Review of Equilibrium

Exchanged quantity	Type of equilibrium
energy	thermal
volume	mechanical
particles	diffusive

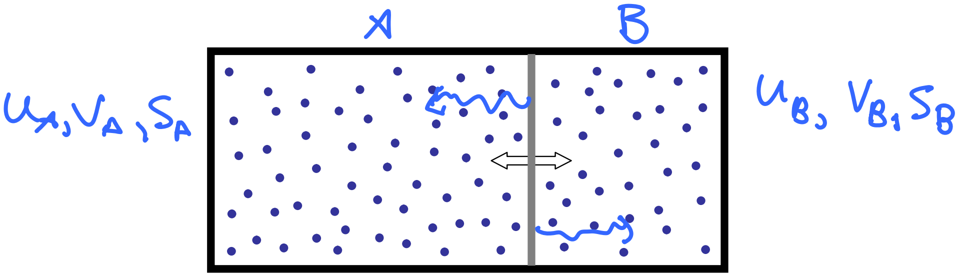
sources 3.4, 3.5 & 5.1, 5.2

Mechanical Equilibrium

- So far, focused on systems where we are exchanging energy
  - To reach thermal equilibrium with N and V fixed
- Now generalize to systems whose volumes can change as they interact
- Just as spontaneous exchange of energy between systems is governed by temperature
  - Spontaneous exchange of volume between systems is governed by pressure
- Want to look for equation that is analogous to $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$

Mechanical Equilibrium

- Consider two systems (e.g. gases) separated by a movable platform



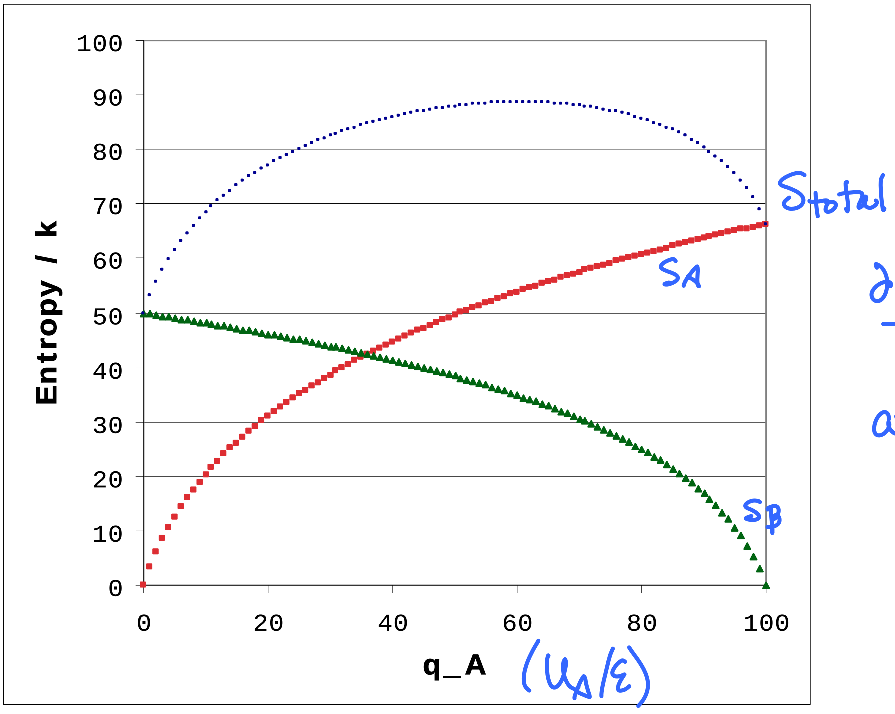
$$\left.\begin{array}{l}\text{total } V = V_A + V_B \\ \text{total } U = U_A + U_B\end{array}\right\} \text{fixed for system}$$

Einstein Solid S vs. U - fixed volume

$N_A = 300$

$N_B = 200$

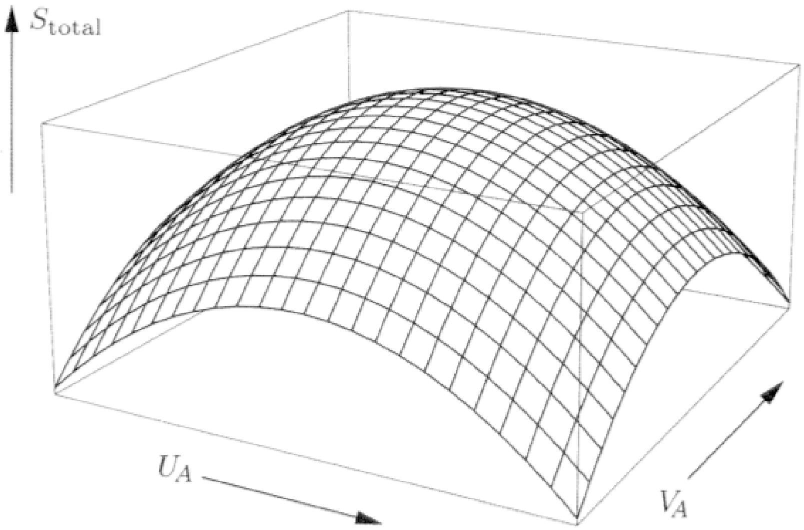
$q = 100$



$$\frac{\partial S_{total}}{\partial U_A} = 0$$

at eq.

Exchange of volume and energy



at eq.

$$\frac{\partial S_{total}}{\partial U_A}=0 \quad \Big\} \quad \frac{\partial S_{total}}{\partial V_A}=0$$

Pressure

- For mechanical equilibrium,

$$\frac{\partial S_A}{\partial V_A}=\frac{\partial S_B}{\partial V_B}$$

$$0=\frac{\partial S_{total}}{\partial V_A}=\frac{\partial S_A}{\partial V_A}+\frac{\partial S_B}{\partial V_A}$$

$$dV_A=-dV_B$$

- Units: dS/dV has units of $\frac{\text{J/K}}{\text{m}^3}=\frac{N/m^2}{K}=\frac{Pa}{K}$

- Propose following relation between entropy and pressure

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

Pressure

- Does this work for an example we know
  - Try ideal monatomic gas

$$S = Nk\ln V + \tfrac{3}{2}Nk\ln U + k\ln f(N)$$

↳ from $\Omega = f(N)V^{N}U^{3N/2}$

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

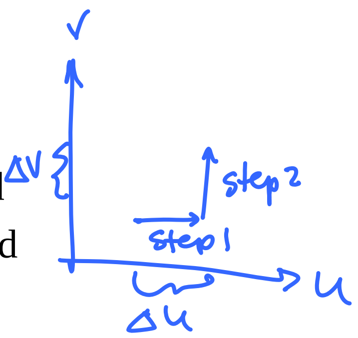
$$= T\frac{\partial}{\partial V}\left(Nk\ln V\right)$$

$$= \frac{NkT}{V} \Rightarrow PV = NkT$$

Volume and Energy Changes

- Looking at a process where both V and U change
  - How much does the entropy change?

- Divide the process into two steps:
  1. Energy changes by ΔU and V is held fixed
  2. Volume changes by ΔV and U is held fixed



- Total change in entropy is

$$\Delta S = (\Delta S)_1 + (\Delta S)_2$$

$$= \left(\frac{\Delta S}{\Delta U}\right)_V \Delta U + \left(\frac{\Delta S}{\Delta V}\right)_U \Delta V$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV = \frac{1}{T}dU + \frac{P}{T}dV$$

Thermodynamic Identity

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

$$dU = TdS - PdV$$

- When V, N are fixed

$$dU = TdS \longrightarrow \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

- Similarly,

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

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- Similarly,

$$P = T\left(\frac{\partial S}{\partial V}\right)_{U,N} \qquad \mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} \Big\} \text{chemical potential}$$

- In general,

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

Chemical Potential

- Recall:

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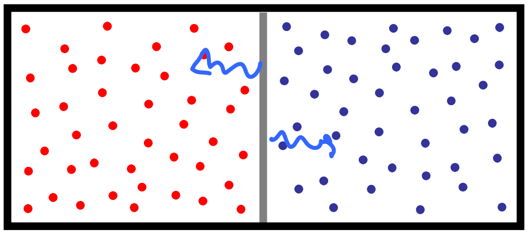
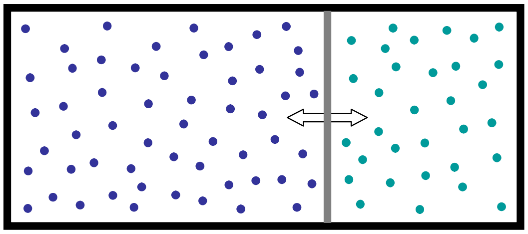
thermal

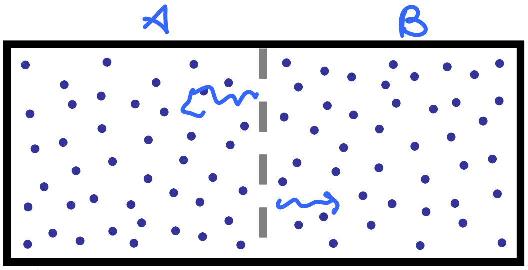


mechanical



Diffusive Equilibrium

- Consider two systems A and B that are same species



U_A, S_A, N_A U_B, S_B, N_B

isolated so $$\left.\begin{aligned} U &= U_A + U_B \\ N &= N_A + N_B \end{aligned}\right\} \text{ fixed}$$

At Equilibrium

- Entropy of system A + B is maximum

$$\left(\frac{\partial S_{total}}{\partial U_A}\right)_{N_A,V_A} = 0 \qquad \left(\frac{\partial S_{total}}{\partial N_A}\right)_{U_A,V_A} = 0$$

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$ at constant U & V

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

particles tend to flow from system with higher μ to one with lower μ

Thermodynamic Identity

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

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

Free Energy

Large systems we have been discussing have macrostates determined by U, N and V

- But what if T is fixed not U or P is fixed rather than V

First need to define some terms

- Recall: Enthalpy $H \equiv U + PV$

Free Energy

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- Helmholtz Free Energy: $F \equiv U - TS$
  - Total energy needed to create something, minus the heat that you can get from the environment at temperature, T
  - Heat is TS where S is final entropy of system
  - If create system out of nothing, F is the energy you need to provide as work to do this at constant temperature, T
  - If annihilate system, energy you get for free is $F = U - TS$

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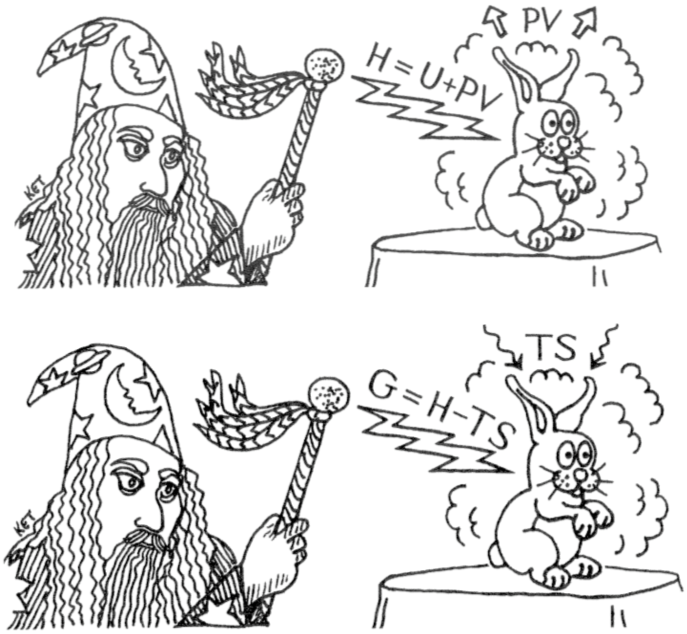
  - If annihilate system, energy you get for free is $F = U - TS$
- Gibbs Free Energy: $G \equiv H - TS \equiv \overbrace{U - TS}^{F} + PV$
  - Additional work is that needed to put the something in the environment

Somewhat silly example…

analogous pair

enthalpy

U total energy

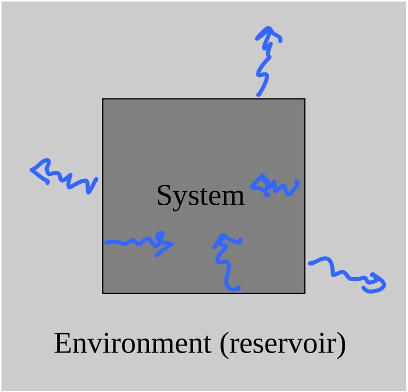


Gibb's free energy

$F = U - TS$ Helmholtz free energy

Meaning of Free Energy

- For an isolated system, entropy tends to increase



reservoir can absorb or release unlimited amounts of energy

→ temperature never changes

- But what about a system in thermal contact with a reservoir?

total entropy tends to increase

Meaning of Free Energy

- For system in thermal contact with reservoir,
  - The total entropy tends to increase now:

$$dS_{\text{total}} = dS + dS_R$$

$$= dS + \frac{1}{T_R} dU_R + \frac{P_R}{T_R} dV_R - \frac{\mu_R}{T_R} dN_R$$

only exchange energy between system & reservoir

$$dS_{total} = dS + \frac{1}{T_R} dU_R$$

$$= dS - \frac{1}{T} dU$$

$$= -\frac{1}{T}(dU - TdS)$$

$$= -\frac{1}{T} dF$$

at eq.

$T = T_R$

$dU = -dU_R$

fixed T, V, N

Where do same for volume

$$dS_{total} = dS - \frac{1}{T}dU - \frac{P}{T}dV$$

$$= -\frac{1}{T}\left(dU - TdS + PdV\right)$$

$$= -\frac{1}{T}dG \qquad T, P, N \text{ fixed}$$

Moving toward Equilibrium

What does system “do” in reaching equilibrium?

- At constant U and V, S tends to increase
- At constant T and V, F tends to decrease
- At constant T and P, G tends to decrease