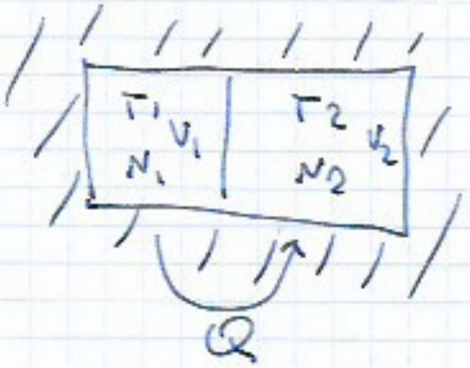
IV GRAND CANONICAL ENSEMBLE

§1. CHEMICAL POTENTIAL

•) We investigated systems in thermal interaction (contact) with exchanging an energy



$T_1 > T_2$

heat Q "flows" from ① to ② until

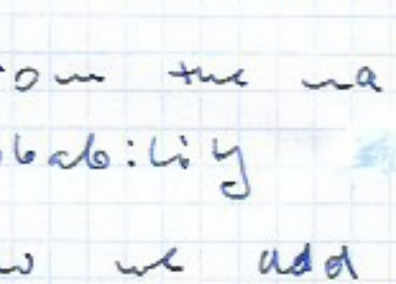
$T_1 = T_2$

$$\frac{1}{T_1} = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} = \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2 N_2} = \frac{1}{T_2}$$

From the maximization of thermodynamic probability $S = k_B \ln \Omega$

•) now we add a chemical interaction (contact) with exchanging particles appart of thermal interaction

thermal + diffusive contact



$T_1 > T_2$

A system is in thermal and in chemical equilibrium if

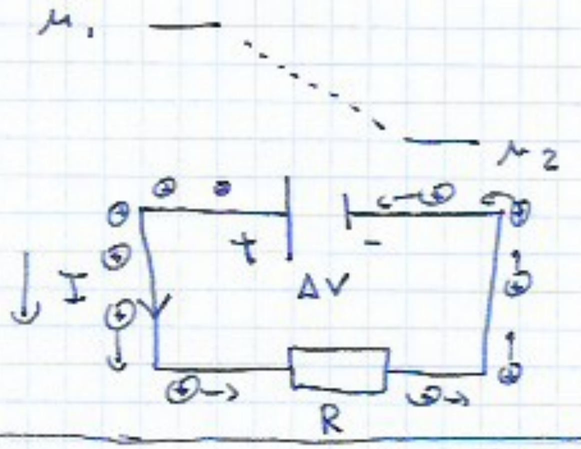
$$\boxed{\begin{array}{c} T_1 = T_2 \\ ?_1 = ?_2 \end{array}}$$

What is $?_1$

A chemical potential governs a flow of particles, e.g. a battery

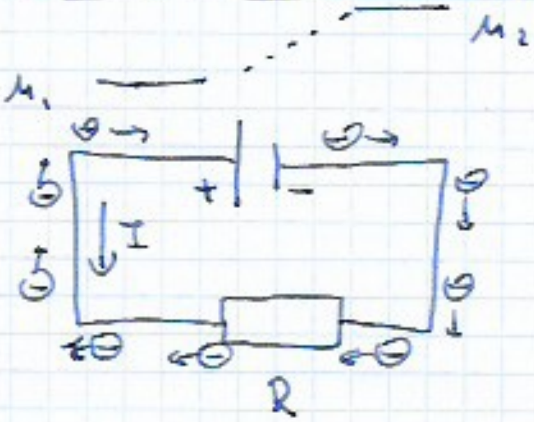
here an electric potential ΔV

$\mu_1 > \mu_2 \Rightarrow$ flow of current I



$\mu_1 - \mu_2 = q\Delta V > 0$

motion of positive $q > 0$ charges from μ_1 to μ_2.

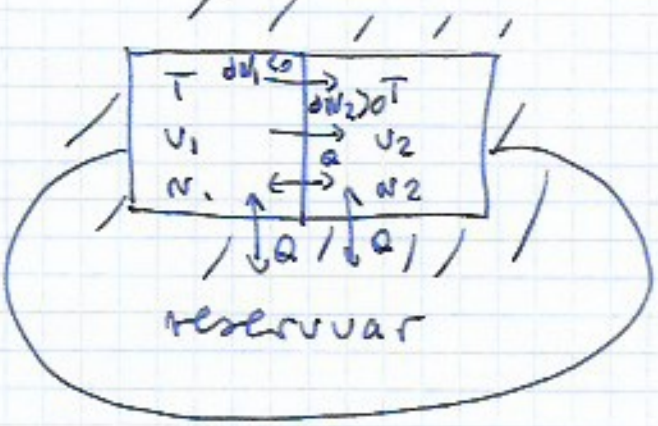


$\mu_1 - \mu_2 = q\Delta V$

motion of negative $q < 0$ charges from μ_2 to μ_2

How to define a chemical potential in thermodynamics?

Consider two subsystems with the same temperature T, which are in a diffusive contact with each other.



one component systems

Helmholtz free energy

$$F = F_1 + F_2 = U_1 + U_2 - T(S_1 + S_2)$$

In thermal equilibrium $N_1 + N_2 = \text{const.} = N$

$$\rightarrow \boxed{dN_1 = -dN_2}$$

Minimizing F

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

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

$$\rightarrow \boxed{\left(\frac{\partial F_1}{\partial N_1}\right)_{T,V_1} = \left(\frac{\partial F_2}{\partial N_2}\right)_{T,V_2}}$$

Def.1 Chemical potential

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

intensive quantity

In thermodynamic equilibrium

$$\boxed{\mu_1(T, V_1, N_1) = \mu_2(T, V_2, N_2)}$$

No particle flow (or flows to left and right are balanced)

From the equation

$$dF = [\mu_1 - \mu_2]\, dN_1$$

we read that if $\mu_1 > \mu_2$ then $dF < 0$ for $dN_1 < 0$. Particles are moved from ① to ② ($dN_2 > 0$) and F - decreases reaching a minimum.

> Spontenous flow of particles is from higher to lower chemical potential.

- •) A difference of the chemical potentials triggers a particle flow.
- •) A difference of the temperatures triggers a heat flow

At thermal equilibrium

$$\boxed{\begin{aligned} \mu_1 &= \mu_2 \\ T_1 &= T_2 \end{aligned}}$$

1) For multicomponent | multi phase systems

$$\boxed{\mu_j = \left(\frac{\partial F}{\partial N_j}\right)_{T, V, N_1 \dots N_{j-1}, N_{j+1} \dots}}$$

e.g. at ~~th~~ thermal equilibrium

$$\mu_{water} = \mu_{ice} \quad \text{at } T = 0°C$$

water-ice coexistence.

2) N is discrete (!) then

$$\boxed{\mu(T, V, N) = F(T, V, N) - F(T, V, N-1)}$$

an energy cost of adding a particle.

<u>Example</u> <u>Ideal gas</u>

$$\overset{\displaystyle \sum_\alpha e^{-\beta \varepsilon_\alpha} \text{ where } \underline{\varepsilon_0 = 0}}{\downarrow}$$

$$F = -k_BT\left[N \ln Z_1 - \ln N!\right], \quad Z_1 = n_Q V = \left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2} V$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_BT\left[\ln Z_1 - \frac{d}{dN}\ln N!\right]$$

$$\frac{d}{dN}\ln N! \simeq \frac{d}{dN}\left[N\ln N - N\right] = \ln N + 1 - 1 = \ln N$$

intensive quantity

$$\boxed{\mu = -k_BT\left[\ln Z_1 - \ln N\right] = k_BT \ln\frac{N}{Z_1} = k_BT \ln\left(\frac{n}{n_Q}\right)}$$

μ - increases with the concentration n.

- For classical gases $n \ll n_Q \rightarrow \mu = k_BT \ln\left(\frac{n}{n_Q}\right) \underline{\underline{< 0}}$
- For ideal gas $pV = Nk_BT \rightarrow n = \frac{p}{k_BT}$

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

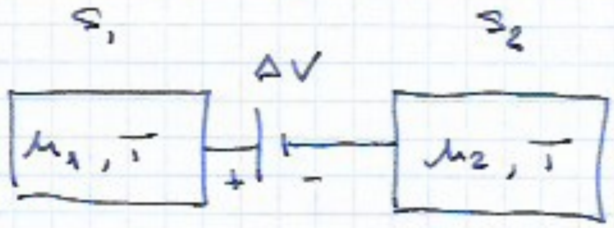
- discrete version $\mu = F(N) - F(N-1) = -k_BT\left[\ln Z_1 - \ln\frac{N!}{(N-1)!}\right] =$

$$= -k_BT\left[\ln Z_1 - \ln N\right] = k_BT \ln(N/Z_1) \text{ ok}$$

- no N! term

$\mu = -k_BT\ln Z_1 = -k_BT\ln(n_Q V) \sim O(\ln V)$ <u>! problem!</u>

internal and external chemical potential



two subsystems with the same temperatures but $\mu_1 \neq \mu_2$

let $\mu_2 > \mu_1$ initially

$$\Delta\mu\,(\text{initial}) = \mu_2 - \mu_1 > 0$$

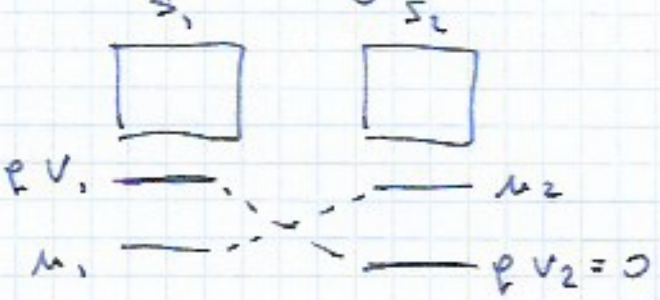
and we apply external potential which balances $\Delta\mu$

i.e. $e\Delta V = e(V_1 - V_2) = \Delta\mu\,(\text{initial})$ electric potential

$mgh = \Delta\mu\,(\text{initial})$ gravity potential

etc.

The potential energy in S_1 is higher than in S_2 (where we set zero)



The external energy adds up to the internal energy U or free energy F

$$U \rightarrow U + N_1\Delta\mu = U + N_1 e\Delta V$$
$$F \rightarrow F + N_1\Delta\mu = F + N_1 e\Delta V$$

This implies that the chemical potential of S_1 ($\mu_1 = \frac{\partial F}{\partial N_1}$) is equal to the chemical potential of S_2

$$\mu_1(\text{final}) = \mu_1(\text{initial}) + [\mu_2(\text{initial}) - \mu_1(\text{initial})]$$
$$= \mu_2(\text{initial}) = \mu_2(\text{final})$$

$\llcorner$ eV_2 is set to zero

In the external potential the systems are in equilibrium

c) The chemical potential is equivalent
a true potential energy per particle

The total chemical potential reads

$$\mu = \underset{\substack{\uparrow \\ \text{total chemical} \\ \text{potential} \\ \text{(mechanopotential,} \\ \text{electropotential,} \\ \text{magnetopotential)}}}{\mu_{tot}} = \underset{\substack{\uparrow \\ \text{potential} \\ \text{energy per} \\ \text{particle} \\ \text{(mechanical,} \\ \text{electric,} \\ \text{magnetic)}}}{\mu_{ext}} + \underset{\substack{\uparrow \\ \text{chemical} \\ \text{potential when} \\ \mu_{ext} = 0}}{\mu_{int}}$$

The condition of the thermal equilibrium
$\mu_1 = \mu_2$ is equivalent to

$$\Delta \mu_{ext} = - \Delta \mu_{int}$$

§ 2. CHEMICAL POTENTIAL AND ENTROPY – – THERMODYNAMIC RELATIONS

We show that

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

similarly to $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$.

Consider $S = S(U,V,N)$ – entropy

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

Let $dV = 0$ (isochoric process) and changes of dS, dU and dN are such that $dT = 0$ (isothermal). Let they be denoted by $(\delta S)_T$, $(\delta U)_T$, $(\delta N)_T$

Then $(\delta S)_T = \left(\frac{\partial S}{\partial U}\right)_{N,V} (\delta U)_T + \left(\frac{\partial S}{\partial N}\right)_{U,V} (\delta N)_T \;\Big|\; : (\delta N)_T$

$$\underset{\underset{\left(\frac{\partial S}{\partial N}\right)_T}{\shortparallel}}{\frac{(\delta S)_T}{(\delta N)_T}} = \underset{\underset{\frac{1}{T}}{\shortparallel}}{\left(\frac{\partial S}{\partial U}\right)_{N,V}} \underset{\underset{\left(\frac{\partial U}{\partial N}\right)_T}{\shortparallel}}{\frac{(\delta U)_T}{(\delta N)_T}} + \left(\frac{\partial S}{\partial N}\right)_U$$

$$\Rightarrow \underbrace{T\left(\frac{\partial S}{\partial N}\right)_{T,V} = \left(\frac{\partial U}{\partial N}\right)_{T,V} + T\left(\frac{\partial S}{\partial N}\right)_{U,V}}_{\text{relation of derivatives with without const. } T}$$

From original definition

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

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

In general one can prove

	$S(U,V,N)$	$U(S,V,N)$	$F(T,V,N)$
T	$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$	$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$	T - independent variable
p	$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$	$-p = \left(\frac{\partial U}{\partial V}\right)_{S,N}$	$-p = \left(\frac{\partial F}{\partial V}\right)_{T,N}$
μ	$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,V}$	$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$	$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$

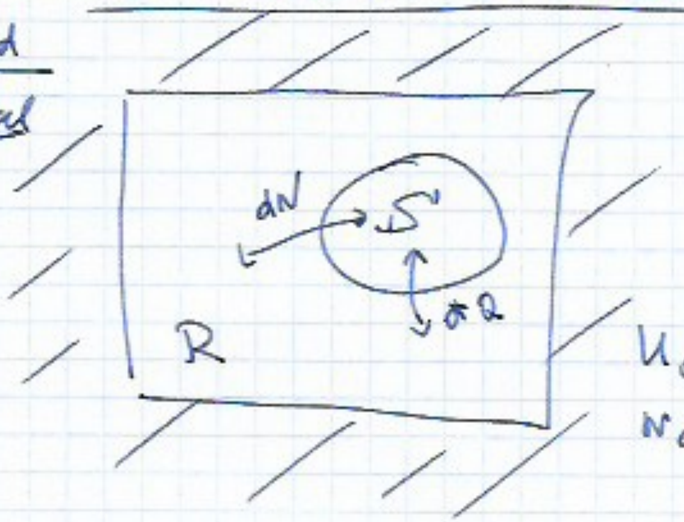
First law of thermodynamics for open systems

$$dS = \underset{\overset{\shortparallel}{\frac{1}{T}}}{\left(\frac{\partial S}{\partial U}\right)_{V,N}} dU + \underset{\overset{\shortparallel}{\frac{p}{T}}}{\left(\frac{\partial S}{\partial V}\right)_{U,N}} dV + \underset{\overset{\shortparallel}{-\frac{\mu}{T}}}{\left(\frac{\partial S}{\partial N}\right)_{U,V}} dN$$

$$\Rightarrow \boxed{\begin{aligned} dU &= T\,dS - p\,dV + \mu\,dN = \\ &= đQ + đW_{mech} + đW_{chem} \end{aligned}}$$

§ 3. GRAND CANONICA ENSEMBLE - GIBBS DISTRIBUTION

Df. Grand canonical ensemble



we investigate a system S coupled to R

$U_0 = U_R + U_S = \text{const}$

$N_0 = N_R + N_S = \text{const}$

What is a probability that S' is in energy ε_s and with particle number N_s?

$$P(\varepsilon_s, N_s) = ?$$

Total number of microstates in R + S

$$\Omega(U_s = \varepsilon_s, N_s; \; U_R = U_0 - \varepsilon_s, N_R = N_0 - N_s) =$$

$$= \Omega_R(U_0 - \varepsilon_s, N_0 - N_s) \cdot \underset{\uparrow \text{ no degeneracy}}{1}$$

From the hypothesis of equal probability a priori

$$\frac{P(\varepsilon_1, N_1)}{P(\varepsilon_2, N_2)} = \frac{\Omega_R(U_0 - \varepsilon_1, N_0 - N_1)}{\Omega_R(U_0 - \varepsilon_2, N_0 - N_2)}$$

from the definition of entropy

$$S = k_B \ln \Omega(U, V, N)$$

we find

$$\frac{P(\varepsilon_1, N_1)}{P(\varepsilon_2, N_2)} = \frac{e^{\frac{1}{k_B} S_R(U_0-\varepsilon_1,\, N_0-N_1)}}{e^{\frac{1}{k_B} S_R(U_0-\varepsilon_2,\, N_0-N_2)}} = e^{\frac{1}{k_B}\Delta S_R}$$

$$\Delta S_R = S_R(U_0-\varepsilon_1, N_0-N_1) - S_R(U_0-\varepsilon_2, N_0-N_2)$$

but $R \gg S$

$$S_R(U_0-\varepsilon, N_0-N) \simeq S_R(U_0, N_0) - \left(\frac{\partial S_R}{\partial U_0}\right)_{N_0}\varepsilon - \left(\frac{\partial S_R}{\partial N_0}\right)_{U_0} N + \dots$$

hence

$$\Delta S_R = -(N_1 - N_2)\underset{\overset{\shortparallel}{-\frac{\mu}{T}}}{\left(\frac{\partial S_R}{\partial N_0}\right)_{U_0}} - (\varepsilon_1-\varepsilon_2)\underset{\overset{\shortparallel}{\frac{1}{T}}}{\left(\frac{\partial S_R}{\partial U_0}\right)_{N_0}}$$

And S and R are in thermal equilibrium

$$\mu \equiv \mu_S = \mu_R, \qquad T \equiv T_R = T_S$$

we obtain

$$\Delta S_R = -\frac{\varepsilon_1 - \varepsilon_2}{k_B T} + \frac{N_1 - N_2}{k_B T}\mu$$

$$\boxed{\frac{P(\varepsilon_1, N_1)}{P(\varepsilon_2, N_2)} = \frac{e^{-\frac{1}{k_B T}(\varepsilon_1 - \mu N_1)}}{e^{-\frac{1}{k_B T}(\varepsilon_2 - \mu N_2)}}}$$

We have obtained a Gibbs distribution

$$\boxed{p(\mathcal{E}, N) = \frac{1}{\Xi(T,V,\mu)}\, e^{-\frac{\mathcal{E}-\mu N}{k_B T}}}$$

Def. Grand partition function

$$\boxed{\Xi(T,V,\mu) = \sum_{N=0}^{\infty} \sum_{\mathcal{E}_s(N)} e^{-\frac{\mathcal{E}_s(N)-\mu N}{k_B T}}}$$

The average X is

$$\langle X\rangle = \sum_{N} \sum_{\mathcal{E}_s(N)} X(N,\mathcal{E}_s)\, \frac{e^{-\frac{\mathcal{E}_s(N)-\mu N}{k_B T}}}{\Xi(T,V,\mu)}$$

The average number of particles

$$\langle N\rangle = \frac{1}{\Xi} \sum_{N=0}^{\infty} \sum_{\mathcal{E}_s(N)} N e^{-\frac{\mathcal{E}_s(N)-\mu N}{k_B T}}$$

note

$$\frac{\partial \Xi}{\partial \mu} = \frac{1}{k_B T} \sum_{N} \sum_{\mathcal{E}_s(N)} N e^{-\beta(\mathcal{E}_s-\mu N)} \qquad \beta = \frac{1}{k_B T}$$

$$\boxed{\langle N\rangle = \frac{k_B T}{\Xi}\frac{\partial \Xi}{\partial \mu} = k_B T \frac{\partial \ln \Xi}{\partial \mu}}$$

let $\boxed{\alpha = e^{\beta\mu}}$ – activity def.

$$\Xi = \sum_{N} \sum_{\mathcal{E}_s(N)} \alpha^N e^{-\beta \mathcal{E}_s(N)}$$

$$\boxed{\langle N\rangle = \alpha \frac{\partial}{\partial \alpha} \ln \Xi}$$

Internal energy

$$U = \langle E \rangle = \sum_N \sum_{E_s(N)} \frac{E_s \, e^{-\beta(E_s - \mu N)}}{\hat{Z}}$$

but $\langle N\mu - E \rangle = \langle N \rangle \mu - U = \frac{1}{\hat{Z}} \frac{\partial \hat{Z}}{\partial \beta} = \frac{\partial}{\partial \beta} \ln \hat{Z}$

$$\boxed{U = \left(\frac{\mu}{\beta} \frac{\partial}{\partial \mu} - \frac{\partial}{\partial \beta} \right) \ln \hat{Z} = \left(k_B T \mu \frac{\partial}{\partial \mu} - \frac{\partial}{\partial \left(\frac{1}{k_B T}\right)} \right) \ln \hat{Z}}$$

Entropy

$$\boxed{\begin{aligned} S &= -k_B \left\langle \ln \frac{e^{-\beta(E-\mu)}}{\hat{Z}} \right\rangle = \\ &= \frac{1}{T} \left(U - \mu \langle N \rangle \right) + k_B \ln \hat{Z} \end{aligned}}$$