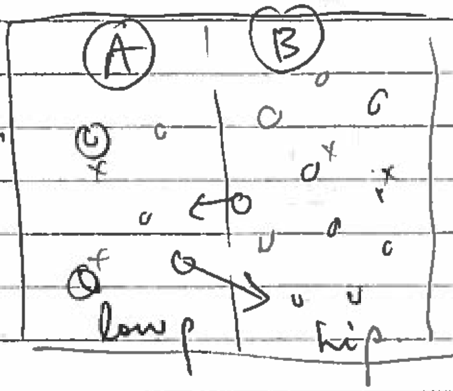
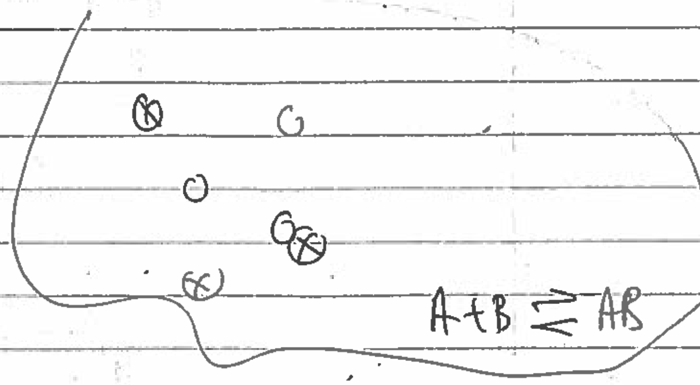
Chap. 9.

Variable Number Particles

same atoms driven by density





Particles pass in/out

Diff in ρ drives particles from $A \to B$.

Chem Reaction.

Total N conserved $\qquad N_A + N_B = \text{cte}$

$dN_A / dN_B = -1$

Chem Reaction. $\qquad N_C + N_{CD} = \text{cte}$

$\qquad N_D + N_{CD} = \text{cte}$

$$\frac{dN_{CD}}{dN_C} = -1 \qquad \frac{dN_{CD}}{dN_D} = -1 \qquad \frac{dN_C}{dN_D} = +1$$

$\boxed{\text{Chem Eqm.}}$

I. Gas Mixture

$$S = S_A + S_B$$

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

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

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

Chem Pot^l. $\mu_x = -T \left(\frac{\partial S_x}{\partial N} \right)_{U,V}$.

S Max^m $dS = 0$ requires $\mu_A = \mu_B$.
Cond^n for Chem Eq^m.

Chem Reaction

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

conserv^n. $N_C + N_{CD} = \text{cte}$ $N_D + N_{CD} = \text{cte}$

$$-dN_C = -dN_D = +dN_{CD}$$

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

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

Cond^n $\boxed{\mu_C + \mu_D = \mu_{CD}}$

$$O_2 + 2H_2 = 2H_2O$$

$$\mu_{O_2} + 2\mu_{H_2} = 2\mu_{H_2O}.$$

$$\sum_i \nu_i \mu_i \Big|_{LHS} = \sum_j \nu_j \mu_j \Big|_{RHS}.$$

$\boxed{\text{No conserv}^n}$ $\quad N_T = N_A + N_B \neq$ ct $\quad \left(\dfrac{dN_A}{dN_B} = 0 \text{ (indep}^t\text{)}\right)$

$S_A + S_B$ $\quad \dfrac{\partial S}{\partial N_A} = \left(\dfrac{\partial S_A}{\partial N_A} + \dfrac{\partial S_B}{\partial N_B}\dfrac{\partial N_B}{\partial N_A}\right) dN_A$

$= 0$ requires $\dfrac{\partial S_A}{\partial N_A} = 0$ or $\mu_A = 0$

E.g. photons in black body radiation
can be absorbed ∴ not conserved.

phonons – not conserved in solid $\quad N_{phon}$ not cte. – absorbed by

All "classical" wave motion $\quad \boxed{\mu = 0}$

$$dS = dN_A\left(\frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B}\right)$$

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

If $\mu_A > \mu_B$, $\dot{N}_A < 0$, particles leave A – side with larger chem pot^l loses particles

Chem.

$$C + D \rightleftharpoons CD$$

$$-dN_C = -dN_D = +dN_{CD}$$

$$S = S_C + S_D + S_{CD}$$

$$\frac{\partial S}{\partial N_C} = \left(\frac{\partial S_C}{\partial N_C} + \frac{\partial S_D}{\partial N_D} - \frac{\partial S_{CD}}{\partial N_{CD}} \right)$$

$$\frac{dS}{dt} = \frac{\partial S}{\partial N_C} \frac{\partial N_C}{\partial t}$$

$$= -\dot{N}_C \left\{ \frac{\mu_C + \mu_D - \mu_{CD}}{T} \right\} \geq 0$$

If $\mu_C + \mu_D > \mu_{CD}$, requires $\dot{N}_C < 0$

\# C atom decr.

Need to determine μ.

Define Gibb's Free Energy

$$G \equiv H - TS = U + PV - TS \qquad \text{Chap 2}$$

Had found

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

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

or $\quad dU = TdS - PdV + \mu dN$

$$A + B \rightleftharpoons C + D$$

$$\mu_A + \mu_B = \mu_C + \mu_D$$

$$G_A + G_B = G_C + G_D$$

Fund^{tl} calc^{n} of μ

Isolated System — Count # states W
+ use equal prob.

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

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

Example $\quad N$ atoms on lattice — $\overset{\text{disting.}}{}$ deg g

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

$$\ln W = N \ln g \qquad \mu = -k_B T \ln g$$

large g
large μ — atom move to side of low g

gas of atoms

$\frac{3}{2}\ln\left(\frac{mk_BT}{2\pi\hbar^2}\right)$ because $\frac{U}{N}=\frac{3}{2}k_BT$

$\boxed{\text{Microcanon ensemble}}$

$$S = Nk_B\left\{\ln\frac{V}{N} + \frac{3}{2}\ln\left(\frac{mU}{3\pi\hbar^2 N}\right) + \frac{5}{2}\right\}$$ over $\longrightarrow$

λ_D^{-1}

$$\mu = -T\frac{\partial S}{\partial N} = -Tk_B\left\{\ln\frac{V}{N} + \frac{3}{2}\ln(\quad) + \cancel{\tfrac{5}{2}}\right\}$$

$$- Nk_BT\left\{-1 - \tfrac{3}{2}\right\}$$

$$\mu = -k_BT\left\{\ln\frac{V}{N} + \frac{3}{2}\ln\frac{mU}{3\pi\hbar^2 N}\right\}$$ see over

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = Nk_B\left(\frac{3U^{-1}}{2}\right) = \frac{3Nk_B}{2}\cdot\frac{1}{U}$$

or $\boxed{U = \frac{3}{2}Nk_BT}$

λ_D^{-1}

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

$$= +k_BT\ln\left(\frac{n}{n_Q}\right)$$ $n = \frac{N}{V}$

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

$n_Q = \frac{1}{\lambda_D^3}$ quantum density

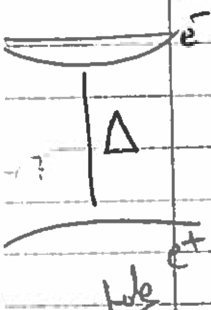
II Consider Helmholtz Free Energy

$$dF = dU - TdS - SdT$$

V varies $$dU = TdS - PdV + \underbrace{\mu dN}_{\text{chem. work}}$$

$$dF = -PdV + \mu dN - SdT$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -k_BT\left(\frac{\partial \ln Z}{\partial N}\right)_{V,T}$$



$$\epsilon(k) = \Delta + \left.\frac{\hbar^2k^2}{2m}\right)^{k_e} \qquad Z = \sum_k e^{-\beta\epsilon(k)}$$

$$Z^{(N)} = Z_1^N/N! \quad \text{(approx.)}$$

$$F = -k_BTN\{\ln Z_1 - \ln N + 1\}$$

$$\mu = -k_BT\left\{\ln\frac{Z_1}{N}\right\} = -k_BT\left\{\ln\frac{\left(\sum_k e^{-\beta\epsilon(k)}\right)}{N}\right\}$$

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

Reactions

binding energy Δ

$$e + p \rightleftharpoons H$$

$\Delta = -13.6\,eV$.

$\sim 1.6\times10^5\,K$

gen. $\mu = kT \ln \frac{n}{n_Q'}$ $g_H = 4$ $T_{sun} \sim 10^7$

m.

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

$g_e = 2$

$g_p = 2$

(spin $\frac{1}{2}$).

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

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

$$\mu_e = kT \ln\left[\frac{n_e}{2}\left(\frac{2\pi\hbar^2}{m_e kT}\right)^{3/2}\right].$$

Eqm

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

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

$$\ln\left(e^{(\Delta/kT)}\right) \qquad + \ln\left\{\frac{n_e}{2}\left(\frac{2\pi\hbar^2}{m_e kT}\right)^{3/2}\right\}$$

$$\frac{n_H}{4}\left(\frac{2\pi\hbar^2}{m_H kT}\right)^{3/2} e^{\Delta/kT} = \frac{n_p n_e}{4}\left(\frac{2\pi\hbar^2}{kT}\right)^3 \left(\frac{1}{m_p m_e}\right)^{3/2}$$

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

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

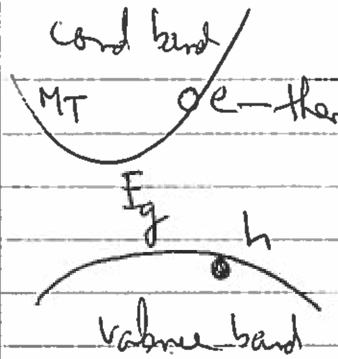
$n_p = n_e$

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

$T = 10^7$

$\frac{n_p}{n_H} \sim 10$

$\Delta = -13.6\text{eV} \Rightarrow \frac{\Delta}{kT} = -0.016$



$e + h \to \underbrace{\text{phonon}}$

$\mu_e + \mu_h = 0$ not cons^d

$$\epsilon_e(k) = E_g + \frac{\hbar^2 k^2}{2m_e}$$

$$\epsilon_h(k) = \frac{\hbar^2 k^2}{2m_h}$$

approach

(treat as lo density gases)

$$\mu_e = E_g + k_B T \ln\left(\frac{n_e}{n'_{Qe}}\right) \qquad n'_{Qe} = 2n_{Qe}$$

$$\mu_h = kT \ln\left(\frac{n_h}{n'_{Qh}}\right) \qquad n'_{Qh} = 2n_{Qh}$$

$$E_g + kT \ln\left(\frac{n_e}{2n_{Qe}}\right) + kT \ln\left(\frac{n_h}{2n_{Qh}}\right) = 0$$

$$\frac{E_g}{kT} + \ln\left(\frac{n_e n_h}{4n_{Qe} n_{Qh}}\right) = 0$$

$$n_e n_h = 4n_{Qe} n_{Qh} e^{-E_g/kT}$$

$n_e = n_h$

$$n_e = 2\left(n_{Qe} n_{Qh}\right)^{1/2} e^{-E_g/2kT}$$

$$\mu_e = \frac{E_g}{2} + \frac{kT}{2} \ln\left(\frac{n_{Qh}}{n_{Qe}}\right)$$

External Chem^l Pot^l

particle in

$$\epsilon_i(r) = \underset{\text{int}^l}{\epsilon_i^0(r)} + \Delta(r)$$

int^n with ext^l field

eg gravity $\Delta(r) = mgz$

E-field $= -e\vec{E}(\vec{r})$ $e = q = $ charge

B-" $= -\mu \cdot B(r)$

$$\mu = \mu_{int} + \Delta$$

particle in grav^n field $\mu = \Delta(r) + \mu_{int}$

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

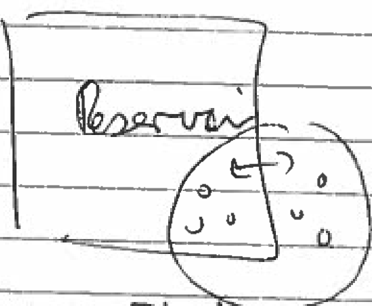
$$n = n_Q e^{(\mu - mgz)/kT}$$

eg $n_{Q_2} \approx e^{-mgz/kT}$ decay expon. with

factor e^{-1} in $z_L = \frac{kT}{mg}$ ~ 8.5 km for O_2

~ 32 km for H_2

Grand Canon^l Ensemble



particles flows in & out
(heat)

can change

Def^n $\quad \frac{1}{T} = k_B \left(\frac{\partial \ln W_R}{\partial U_R} \right)_{N_R} = \frac{\partial S}{\partial U}$ — for reservoir

& T const for LARGE reservoir

$$\mu = -k_B T \left(\frac{\partial \ln W_R}{\partial N_R} \right)_{U_R} = -T \frac{\partial S}{\partial N}$$

Solve above

$$\ln W_R = K + \frac{U_R - \mu N_R}{kT}$$

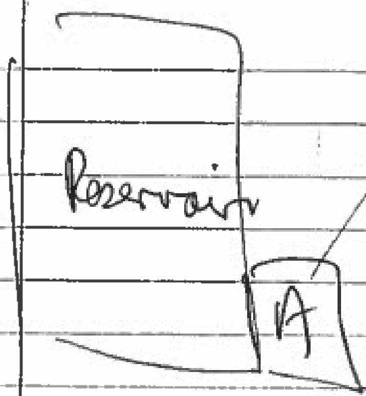
$$W_R = \alpha \exp\left[(U_R - \mu N_R)/kT \right]$$

$$W_R(U_R, N_R) = \gamma e^{(U_R - \mu N_R)/kT}$$

te

$$W(\epsilon_i, n_i) = W_R(U_T - \epsilon_i, N_T - N_i) = \gamma e^{(U_T - \mu N_T)/kT} e^{-(\epsilon_i - \mu n_i)/kT}$$

$$p_i \propto e^{-(\epsilon_i - \mu n_i)/kT}$$



System A in contact w R

total isolated

$$U_T = U_R + U_A \qquad U_R = U_T - U_A$$

$$N_T = N_R + N_A \qquad N_R = N_T - N_A$$

$$W_R = \alpha\, e^{\{(U_T - U_A) - \mu(N_T - N_A)\}/kT}$$

T, U_T const.

$$= \underbrace{\alpha'}_{\text{const}}\, e^{-(U_A - \mu N_A)/kT}$$

single qu. state $\psi_i = |i\rangle$

summing e fn both E_i + N not always OK

$$W_i = \alpha' e^{-(E_i - \mu N_i)/kT}$$

└ total # accessible states

Total # states for all possible $|i\rangle$ $\quad W = \sum W_i$

$$p_i = \frac{W_i}{W}$$

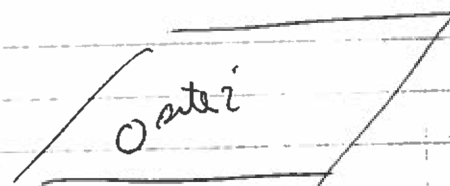
$$= e^{-(E_i - \mu N_i)/kT} \Big/ \sum_i e^{-(E_i-\mu N_i)/kT}$$

Now consider ensemble of replicas with E_i, N_i;

en + part. # flowing $\hookrightarrow$ grand canon^l ensemble

$$\boxed{\Xi = \sum_i e^{-(E_i - \mu N_i)/k_BT}}$$

e.g. particles on a surface



$$\begin{array}{ccc} n_i = 1 & \text{or} & 0 \\ \updownarrow & & \updownarrow \\ E_i = \epsilon_i & & 0 \end{array}$$

$$\Xi = 1 + e^{-(\epsilon_i - \mu)/k_BT}$$

$$p_{\substack{\text{site}\\ \text{occup}}} = \frac{e^{-(\epsilon_i-\mu)/kT}}{\Xi} = \frac{1}{e^{(\epsilon_i-\mu)/kT}+1}$$

Grand Potential

$$S = -k_B \sum_i p_i \ln(p_i)$$

$$p_i = e^{-(E_i - \mu N_i)/kT} / \Xi$$

$$S = -k_B \sum_i p_i \left\{ \left(-\frac{E_i - \mu N_i}{kT} \right) - \ln \Xi \right\}$$

$$= \frac{\bar{U}}{T} - \mu \frac{\bar{N}}{T} + k_B \ln \Xi$$

$$\boxed{\bar{U} - \mu N - TS = -k_B T \ln \Xi = \Phi_G}$$ ← grand potential

Can det thermo fn from Φ_G

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} d\bar{U} + \left(\frac{\partial S}{\partial V}\right)_{N,U} dN + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

$$= \frac{d\bar{U} + PdV - \mu dN}{T}$$

$$d\bar{U} = -PdV + \mu dN + TdS$$

$$\Phi_G = \bar{U} - \mu N - TS$$

$$d\Phi_G = d\bar{U} - d(\mu N) - d(TS)$$

$$= -PdV - \bar{N}d\mu - SdT$$

$$S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu} = \frac{\partial}{\partial T}\left(k_B T \ln \Xi\right)_{V,\mu}$$

$$P = \frac{\partial}{\partial V}\left(k_B T \ln \Xi\right)_{T,\mu}$$

$$\bar{N} = \frac{\partial}{\partial \mu}\left(kT \ln \Xi\right)_{T,V}$$