN_B$$

$$= \left\{ \frac{\partial S_A}{\partial N_A} + \frac{\partial S_B}{\partial N_B} \underbrace{\frac{\partial N_B}{\partial N_A}}_{-1} \right\} dN_A$$

$$= -\frac{dN_A}{T}(\mu_A - \mu_B)$$

Chemical potential

$$\mu_x = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}.$$

If there is no conservation of N
e.g. photons, phonons...

$$N_T = N_A + N_B \neq \text{constant}$$

$$\frac{dN_A}{dN_B} = 0$$

$$dS = \frac{\partial S}{\partial N_A} dN_A = \left[\frac{\partial S_A}{\partial N_A} + \frac{\partial S_B}{\partial N_B}\underbrace{\left(\frac{\partial N_B}{\partial N_A}\right)}_{=0}\right] dN_A$$

$$\frac{\partial S}{\partial N_A} = 0 \quad \text{for equilibrium.}$$

If require equilibrium for a given system

$$\frac{\partial S_A}{\partial N_A} = 0 \quad \text{or} \quad \mu_A = 0.$$

All classical wave motion $\mu = 0$.

VIP $$dS = -\left(\frac{\mu_A - \mu_B}{T}\right) dN_A$$

Must have $$\frac{dS}{dt} = -\left(\frac{dN_A}{dt}\right)(\mu_A - \mu_B) \geq 0$$

THUS If $\mu_A > \mu_B$, $\dot{N}_A < 0$, particles leave A

- side with largest chemical potential loses atoms

Need to relate μ to expt^{l} determ^{n}.

Define Gibb's Free Energy

$$G = H - TS = \bar{U} + PV - TS$$

Entropy is a state function $S(U, V, N)$

$$\therefore \quad dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

$$\boxed{dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN}$$

or

$$\boxed{dU = TdS - PdV + \mu dN}$$

Now

$$G = \bar{U} + PV - TS$$

$$dG = dU + PdV + VdP - SdT - TdS$$

use

$$dG = -SdT + \mu dN + VdP$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

G extensive.

$$\frac{\partial G}{\partial N} = \frac{G}{N} \quad \text{so} \quad \boxed{\mu = \frac{G}{N}}$$

$\boxed{\text{Determine } \mu \text{ for isolated system}}$

Count # states W. Assign equal probability

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} \qquad S = k_B \ln W$$

$$= -k_B T\left(\frac{\partial}{\partial N}\ln W\right)$$

Trivial example — N atoms on distinguishable lattice sites

degeneracy g

$$S = k_B \ln W = N k_B \ln g$$

$\ln W = \ln g$

$$\mu = -k_B T \ln g$$

atoms move to side of low g.

Microcanonical Ensemble

$$\phi = A \sin\frac{n_1 \pi x}{L_x} \sin\frac{n_2 \pi x}{L_y} \sin\frac{n_3 \pi x}{L_z}$$

$$\epsilon = \frac{\hbar^2 \pi^2}{2mL^2}\left(n_1^2 + n_2^2 + n_3^2\right) \qquad k_1 = \frac{n_1 \pi}{L}$$

$$Z = Z_{(n_1)} Z_{(n_2)} Z_{(n_3)}$$

$$\sum_n e^{-\gamma n^2} \rightarrow \int e^{-\gamma n^2} = \frac{\sqrt{\pi}}{2\sqrt{\gamma}}$$

$$Z_{n_1} = L\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{1/2}$$

$$= \frac{L}{\lambda_{DeB.}}$$

$$Z_{tot}^{trans.} = V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} = V/\lambda_{dB}^3$$

Distinguishability

$$Z^{(N)} = \frac{\left(Z_{tran}\right)^N}{N!}$$

Helmholtz free energy

$$F = -Nk_BT\left\{\ln V + \frac{3}{2}\ln\left(\frac{mk_BT}{2\pi\hbar^2}\right)\right. - k_BT\left\{N\ln N - N\right\}$$

$$F = -Nk_BT\left\{\ln\frac{V}{N} + \frac{3}{2}\ln\left(\frac{mk_BT}{2\pi\hbar^2}\right) + 1\right\}$$

$$S = -\frac{\partial F}{\partial T} = Nk_B\left\{\ln\frac{V}{N} + \frac{3}{2}\ln\underbrace{\left(\frac{mk_BT}{2\pi\hbar^2}\right)}_{\lambda_D^2} + \frac{5}{2}\right\}$$

chem. Pot.

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$$

$$= -k_BT\left\{\ln\underbrace{\frac{V}{N}}_{\frac{1}{n}} - \ln\left(\lambda_D^3\right)\right\}$$

n = number density

$$\mu = k_BT\left(\ln\frac{n}{n_Q}\right)$$

If atoms have degeneracy g $n_Q \rightarrow n_Q'$

$n_Q' = g\,n_Q$

quantum density

$$\mu = k_BT\ln\left(\frac{n}{n_Q'}\right)$$

For gas $n_Q = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}$

Chemical Reactions

$$C + D \rightleftharpoons CD$$

$N_C + N_{CD} =$ constant

$N_D + N_{CD} =$ constant.

$$\frac{dN_{CD}}{dC} = -1$$

$$\frac{dN_{CD}}{\partial N_D} = -1.$$

But $\dfrac{dN_C}{dN_D} = +1$

$$S = S_C(N_C) + S_D(N_D) + S_{CD}(N_{CD})$$

$$dS = \left[\frac{\partial S_C}{\partial N_C} + \frac{\partial S_D}{\partial N_D}\underbrace{\left(\frac{\partial N_D}{\partial N_C}\right)}_{+1} + \frac{\partial S_{CD}}{\partial N_{CD}}\underbrace{\frac{\partial N_{CD}}{\partial N_C}}_{-1}\right] dN_C$$

$$= -dN_C\left(\mu_C + \mu_D - \mu_{CD}\right)$$

equilibrium $\boxed{\mu_C + \mu_D = \mu_{CD}}$

$$e^- + p^+ \rightleftharpoons H$$

binding energy Δ

~~$\Delta = -13.6\,eV$~~

general

$$\mu = k_B T \ln \frac{n}{n_Q'}$$

$g_H = 4$

$g_e = 2$

$g_p = 2$

$$\mu_H = k_B T \ln \left[\frac{n_H}{4 \cdot \left(\frac{m_H kT}{2\pi\hbar^2} \right)^{3/2}} \right]$$

$$\mu_p = k_B T \ln \left[\frac{n_p}{2 \left(\frac{m_p kT}{2\pi\hbar^2} \right)} \right]$$

$$\mu_e = k_B T \ln \left[\frac{n_e}{2 \left(\frac{m_e kT}{2\pi\hbar^2} \right)} \right]$$

$$\mu_H = \mu_e + \mu_p$$

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$\ln\left[e^{\frac{\Delta}{k_B T}}\right]$.

$$\ln\left[\frac{n_H}{4}\left(\frac{2\pi\hbar^2}{m_H kT}\right)^{3/2}\right] + \frac{\Delta}{kT}$$

$$= \ln\left[\frac{n_p}{2}\left(\frac{2\pi\hbar^2}{m_p kT}\right)^{3/2}\right]$$

$$+ \ln\left[\frac{n_e}{2}\left(\frac{2\pi\hbar^2}{m_e kT}\right)\right]$$

$$n_p n_e = n_H \left(\frac{\cancel{m_p} m_e}{\cancel{m_H}}\right)^{3/2}\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2} e^{\Delta/kT}.$$

$n_p = n_e$

$Q = 0$

$$n_e = n_p = n_H^{1/2}\left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2} e^{\Delta/kT}.$$

$T \sim 10^7$ $\quad \frac{\Delta}{k_B T} = -0.16$ $\quad \frac{n_p}{n_H} \sim 10$.

$\rho_H = 1.4 \times 10^3\ kg/m^3$

$m_H \quad 1.6 \times 10^{-27}\ kg$.

$n_H \sim 0.7 \times 10^{30} \sim 7 \times 10^{29}$

$-\Delta = 13.6\,eV$

$1.6 \times 10^5\ k_B$

$T_{sun} \simeq 10^7\,K$.

no free H