

What is the chemical potential?

# Why is the chemical potential difficult to grasp?

- We understand what we experience/measure
  - $T$  – radiation or equilibrium with sensor
  - $V$  – lengths
  - $P$  – Equilibrium with liquid columns, bent membranes
  - $N$  – mass, weight
  - $Q$  – known dissipation (for example  $P = \frac{dQ}{dt} = RI^2$ )
  - $W = P\Delta V$
  - $C_V = Q/\Delta T$
- Cannot be measured directly
  - $U$  – 1<sup>st</sup> law:  $Q + P\Delta V, G, H, F$
  - $S$  – needs integration of  $C_V$
  - $\mu$  – derivative of  $S, G, F...$

# What are the fundamental principles of equilibrium?

Mechanics

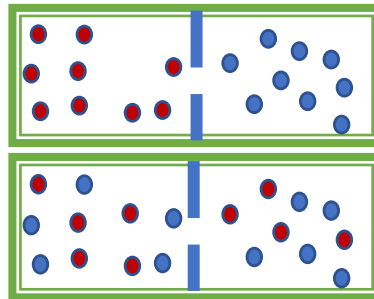
$$\sum_i F_i = -\sum_i \nabla U_i = 0$$

minimize energy

Thermodynamics

maximize entropy

particle number



identical, coloured,  $dU=0$

$dS>0$ ,  $\mu_1 = \mu_2$

The two principles are related by TDI

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

$$dH = TdS + VdP + \mu dN$$

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

$$dG = -SdT + VdP + \mu dN$$

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

# What is the chemical potential?

From

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

$$dH = TdS + VdP + \mu dN$$

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

$$dG = -SdT + VdP + \mu dN$$

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

Most useful definitions

F=U-TS

energy to create a system minus the energy from the environment

G=U+PV-TS

energy to create a system and make room for it minus the energy from the environment

OK, but how do we calculate or measure this?

# Chemical potential of ideal gas

(thermodynamics)

Ideal gas:  $PV = NkT$

expression for  $\mu$ :  $\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T} = \left(\frac{\partial F}{\partial N}\right)_{V,T}$

We need some relation between energies,  $G$  or  $F$  and  $P, V, N, T$

TDI ( $F$ ):  $dF = -SdT - PdV + \mu dN$

TDI ( $G$ ):  $dG = -SdT + VdP + \mu dN$

=> at constant  $T$  &  $N$ :  $dG = VdP, \quad dF = -PdV$

$$dG = VdP = \frac{NkT}{P} dP$$

$$\int dG = G - G_0 = NkT \int \frac{dP}{P} = NkT \ln \frac{P}{P_0}$$

$$\mu = \frac{G}{N} = \mu_0 + kT \ln \frac{P}{P_0}$$

$$dF = -PdV = \frac{NkT}{V} dV$$

$$\int dF = F - F_0 = -NkT \int \frac{dV}{V} = -NkT \ln \frac{V}{V_0}$$

$$\mu = \frac{F}{N} = \mu_0 - kT \ln \frac{V}{V_0} = \mu_0 + kT \ln \frac{P}{P_0}, \quad \left(\frac{V}{V_0} = \frac{P_0}{P}\right)$$

# Chemical potential of ideal gas

(stat. mech. of quantum ideal gas)

Helmholtz free energy of quantum ideal gas (**error** last Thursday):

$$F_N(T, V) = -NkT \left[ \ln \left( \frac{V}{Nv_Q} \right) + 1 \right]$$

How do we find the chemical potential?  $\mu = \left( \frac{\partial F}{\partial N} \right)_{V, T}$

...

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{V, T} = -kT \left[ \ln \left( \frac{V}{Nv_Q} \right) + 1 \right] + NkT \left[ \frac{d \ln N}{dN} \right]$$

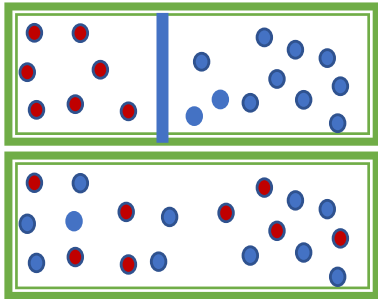
.  $\mu = -kT \ln \left( \frac{V}{V_0} \right), \quad V_0 = Nv_Q, \quad n_Q = v_Q^{-1}$

.  $\mu = kT \ln \left( \frac{n}{n_Q} \right), \quad n = \frac{N}{V}$

.  $\mu = kT \ln \left( \frac{P}{P_0} \right), \quad P_0 = n_Q kT$

# Chemical potential of ideal mixtures

$$\begin{matrix} V_1 & V_2 \\ N_1 & N_2 \\ T_1 & = & T_2 \\ P_1 & = & P_2 \end{matrix} \Rightarrow \mu_1^0(P, T) = \mu_2^0(P, T)$$



Remove wall:  $V=V_1+V_2$

$$\frac{F}{N} = \mu = \mu_0 - kT \ln \frac{V}{V_0}$$

$$\Delta\mu_1 = -kT \ln \frac{V_1 + V_2}{V_1}$$

$$\frac{V_1 + V_2}{V_1} = \frac{N_1 + N_2}{N_1} = \frac{1}{x_1}$$

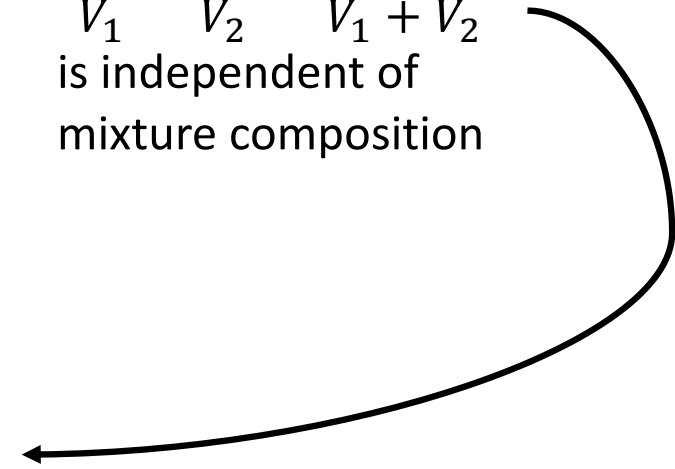
$$\Delta\mu = kT \ln x_1$$

$$\mu_i(P, T, x_i) = \mu_i^0(P, T) + kT \ln x_i$$

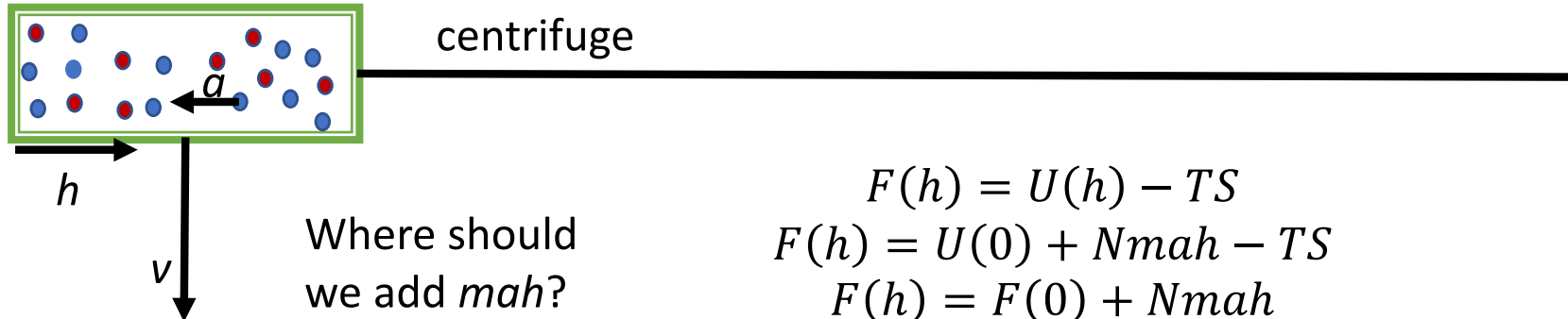
Ideal mixture:

$$\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N_1 + N_2}{V_1 + V_2}$$

is independent of mixture composition



# Potential energy and the chemical potential



$$F(h) = U(h) - TS$$

$$F(h) = U(0) + Nmah - TS$$

$$F(h) = F(0) + Nmah$$

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{V,T} = \mu(0) + mah$$

$$\mu_{tot} = \mu_{int} + \mu_{ext}$$

Barometric pressure: Can we use this to calculate  $p(z)$ ?

equilibrium:  $\mu(z) = \mu_0 = \mu_0 + kT \ln \frac{P(z)}{P_0} + mgz$

$\Rightarrow \frac{P(z)}{P_0} = e^{-mgz/kT} = e^{-z/z_c}$

,  $z_c = kT/mg$

Nitrogen ( $m=28$ )  $z_c=8.5\text{km}$ , Oxygen ( $m=32$ )  $z_c = 7.4 \text{ km}$ , Mount Everest:  $P = 0.37 P(0)$



# Electrolytes in container and electric field

batteries, cells in our bodies in em field, nerve signals...

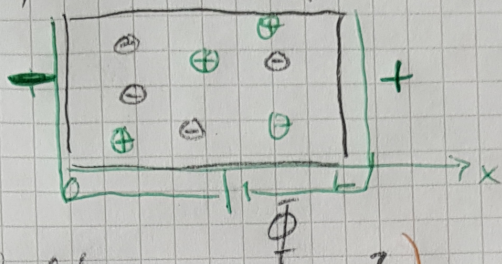
# The chemical potential, $\mu$

only for chemists?

- Ch. 2.6, pp 79-83: entropy of mixing
- Ch. 3.5, pp 115-121: diffusive equilibrium and the chemical potential
- Ch. 5.1,  $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = \left(\frac{\partial F}{\partial N}\right)_{T,V}$ ,  $\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_i}$
- Ch. 5.2,
  - $G = \sum_i N_i \mu_i$
  - ideal gas:  $\mu(T, P) = \mu^0(T) + kT \ln\left(\frac{P}{P_0}\right)$
  - ideal mixture:  $\mu(T, P, x) = \mu^0(T, P) + kT \ln(x)$
  - Grand potential
- Ch. 6.7,  $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT \ln\left(\frac{V Z_{int}}{N v_Q}\right)$ ,  $G = N\mu$
- Thursday: Ch 7.1, open systems & the Gibbs factor
- Next week: Ch 7.2-7.6, quantum statistics, semi-conductors...

Barrier, eller i kroppen var.

- elektrolytter
- elektrisk felt
- vægter



⊕ ions mobile

⊖ ions fixed

(How does ion distribution eq?)

electrical potential  $\Phi(x)$   $[\Phi] = V$

electric field  $E = -\Phi(x)/x$

Potential energy of <sup>pos</sup> charges  $V(x) = -q E x = -q \Phi$

Force  $F = -\frac{\partial V}{\partial x} = -q E$

⇒ ions move while there is an electric field

(What will happen?)

(stop at wall and eliminate field)

$$\text{Poisson} \quad \nabla^2 \Phi = -\frac{\rho}{\epsilon}$$

We seek equilibrium distribution of ions  $n(x)$  &  $\Phi(x)$

$$\mu(x) = \text{const} = \mu_{\text{int}} + \mu_{\text{ext}}$$

$$\mu(x) = kT \ln \frac{n(x)}{n_0} + q \Phi(x)$$

$$\text{BC: } \Phi(0) = \Phi_0 = 0 \quad \Phi(L) = \Phi_L$$

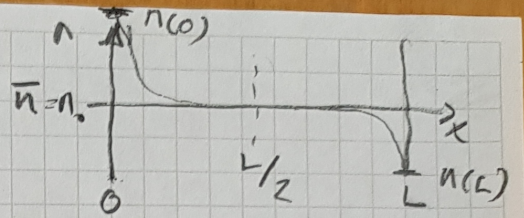
$$\text{eq: } \mu(0) = \mu(L)$$

$$kT \ln \frac{n(0)}{n_0} = kT \ln \frac{n(L)}{n_0} + q \Phi_L$$

$$\Rightarrow \frac{n(0)}{n(L)} = e^{\frac{q \Phi_L}{kT}}$$



Assume antisymmetric  $n(x)$



$$\Rightarrow n(0) - n_0 = -(n(L) - n_0)$$

$$2n_0 = n(0) + n(L) e^{q\phi_L/kT}$$
$$= n(L) (1 + e^{q\phi_L/kT})$$

$$\Rightarrow n(L) = \frac{2n_0}{(1 + e^{q\phi_L/kT})}$$

$$n(0) = \frac{2n_0}{(1 - e^{-q\phi_L/kT})}$$

$$\mu(x) = kT \ln \frac{n(x)}{n_0} + q\phi = \mu_0 = \text{const}$$

$$\Rightarrow \frac{n(x)}{n_0} = e^{(q\phi(x) - \mu_0)/kT}$$

The model has no length scale (so far)

Ion distribution at walls shield  $E$  inside