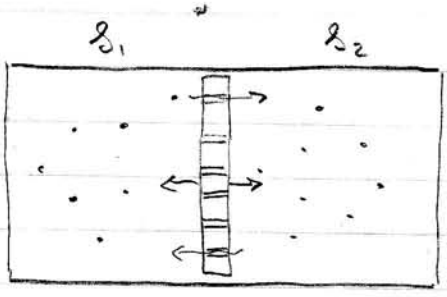
Lecture 11

Consider two systems that can exchange energy, volume, and particles. Total system is isolated



$U_1, V_1, N_1 \quad U_2 V_2 N_2$

$U = U_1 + U_2$ fixed
$V = V_1 + V_2$ fixed
$N = N_1 + N_2$ fixed

but individual quantities can be exchanged

At equilibrium, the total entropy S is maximum so $dS = 0$
In general $S = S(U, V, N)$ so:

$$dS = 0 = dS_1 + dS_2$$

$$dS_1 = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} dU_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{U_1,N_1} dV_1 + \left(\frac{\partial S_1}{\partial N_1}\right)_{U_1,V_1} dN_1$$

similarly for dS_2. Also $dU_2 = -dU_1$, $dV_2 = -dV_1$, $dN_2 = -dN_1$

$$\Rightarrow \quad 0 = \left(\frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2}\right) dU_1 + \left(\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2}\right) dV_1 + \left(\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2}\right) dN_1$$

thermal equil.	mechanical equil.	diffusive equil.
$\frac{1}{T_1} = \frac{1}{T_2}$	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$	$\frac{-\mu_1}{T_1} = \frac{-\mu_2}{T_2}$

Define chemical potential

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

At equilibrium $\mu_1 = \mu_2$

Notice μ is intensive since S, N are extensive
Also, $-$ sign means that $\mu < 0$ if entropy ↑ as N ↑
(as in the ideal gas)

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

Write in terms of dU, get thermodynamic identity:

$$dU = \underbrace{T dS}_{\text{heat}} \underbrace{- p dV}_{\text{"mechanical" work}} + \underbrace{\mu dN}_{\text{"chemical" work}}$$

← 3 ways to transfer energy

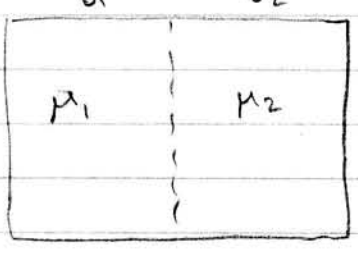
$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN \qquad U = U(S, V, N)$$

$$\therefore \quad \mu \equiv \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

Change in energy upon changing N for fixed S, V

Does sign make sense? Think of ideal gas. If we add a particle, Ω and S increase. To hold S constant, we must decrease U, so $\mu < 0$.

Just as difference in T drives heat flow (or Δp drives volume change), difference in μ drives particle flow



Let's say initially $\mu_1 > \mu_2$

so $\frac{\partial S_1}{\partial N_1} < \frac{\partial S_2}{\partial N_2}$. S_2 gains more entropy than S_1 loses for flow of particles from 1 → 2

i.e. $dS = dS_1 + dS_2 = \left(\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2}\right) dN_1 \geq 0$

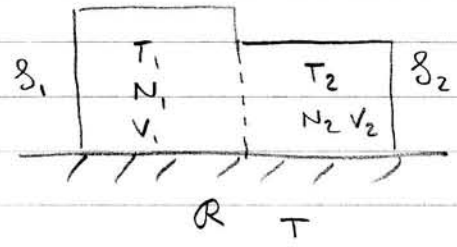
≤ 0 so $dN_1 \leq 0$ i.e. particles flow $1 \rightarrow 2$

So <u>particles flow from high μ to low μ</u>

Chemical potential is equivalent to a potential energy
$\Delta\mu$ drives motion of particles, until $\Delta\mu = 0$

In most practical situations, we don't deal with isolated system. More often, we encounter systems in thermal equilibrium with a reservoir.

Imagine two systems S_1, S_2 in thermal equilibrium with reservoir R (and each other). They can exchange particles



$T_1 = T_2 = T$

We saw earlier that Helmholtz free energy of $S_1 + S_2$ is <u>minimized</u>

$F = F_1(N_1, V_1, T) + F_2(N - N_1, V_2, T)$ $\quad N = N_1 + N_2$

$$dF = 0 = dF_1 + dF_2$$
$$= \left(\frac{\partial F_1}{\partial N_1}\right)_{T,V_1} dN_1 + \left(\frac{\partial F_2}{\partial N_2}\right)_{T,V_2} dN_2$$
$$= \left(\frac{\partial F_1}{\partial N_1} - \frac{\partial F_2}{\partial N_2}\right) dN_1$$

(Assume for simplicity $dV = 0 = dT$)

So equilibrium is reached when $\frac{\partial F_1}{\partial N_1} = \frac{\partial F_2}{\partial N_2}$

Propose that $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$

Check: $dU = TdS - pdV + \mu dN$

$dF = dU - SdT - TdS$ $\qquad F = U - TS$

$= -SdT - pdV + \mu dN$ $\qquad \therefore \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$

So: $\boxed{\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V}}$ All equivalent

Ex: ideal gas

$F = -k_B T \ln Z \qquad Z = \frac{(n_Q V)^N}{N!} \qquad n_Q = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$

$\therefore \quad F \approx -N k_B T \ln(n_Q V) + N k_B T \ln N - N k_B T$

$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_B T \ln(n_Q V) + k_B T \ln N + \cancel{N} k_B T \frac{1}{\cancel{N}} - \cancel{k_B T}$

$= -k_B T \ln\left(\frac{n_Q V}{N}\right)$

$\mu_{ideal} = k_B T \ln\left(\frac{n}{n_Q}\right)$

Recall that for classical ideal gas $n \ll n_Q$ so $\mu_{ideal} < 0$

Ex: Argon at $T = 300\,K$, $p = 1\,atm$

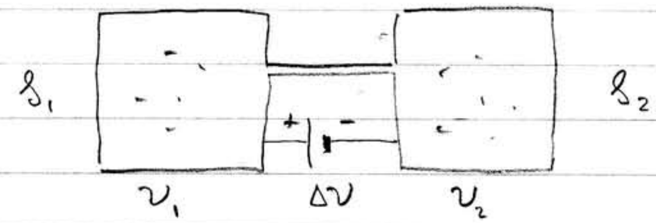
$n = \frac{N}{V} = 2.5 \times 10^{25}\ m^{-3} \qquad n_Q = 2 \times 10^{32}\ m^{-3}$

$\mu_{Ar} = -0.42\ eV < 0$

Note that $\mu \sim \ln n$ so if two identical gases are brought into diffusive equilibrium $\mu_1 = \mu_2$ means $n_1 = n_2$. Makes sense.

If chemical potential is like a potential energy, we should be able to counteract $\Delta\mu$ with a difference in potential energy in the opposite direction

Imagine a gas with charge q $\qquad$ $\mathcal{S}_1$ + $\mathcal{S}_2$ are in thermal + diffusive equilibrium, but we have a voltage difference between them



For each system $\mathcal{S}$

$$E = K.E. + P.E.$$

$$K.E. = \frac{p^2}{2m} \qquad P.E. = q\mathcal{V}$$

$$Z_1 = \frac{1}{N_1!}\left(e^{-\beta q \mathcal{V}_1} \sum_i e^{-\frac{\beta p_i^2}{2m}}\right)^{N_1} = \frac{1}{N_1!}\left(e^{-\beta q \mathcal{V}_1} n_Q V\right)^N$$

$$F_1 = -k_B T \ln Z_1 = -N_1 k_B T \ln\left(e^{-\beta q \mathcal{V}_1} n_Q V\right) + N k_B T \ln N - N k_B T$$

$$\mu_1 = \underbrace{k_B T \ln\left(\frac{n_1}{n_Q}\right)}_{\mu_{int,1}\text{ internal}} + \underbrace{q\mathcal{V}_1}_{\mu_{ext,1}\text{ external}}$$

same for $\mathcal{S}_2$

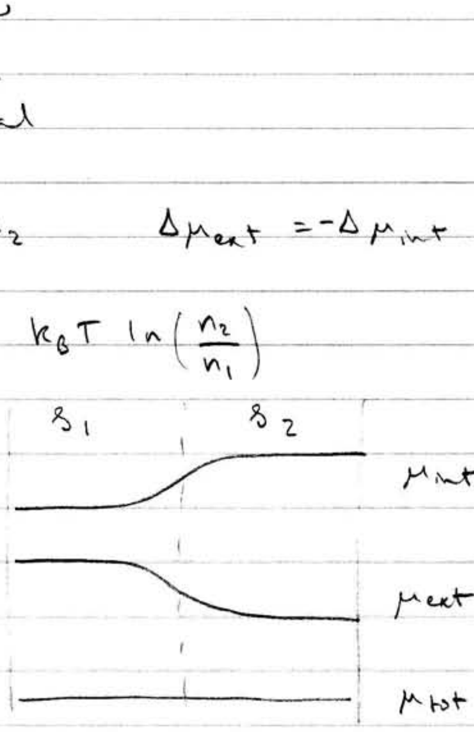
$\therefore$ At equilibrium $\mu_1 = \mu_2$ $\qquad$ $\Delta\mu_{ext} = -\Delta\mu_{int}$

$$q\Delta\mathcal{V} = q\mathcal{V}_1 - q\mathcal{V}_2 = k_B T \ln\left(\frac{n_2}{n_1}\right) \qquad \text{Nernst equation}$$

If $\mu_{int,2} > \mu_{int,1}$

Then $\mu_{ext,2} < \mu_{ext,1}$

$\mathcal{V}_2 < \mathcal{V}_1$

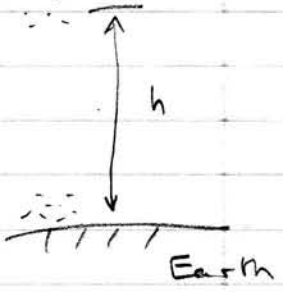


So ΔV maintains a concentration gradient between β_1 + β_2. This is what happens in a cell. Molecular pumps move ions across cell membrane, establish ΔV between inside + outside of cell, and concentration gradient (of course, ions in solution are not an ideal gas. Will see this later when we talk about dilute solutions)

Ex: atmospheric density

Atoms in atmosphere are in gravitational field of the earth, so:

$$\mu(h) = \underbrace{mgh}_{\mu_{ext}} + \underbrace{k_B T \ln \frac{n(h)}{n_Q}}_{\mu_{int}}$$



Assume equilibrium so $\mu(0) = \mu(h)$

$$mgh + k_B T \ln \frac{n(h)}{n_Q} = k_B T \ln \frac{n(0)}{n_Q}$$

$$\therefore \quad n(h) = n(0) \exp\left(-\frac{mgh}{k_B T}\right)$$

Since $p = \frac{Nk_BT}{V} = n k_B T$ $\qquad p(h) = p(0)\, e^{-mgh/k_BT}$

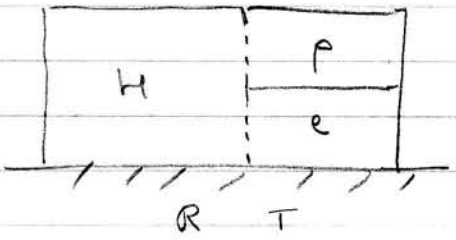
Roughly how atmospheric density varies with height, although atmosphere is clearly not isothermal.

Ex: Ionization of H atom in the sun

In the sun $H \leftrightarrow p + e$ ionization energy is $\Delta = 13.6\,eV$
(i.e. binding energy for H is $-\Delta$)

Treat sun as fixed V, T ($T = 5800\,K$), so F will be minimized

$$F_{tot} = F_H + F_p + F_e$$



Equivalent to 3 systems $\mathcal{S}_H$, $\mathcal{S}_p$, $\mathcal{S}_e$ with $\mathcal{S}_H$ in diffusive equilibrium with $\mathcal{S}_p + \mathcal{S}_e$

$$dF_{tot} = 0 = dF_H + dF_p + dF_e$$

$$= \frac{\partial F_H}{\partial N_H} dN_H + \frac{\partial F_p}{\partial N_p} dN_p + \frac{\partial F_e}{\partial N_e} dN_e$$

But, from reaction $dN_H = -dN_e = -dN_p$, $N_e = N_p$
(i.e. gaining 1 H atom means losing one e^- and one p)

$$\therefore \quad 0 = \left(\frac{\partial F_H}{\partial N_H} - \frac{\partial F_p}{\partial N_p} - \frac{\partial F_e}{\partial N_e} \right) dN_H = \mu_H - \mu_p - \mu_e$$

Equilibrium is $\mu_H = \mu_p + \mu_e$

Treat each as ideal gas, except for H we must account for binding energy $-\Delta$

$$\therefore \quad \mu_H = -\Delta + k_B T \ln \frac{n_H}{n_Q(H)} \qquad \mu_p = k_B T \ln \frac{n_p}{n_Q(p)} \qquad \mu_e = k_B T \ln \frac{n_e}{n_Q(e)}$$

Equilibrium gives: $$-\frac{\Delta}{k_B T} = \ln \left[\frac{n_e n_p}{n_H} \cdot \frac{n_Q(H)}{n_Q(e)\, n_Q(p)} \right]$$

$$\frac{n_q(H)}{n_q(e)\, n_q(p)} = \left(\frac{m_H}{m_p m_e}\right)^{3/2} \left(\frac{h^2}{2\pi k_B T}\right)^{3/2}$$

since $n_q = \left(\frac{2m k_B T}{h^2}\right)^{3/2}$

so: $$\frac{n_e n_p}{n_H} = \left(\frac{2\pi k_B T}{h^2}\right)^{3/2} \left(\frac{m_p m_e}{m_H}\right)^{3/2} e^{-\Delta/k_B T}$$

Simplify $n_e = n_p$ and $m_H \approx m_p$ $(m_p \sim 2000\, m_e)$

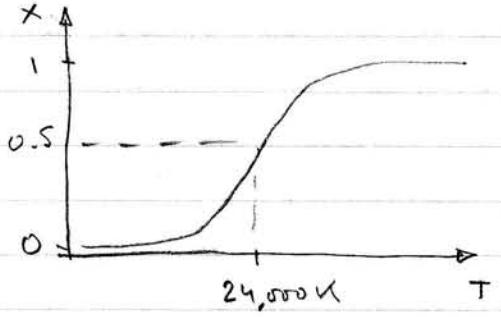
$$\frac{n_p^2}{n_H} = \left(\frac{2\pi m_e k_B T}{h^2}\right)^{3/2} e^{-\Delta/k_B T}$$

Saha equation

Look at fraction of ionized atoms $x = \frac{N_p}{N_{tot}}$ $\quad N_{tot} = N_H + N_p$

$$n_p = \frac{N_p}{V} = x\frac{N_{tot}}{V}, \quad n_H = \frac{N_H}{V} = (1-x)\frac{N_{tot}}{V}$$

so $$\frac{x^2}{1-x} = \frac{V}{N_{tot}} \left(\frac{2\pi m_e k_B T}{h^2}\right)^{3/2} e^{-\Delta/kT} \Rightarrow \text{solve for } x$$



½ are ionized at $T_{1/2} = 24{,}000$ K
(much less at surface of sun $T = 5800$ K)

$k_B T_{1/2} \approx 2\text{ eV} < 13.6\text{ eV} = \Delta$