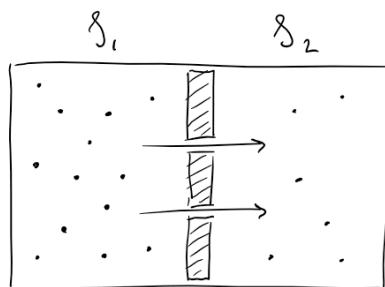


## Lecture 10 – Chemical potential

LAST TIME: We've considered systems in thermal contact exchanging energy, but not particles

TODAY: Systems that can exchange energy, change volume, and particles.

Since total combined system is closed:



$U = U_1 + U_2$  is fixed

$V = V_1 + V_2$  is fixed

$N = N_1 + N_2$  is fixed

but individual quantities can vary

KEY CONCEPT: Diffusive equilibrium

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

$$dS = 0 = dS_1 + dS_2$$

with

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

and a similar expression for  $dS_2$ .

Since  $dU_1 = -dU_2$ ,  $dV_1 = -dV_2$ , and  $dN_1 = -dN_2$  it follows that

$$0 = \underbrace{\left( \frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2} \right)}_{\frac{1}{T_1} - \frac{1}{T_2} = 0} dU_1 + \underbrace{\left( \frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} \right)}_{\frac{p_1}{T_1} - \frac{p_2}{T_2} = 0} dV_1 + \underbrace{\left( \frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2} \right)}_{-\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2} = 0} dN_1$$

"thermal equilibrium"
"mechanical equilibrium"
"diffusive equilibrium"

$\mu$  is called the chemical potential:  $\mu \equiv -T \left( \frac{\partial S}{\partial N} \right)_{U, V}$

Under diffusive equilibrium  $\mu_1 = \mu_2$ .

Note: negative sign in definition means that  $\mu < 0$  if entropy  $S$  increases as particle number  $N$  increases for fixed  $U$  and  $V$  (as in an ideal gas).

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

If we write this in terms of  $dU$ , we get a new thermodynamic identity:

$$dU = \underset{\substack{\uparrow \\ \text{heat}}}{TdS} - \underset{\substack{\uparrow \\ \text{mechanical} \\ \text{work}}}{pdV} + \underset{\substack{\uparrow \\ \text{chemical} \\ \text{work}}}{\mu dN}$$

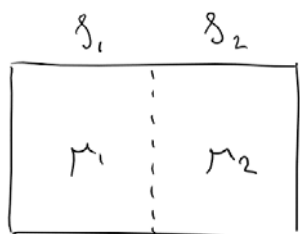
3 ways to transfer energy:

Also, since  $dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$ , we can also write  $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$ .

KEY CONCEPT: chemical potential

Just as difference in temperature drives heat flow (or difference in pressure drives volume change), difference in  $\mu$  drives particle flow.

Consider two systems  $\mathfrak{S}_1$  and  $\mathfrak{S}_2$  in thermal and mechanical equilibrium that can exchange particles.  $\mathfrak{S}_1 + \mathfrak{S}_2$  is closed.



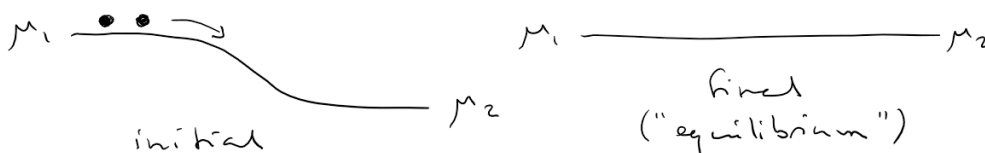
If initially  $\mu_1 > \mu_2$ , then  $\frac{\partial S_1}{\partial N_1} < \frac{\partial S_2}{\partial N_2}$ .

Therefore, system  $\mathfrak{S}_2$  gains more entropy than  $\mathfrak{S}_1$  loses for flow of particles from 1  $\rightarrow$  2:

$$dS = dS_1 + dS_2 = \underbrace{\left(\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2}\right)}_{<0} dN_1 \geq 0$$

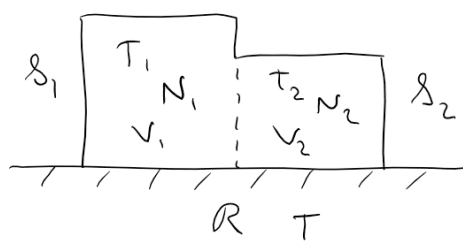
so  $dN_1 < 0$ , i.e. particles flow from 1  $\rightarrow$  2

Particles flow from high  $\mu$  to low  $\mu$ .



Chemical potential is similar to a gravitational or electric potential (with particles flowing "downhill").  $\Delta\mu$  drives motion of particles, until  $\Delta\mu = 0$ .

Imagine two systems  $\mathfrak{S}_1$  and  $\mathfrak{S}_2$  in thermal equilibrium with a reservoir  $\mathcal{R}$  that can exchange particles with each other.



$$T = T_1 = T_2$$

We saw in Lect. 7 that the Helmholtz free energy of  $\mathfrak{S}_1 + \mathfrak{S}_2$  is minimized

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

Assume for simplicity that  $dV = 0$  and  $dT = 0$ , then:

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

Equilibrium is reached when  $\left( \frac{\partial F_1}{\partial N_1} \right)_{T, V_1} = \left( \frac{\partial F_2}{\partial N_2} \right)_{T, V_2}$ .

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

### Question 1: Prove the above statement.

Hint: use the thermodynamic identity  $dU = TdS - pdV + \mu dN$

$F = U - TS$ , so

$$\begin{aligned} dF &= dU - SdT - TdS \\ &= -SdT - pdV + \mu dN \\ &= \left( \frac{\partial F}{\partial T} \right)_{V, N} dT + \left( \frac{\partial F}{\partial V} \right)_{T, N} dV + \left( \frac{\partial F}{\partial N} \right)_{T, V} dN \end{aligned}$$

Therefore  $\mu = \left( \frac{\partial F}{\partial N} \right)_{T, V}$ , QED.

Ex: chemical potential of an ideal gas

Recall that  $F = -k_B T \ln Z$  and  $Z = \frac{(n_Q V)^N}{N!}$  for an ideal gas so:

$$F_{ideal} \approx -Nk_B T \ln(n_Q V) + Nk_B T \ln N - Nk_B T$$

where we applied the Stirling approximation. So,

$$\begin{aligned} \mu_{ideal} &= \left( \frac{\partial F}{\partial N} \right)_{T,V} = -k_B T \ln(n_Q V) + k_B T \ln N + \cancel{Nk_B T \frac{1}{N}} - \cancel{k_B T} \\ &= -k_B T \ln\left(\frac{n_Q V}{N}\right) = k_B T \ln\left(\frac{n}{n_Q}\right) \end{aligned}$$

where  $n = N/V$  is the number density. Recall that for a classical ideal gas  $n \ll n_Q$  so  $\mu_{ideal} < 0$ .

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

$$n_{Ar} = 2.5 \times 10^{25} \text{ m}^{-3}$$

$$n_Q = 2 \times 10^{32} \text{ m}^{-3}$$

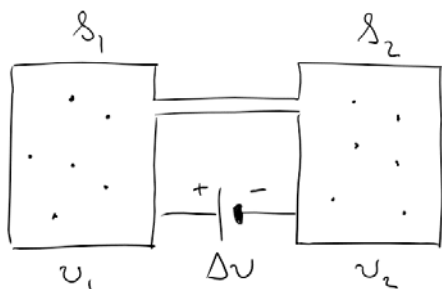
$$\mu_{Ar} = -0.42 \text{ eV}$$

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.

KEY CONCEPT: Internal and external chemical potential

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

Ex: the Nernst equation



Imagine an ideal gas with charge  $q$ . Systems  $\mathfrak{S}_1$  and  $\mathfrak{S}_2$  are in thermal & diffusive equilibrium, but we apply a voltage (electric potential) difference between them

For each particle  $i$  in system  $\mathfrak{S}_{1,2}$ :

$$\varepsilon_i = \frac{p_i^2}{2m} + qv_{1,2}$$

Every particle in each system experiences the same electric potential  $v_1$  or  $v_2$

**Question 2: Determine the chemical potential for particles in system  $\mathfrak{S}_1$  and compare it to an uncharged ideal gas.**

We follow the same derivation as for an uncharged ideal gas. The partition function for gas particles in system  $\mathfrak{S}_1$  is

$$Z_{tot,1} = \frac{1}{N_1!} \left( \sum_i e^{-\beta \varepsilon_i} \right)^{N_1} = \frac{1}{N_1!} \left( e^{-\beta q v_1} \sum_i e^{-\beta p_i^2 / 2m} \right)^{N_1} = \frac{1}{N_1!} \left( e^{-\beta q v_1} n_Q V_1 \right)^{N_1}$$

The electric potential factor comes out of the sum because it is the same for every microstate. So,

$$F_1 = -N_1 k_B T \ln(e^{-\beta q v_1} n_Q V_1) + N_1 k_B T \ln N_1 - N_1 k_B T$$

$$\mu_1 = \left( \frac{\partial F_1}{\partial N_1} \right)_{T,V} = -k_B T \ln(e^{-\beta q v_1} n_Q V) + k_B T \ln N_1 + \cancel{N_1 k_B T \frac{1}{N_1}} - \cancel{k_B T} = k_B T \ln \left( \frac{n_1}{n_Q} \right) + q v_1$$

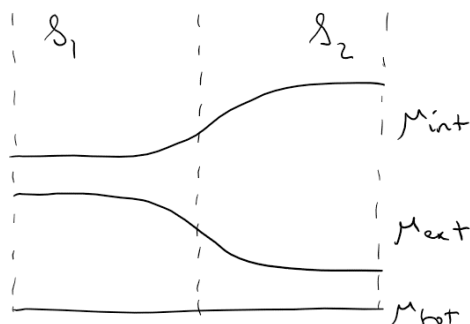
In other words,

$$\mu_1 = \underbrace{k_B T \ln(n_1/n_Q)}_{\mu_{\text{int},1}} + \underbrace{q v_1}_{\mu_{\text{ext},1}}$$

$\uparrow$                        $\uparrow$   
 “internal”    “external”    chemical potential

At equilibrium  $\mu_1 = \mu_2$ , so  $\Delta\mu_{\text{ext}} = -\Delta\mu_{\text{int}}$ :

$$q\Delta v = q v_1 - q v_2 = k_B T \ln \left( \frac{n_2}{n_1} \right) \quad \text{“Nernst equation”}$$



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

Then  $\mu_{\text{ext},2} < \mu_{\text{ext},1}$  and  $v_2 < v_1$

$\Delta v$  maintains a concentration gradient between  $S_1$  and  $S_2$ . This is what happens in a cell. Molecular pumps move ions across the cell membrane establish  $\Delta v$  between the inside and outside of the cell, and concentration gradient.

(Note: ions in solution are not an ideal gas, they are a dilute solution, i.e. a solution where the solvent is much more abundant than the solute. It turns out that dilute solutions have the same basic form for the chemical potential as an ideal gas. The chemical potential  $\mu_{\text{sol}}$  of a solute species is:

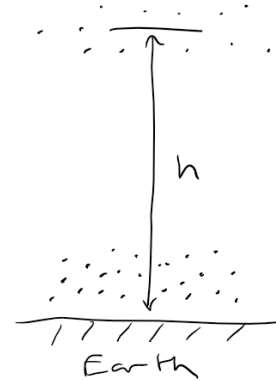
$$\mu_{\text{sol}} = \mu_{\text{sol}}^0 + k_B T \ln \left( \frac{n_{\text{sol}}}{n_0} \right)$$

where the index 0 refers to some standard state. By convention, in an aqueous solution,  $n_0 = 1$  mole of solute/1 L of  $\text{H}_2\text{O} = 1$  molar. The Nernst equation works equally well for dilute solutions. This expression will also be useful for chemical equilibrium in the next lecture.)

Ex: atmospheric density

Consider the atmosphere above the earth. Atoms in atmosphere are in the gravitational field of the earth so:

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




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**Question 3: Assuming the atmosphere at the earth's surface  $y = 0$  and at an altitude  $y = h$  are in thermal and diffusive equilibrium, determine how density changes with altitude.**

We assume equilibrium so  $\mu(h) = \mu(0)$ .

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

Therefore

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

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Also, since  $p = \frac{Nk_B T}{V} = nk_B T$ ,  $p(h) = p(0) \exp\left(-\frac{mgh}{k_B T}\right)$

This is roughly how atmospheric density varies with height, although atmosphere is clearly not isothermal