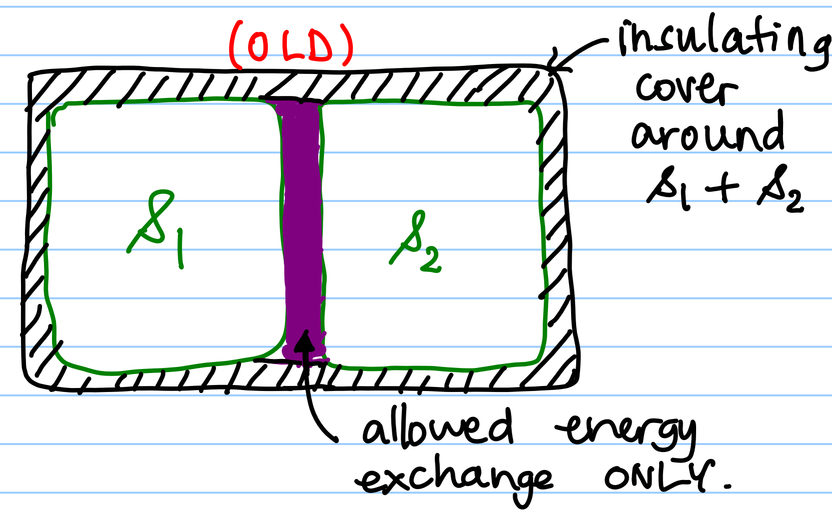
**Today:**

- Redo the $\mathcal{S}_1 + \mathcal{S}_2$ thought [gedanken] experiment but, this time, allow exchange of BOTH energy & particles.
- Find the extra condition(s) for thermal equilibrium → Chemical Potential $\mu$
- Find the new 1st Law of Thermodynamics ($dU = đQ - đW$)
- Example: Ideal Gas Atmosphere

Recall our old friends: system $\mathcal{S}_1$ & system $\mathcal{S}_2$

Previously, we found that maximizing the total entropy led to $\frac{1}{\tau} \equiv \left(\frac{\partial \sigma}{\partial U}\right)_{V,N,\ldots}$ and that thermal equilibrium requires $\tau_1 = \tau_2$.



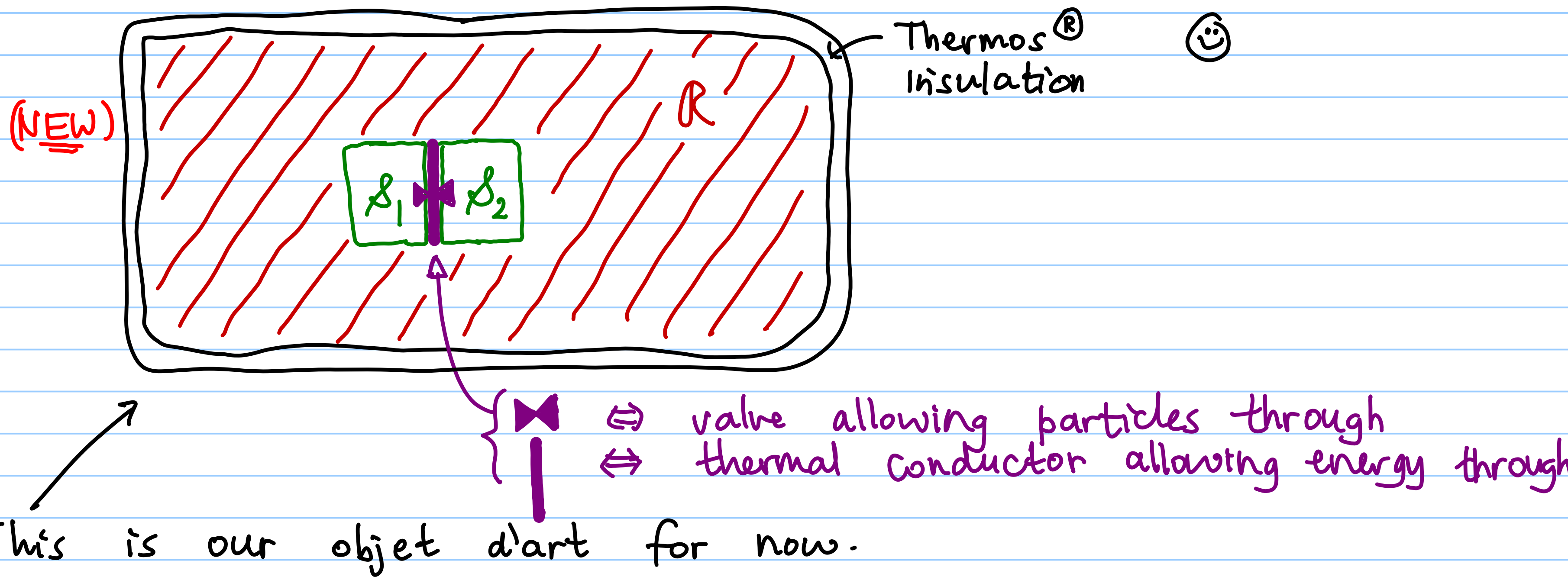

- Consider new: allowing not just $U_1$ & $U_2$ to vary subject to $U_1 + U_2 = U$ but also $N_1$ & $N_2$ " " " " $N_1 + N_2 = N$ where $U$ & $N$ are fixed.

# CHEMICAL POTENTIAL

We want to maximize entropy, with $U_i$ & $N_i$ varying ($i=1,2$).
Previously, we learned that

maximizing $\sigma$ $\leftrightarrow$ minimizing $F$ at fixed $(\tau, V)$

$\Rightarrow$ if we want to use all we know about $F$, we had better make sure $\tau$ is kept constant via a reservoir $\mathcal{R}$:




- We want $dF = 0$ with $F = F(N, \tau, V)$
  subject to $dN = 0 = dN_1 + dN_2$

⇒ Define $\boxed{\mu := \left(\frac{\partial F}{\partial N}\right)_{\tau, V, \ldots}}$

Then

$$dF = dF_1 + dF_2 \quad \leftarrow \text{(because } \sigma \text{ \& } U \text{ are additive for independent systems)}$$

$$= \left(\frac{\partial F_1}{\partial N_1}\right)_{N_2,\tau,V} dN_1 + \left(\frac{\partial F_2}{\partial N_2}\right)_{N_1,\tau,V} dN_2 \quad \leftarrow \text{(because } (\tau, V) \text{ fixed)}$$

$$= \mu_1\, dN_1 + \mu_2\, dN_2$$

$$= (\mu_1 - \mu_2)\, dN_1 \quad \Rightarrow \quad \boxed{\mu_1 = \mu_2} \text{ for diffusive equilibrium}$$

Thermal equilibrium also requires $\boxed{\tau_1 = \tau_2}$, of course. ☺

## More than 2 component systems:

- In fact, for $n$ systems in diffusive & thermal equilibrium,

$$\begin{cases} \tau_i = \tau_j, & i \neq j \quad i, j = 1, \ldots, n \\ \mu_i = \mu_j, & \end{cases}$$

where $\mu_i = \left(\frac{\partial F_i}{\partial N_i}\right)_{N_{j \neq i}, \tau, V, \ldots}$

⊛ A prototypical example: 3 different kinds of gas molecules in one box.

- Recall that, if $\tau_1 > \tau_2$, energy moves from hotter to colder body, i.e. down the $\tau$-gradient.

Here, **if $\mu_1 > \mu_2$, particles move down the $\mu$-gradient.** (e.g. osmosis)

**NEW 1ST LAW** [KK's "Thermodynamic Identity"]

The most straightforward way I know of deriving this is to concentrate on entropy ($\sigma$), in two stages:

(i) first consider $\sigma(U,N)$ keeping $\tau$ & $V$ fixed;

(ii) then bring in $V$ as well → consider $\sigma(U,N,V)$ at fixed $\tau$.

- If $\sigma = \sigma(U,N)$ then $d\sigma = \left(\frac{\partial\sigma}{\partial U}\right)_{N,V} dU + \left(\frac{\partial\sigma}{\partial N}\right)_{U,V} dN$

$$\Rightarrow \left(\frac{\partial\sigma}{\partial N}\right)_{U,V} = -\left(\frac{\partial\sigma}{\partial U}\right)_{N,V,\tau}\left(\frac{\partial U}{\partial N}\right)_{\tau,V} + \underbrace{\left(\frac{\partial\sigma}{\partial N}\right)_{U,V,\tau}}_{\text{not same as } (\partial\sigma/\partial N)_{U,V}}$$

$$= -\frac{1}{\tau}\left(\frac{\partial U}{\partial N}\right)_{\tau,V} + \left(\frac{\partial\sigma}{\partial N}\right)_{U,V,\tau} \qquad (*)$$

(Hmm... seems we're stuck. Let's bring in $\mu$:) $\mu = \left(\frac{\partial F}{\partial N}\right)_{\tau,V}$

Also, we know $F = U - \tau\sigma$ ← (aha!)

$$\Rightarrow \left(\frac{\partial F}{\partial N}\right)_{\tau,V} = \left(\frac{\partial U}{\partial N}\right)_{\tau,V} - \tau\left(\frac{\partial \sigma}{\partial N}\right)_{\tau,V}$$

i.e. $$\mu = \left(\frac{\partial U}{\partial N}\right)_{\tau,V} - \tau\left(\frac{\partial \sigma}{\partial N}\right)_{\tau,V} \qquad (\phi)$$

(*) & ($\phi$) ⇒ $$\boxed{\mu = -\tau\left(\frac{\partial \sigma}{\partial N}\right)_{U,V,\tau}}$$

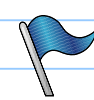
- Let's bring in volume dependence. We know that now

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

Earlier in the course, we found that

$$p = \tau\left(\frac{\partial \sigma}{\partial V}\right)_{U,N}$$

So $$d\sigma = \frac{1}{\tau}dU - \frac{\mu}{\tau}dN + \frac{p}{\tau}dV$$

i.e. $$\boxed{dU = \tau d\sigma - p dV + \mu dN}$$ 

Since $dU = đQ - đW$, with $đQ = \tau d\sigma$, we see that

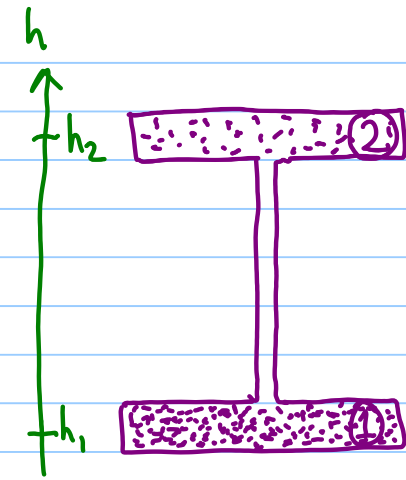
$$\boxed{đW = +p dV - \mu dN}$$

i.e. work done by system has contribution of $-\mu dN$
or " " on " " " " $+\mu dN$

i.e. doing work on system, of magnitude $\int_{path} \mu dN$, raises system energy.

## $\mu$ as an energy

- Consider a thought experiment in which 2 bits of gas start at heights $h_1 \neq h_2$, and have chemical potentials $\mu_1 \neq \mu_2$. Let $\tau_1 = \tau_2 = \tau$.




($\tau$ = constant)

- Suppose that $\mu_1 > \mu_2$.

(?) Equilibrium requires $\mu_1 = \mu_2$, so particles move down $\mu$-gradient, which happens to be upwards ↑ in this experiment setup.

- Work we do taking $\Delta N$ particles ① → ② is $\Delta W = -\int_{path} \mu \, dN$

  i.e. $\Delta W = -(\mu_2 - \mu_1)\Delta N$

  but work done against gravity is $\Delta W = \Delta N \cdot mg(h_2 - h_1)$ !

  $\Rightarrow \quad \mu_1 - \mu_2 = mg(h_2 - h_1)$ $\quad (\Delta W_{total} = 0)$

  ⊛ $\mu$ has units of energy. Also, note that $\mu_1 + mgh_1 = \mu_2 + mgh_2$.

  ($\mu_1$: internal $(\partial F/\partial N)$; $mgh_1$: external potential energy)

- Quite generally: $\boxed{\mu = \mu_{int} + \mu_{ext}}$

## Example: Isothermal Ideal Gas Atmosphere

Ideal gas : $Z_1 = n_Q V$ with $n_Q = \sqrt{\frac{m\tau}{2\pi\hbar^2}}$ (in 3 dimensions of space)

Also : $F = -\tau \log Z_N = -\tau \log\left(\frac{Z_1^N}{N!}\right) = +\tau N \log N - \tau N - N\tau \log(n_Q V)$

$= -N\tau \log\left(\frac{n_Q}{n}\right) - \tau N$ where $n = \frac{N}{V}$

Know $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,\tau,\ldots} = +\frac{\partial}{\partial N}\left[-N\tau \log\left(\frac{n_Q V}{N}\right) - \tau N\right]$

$= -\tau\left[\log\left(\frac{n_Q V}{N}\right) - 1 + 1\right] = -\tau \log\left(\frac{n_Q}{n}\right)$

so $\mu = \mu_{int} + \mu_{ext}$

$= \tau \log\left(\frac{n}{n_Q}\right) + mgh = \text{constant } \forall h$

and $\tau = \text{constant } \forall h$ ("isothermal")

Rearranging $\Rightarrow$ $n(h) = n_Q(\tau) \exp\left(\frac{\mu}{\tau} - \frac{mgh}{\tau}\right)$

or $\boxed{n(h) := n_0\, e^{-mgh/\tau}}$ where $n_0 = \sqrt{\frac{m\tau}{2\pi\hbar^2}}\, e^{\mu/\tau}$

Exercise: work out how low atmospheric pressure would be on Everest by comparison to Toronto, assuming (unrealistic) that $\tau \approx$ const.

Next time: GIBBS FACTOR ☺