Phys 344.

Lecture 13. Mechanical Equilibrium and Pressure.

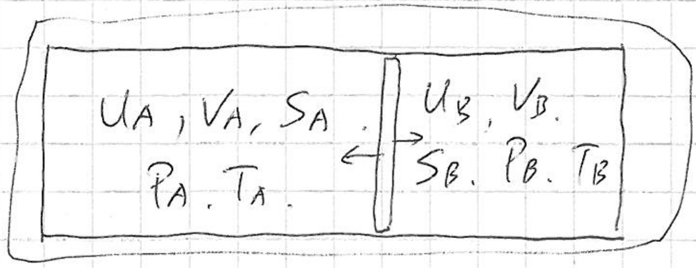
- Question.

  How does S depend on V, P, [illegible] ?

- Two systems — can exchange energy and volume.

$$U = U_A + U_B \qquad V = V_A + V_B.$$

$$S_{Total} = S = S_A + S_B$$



U and V are fixed.

S varies as U_A and V_A varies.

- At ~~thermal~~ equilibrium.

$$\frac{\partial S}{\partial U_A} = 0. \qquad \frac{\partial S}{\partial U_A} = 0.$$

$$\Downarrow$$

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}.$$

Mechanical equilibrium.

Same temperature

(Thermal equilibrium).

- $\frac{\partial S}{\partial V_A} = 0 = \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = \frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B}$

$$\therefore \left(\frac{\partial S_A}{\partial V_A}\right)_{U_A, N_A} = \left(\frac{\partial S_B}{\partial V_B}\right)_{U_B V_B}$$

The piston is a macroscopic object and should obey Newton's law of equilibrium, $P_A = P_B$.

$$\therefore P \propto \frac{\partial S}{\partial V}.$$

$S - J/K = N \cdot m/K$.

$V - m^3$

$P = \frac{N}{m^2}$.

$\frac{\partial S}{\partial V} - N/m^2 \cdot K$.

$$\therefore P \propto T \frac{\partial S}{\partial V}.$$

- Definition of Pressure : $P = T\left(\frac{\partial S}{\partial V}\right)_{U,N}$.

· e.g. Monotomic ideal gas

$\cancel{S} =$ Sackur-Tetrode equation

$$S = Nk\left\{\ln\left[\frac{V}{N}\left(\frac{4\pi m U}{3Nh^2}\right)^{3/2}\right] + \frac{5}{2}\right\}$$

(can be obtained from ~~probability of~~ Ω)

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

$$= T \cdot N \cdot k \frac{\frac{1}{N}\left(\frac{4\pi m U}{3Nh^2}\right)^{3/2}}{\frac{V}{N}\left(\frac{4\pi m U}{3Nh^2}\right)^{3/2}}$$

$$= \frac{TNk}{V}$$

$PV = NkT$ —— ideal gas law.

if $S = S(U, V)$

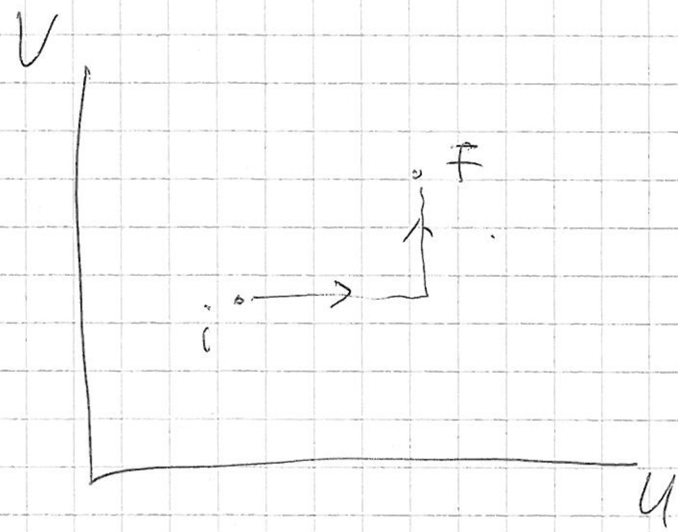
$$\therefore \quad dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

Thermodynamic identity.

$$\boxed{dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV} \qquad (3.45)$$

OR $\quad dU = T\,dS - P\,dV$.

To find ΔS.



definition of T:

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}.$$

definition of P:

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}.$$