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 $\mathrm{P} = \frac{dQ}{dt} = RI^2$)
  - $W = P\Delta V$, we feel it when working
  - $C_V = Q/\Delta\mathrm{T}$, we feel the difference between plastic and rocks
- Cannot be measured directly
  - *U* – 1st law: $\mathrm{Q} + W$, *G, H, F*
  - S – needs integration of C_v
  - μ – derivative of *S, G, F*...

What are the fundamental principles of equilibrium?

Mechanics

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

minimize energy

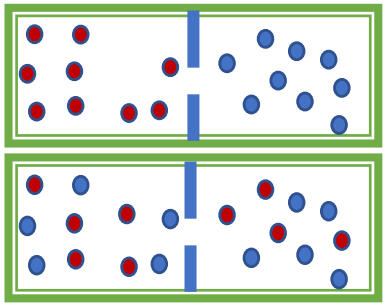
Thermodynamics

maximize entropy

(minimize F or G)

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

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: $dG = VdP, \quad dF = -PdV$

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

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

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T} = \mu_0 + kTln\frac{P}{P_0}$$

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

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

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu_0 - kTln\frac{V}{V_0} = \mu_0 + kTln\frac{P}{P_0},$$

$$\left(\frac{V}{V_0} = \frac{P_0}{P}\right)$$

Chemical potential of ideal gas

(stat. mech. of quantum ideal gas)

Helmholtz free energy of quantum ideal gas:

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

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

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

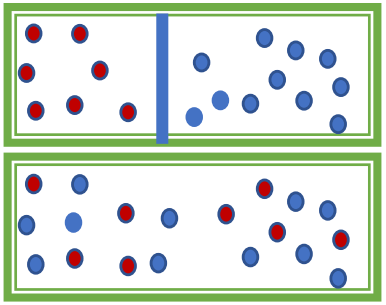
$$\mu = -kTln\left(\frac{V}{V_0}\right),\ V_0 = Nv_Q, \qquad n_Q = v_Q^{-1}$$

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

$$\mu = kTln\left(\frac{P}{P_0}\right), \quad P_0 = n_QkT$$

Chemical potential of ideal mixtures

V_1 V_2
N_1 N_2
$T_1 = T_2$
$P_1 = P_2$ => $\mu_1^0(P,T) = \mu_2^0(P,T)$



$$\mu = \mu_0 - kTln\frac{V}{V_0}$$

Remove wall: $V=V_1+V_2$

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

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

$$\Delta\mu_1 = kTlnx_1$$

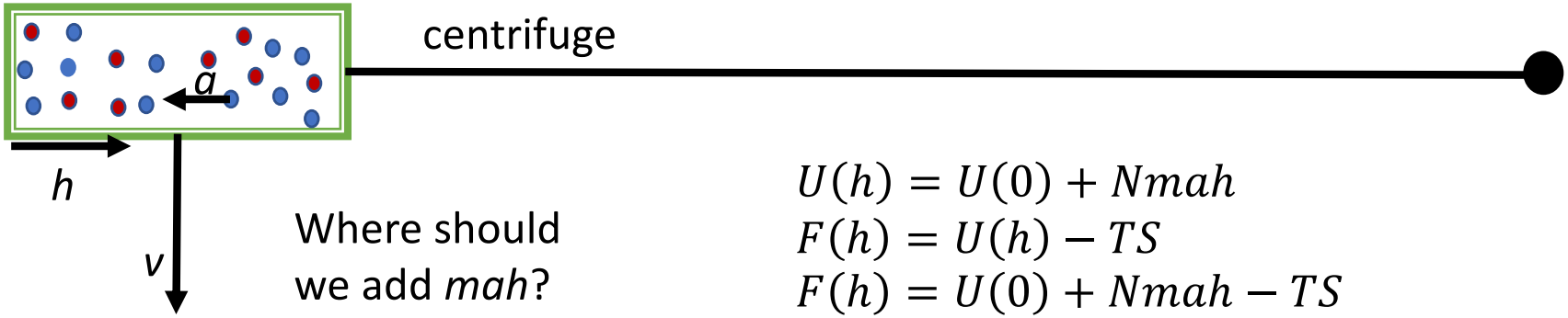
$$\mu_i(P,T,x_i) = \mu_i^0(P,T) + kTlnx_i$$

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



Where should we add *mah*?

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

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

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

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

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

$z_c = kT/mg$

Nitrogen (*m*=28) z_c=8.5km, Oxygen (*m*=32) z_c = 7.4 km, Mount Everest: *P = 0.37 P(0)*

The chemical potential, μ

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, $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = \left(\frac{\partial F}{\partial N}\right)_{T,V}, \quad \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_i}$
- Ch. 5.2,
  - $G = \sum_i N_i \mu_i$
  - ideal gas: $\mu(T,P) = \mu^0(T) + kTln\left(\frac{P}{P_0}\right)$
  - ideal mixture: $\mu(T,P,x) = \mu^0(T,P) + kTln(x)$
  - Grand potential
- Ch. 6.7, $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kTln\left(\frac{VZ_{int}}{Nv_Q}\right), \quad G = N\mu$
- Next lecture: Osmosis and freezing of cells
- Next week: Ch 7.2-7.6, quantum statistics, semi-conductors...

Electrolytes in container and electric field

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

