Lecture 14

- Thermodynamic Identity

$$dU = TdS - PdV$$

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

- Quasistatic process:

$$dS = \frac{đQ}{T}$$

$\underline{\text{Adiabatic}}$ quasistatic : $dS = 0$.

↑ $đQ=0$ or: $S = \text{const}$.

called isentropic process

$$T = \left(\frac{\partial U}{\partial S}\right)_V, \quad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

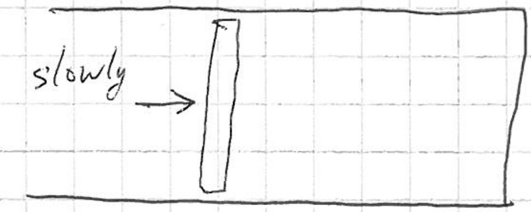
← S fixed
isentropic

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_U$$

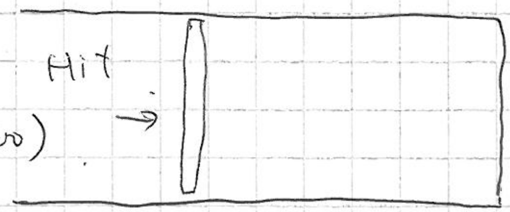
- Non-quasistatic process.

$$dS > \frac{đQ}{T}.$$

Why? $dU = đQ + đW$.



slowly: $dS = \dfrac{đQ_{quasistatic}}{T}.$



Hit: and wait.

same dU as before, (same dS too) — because same initial and final states.

but more work $đW$.

$\therefore$ less $đQ$

$$\therefore\ dS > \frac{đQ_{non\text{-}quasistatic}}{T}$$

Note: Non-quasistatic processes always create additional entropy!

(so they are always irreversible).

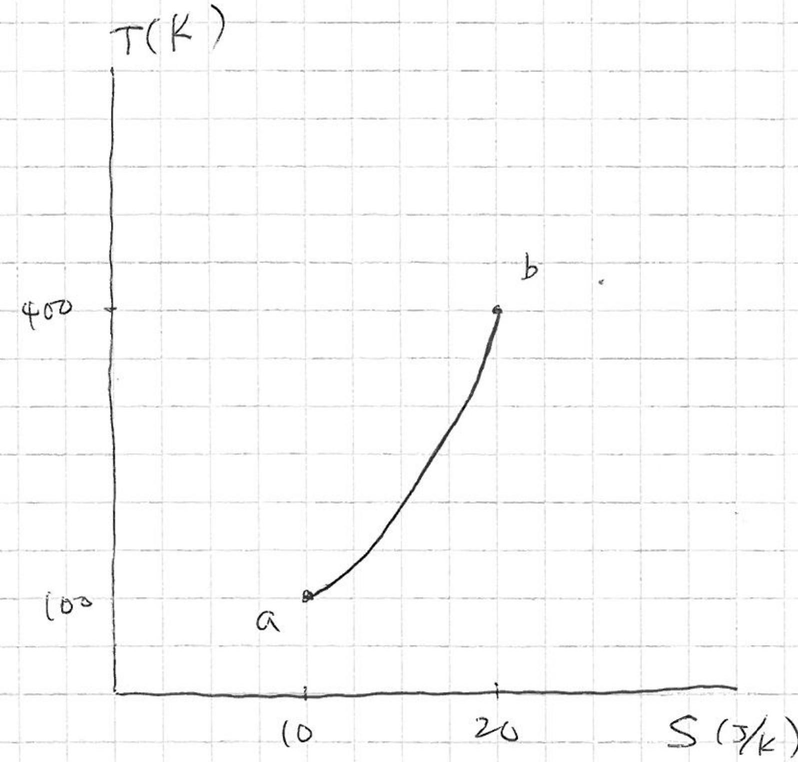
e.g. 1 mol. of monatomic ideal gas.

for a quasistatic process $S^2 = nT$ ($n = 1$ mol.)

$a \to b$.

$T_a = 100\,K$

$T_b = 400\,K$.



① Heat input $Q = ?$

② work on system : $W = ?$

①: $đQ = TdS$

$$Q = \int_a^b đQ$$

$$= \int_a^b T\,dS$$

$$= \int_a^b S^2 dS = \frac{1}{3}S^3\Big|_{10}^{20} = \frac{1}{3}\left(20^3 - 10^3\right) = 2333\,J = 2.33\,kJ.$$

②. $\Delta U = W + Q$. $W = \Delta U - Q$

$U = \frac{3}{2}nRT$, $\Delta U = \frac{3}{2}R\Delta T$ ($n=1$)

$$= \frac{3}{2} \times 8.31 \times (400-100)$$

$$= 3.74\ kJ.$$

$$W = 3.74 - 2.33 = 1.41\ kJ.$$

e.g. For a photon gas (black body radiation).

$$U(S, V) = a V^{-1/3} S^{4/3} \quad (a - \text{positive const.})$$

Find. $S(V, T)$, $H(S, V)$.

① $S(V, T)$: $dU = TdS - pdV$.

$$T = \left(\frac{\partial U}{\partial S}\right)_V = a V^{-1/3} \cdot \frac{4}{3} S^{1/3} = \frac{4a}{3}\left(\frac{S}{V}\right)^{1/3}$$

$$\therefore \quad S = \left(\frac{3}{4a}\right)^3 V T^3$$

② $H(S, V)$.

$$H = U + PV \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

$$= -a\left(-\frac{1}{3}\right) V^{-4/3} S^{4/3}$$

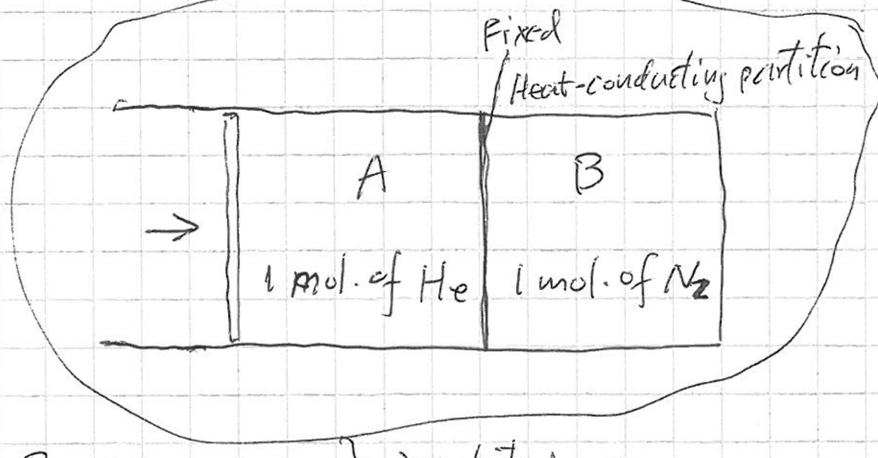
$$= \frac{a}{3}\left(\frac{S}{V}\right)^{4/3}$$

$$H = a V^{-1/3} S^{4/3} + \frac{a}{3} V^{-4/3} S^{4/3} \cdot V$$

$$= \frac{4a}{3} V^{-1/3} S^{4/3}.$$

e.g. Ideal gases near room Temp.

You push the piston slowly and do work W.



insulated.

Find: ① change in U for B. (N_2 gas) } i.e. $\Delta U_B = ?$

② Heat capacity of A.

③ Equation of process for A.

①. Find ΔT for the whole system and then ΔU_A.

whole system: $\Delta U = W + Q = W \quad (Q=0)$.

$$U = \frac{3}{2} n_A RT + \frac{5}{2} n_B RT = \frac{3}{2} RT + \frac{5}{2} RT = \frac{8}{2} RT$$

$$= 4RT.$$

$$\Delta U = 4R\Delta T = W. \qquad \Delta T = \frac{W}{4R}.$$

$$U_B = \frac{5}{2} RT.$$

$$\Delta U_B = \frac{5}{2} R\Delta T = \frac{5}{2} R \cdot \frac{W}{4R} = \frac{5}{8} W.$$

(Note: $\Delta U_A = \frac{3}{2} R\Delta T = \frac{3}{8} W$)

B has more degrees of freedom — larger heat capacity

A and B are in thermal equilibrium. (Same ΔT).

∴ B gains more energy.

② . Total system : $đQ = 0 = đQ_A + đQ_B$.

$$0 = C_A\,dT + C_B\,dT.$$

$$C_A = -C_B \qquad C_B = C_V = \frac{f}{2}nR = \frac{5}{2}nR.$$

$n = 1$.

$$\therefore\ C_A = -\frac{5}{2}R$$

↑

negative : in this process, A loses heat,

but T_A increases.

(because you do work on A)

For A:

③ . $$đQ_A = dU_A - đW_A$$

$$PV = RT.$$

$$P = \frac{RT}{V}.$$

$$-\frac{5}{2}R\,dT = \frac{3}{2}R\,dT + P\,dV.$$

$$-4R\,dT = \frac{RT}{V}\,dV.$$

$$\frac{-4\,dT}{T} = \frac{dV}{V}.$$

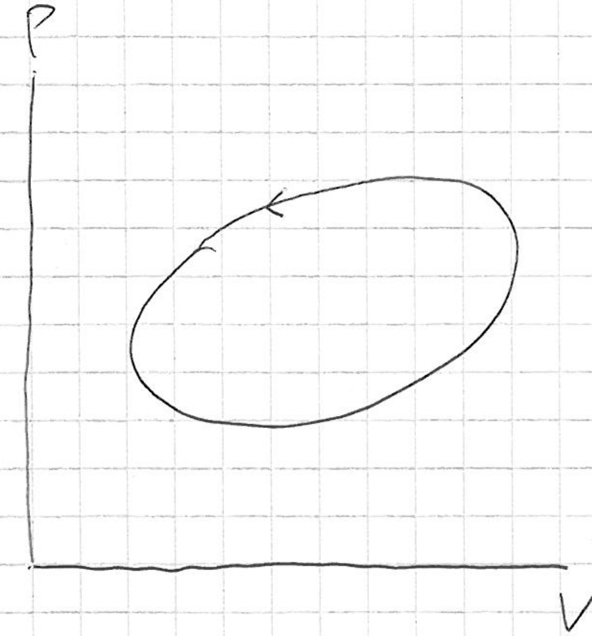
$$-4\ln T = \ln V + \ln C_i = \ln(CV) \qquad C - \text{const}.$$

$$T^{-4} = CV$$

$$\therefore\ \boxed{VT^4 = \text{const}.}$$

$$V \cdot P^4 V^4 = \text{const}. \qquad \therefore\ \boxed{P^4 V^5 = \text{const}.}$$

e.g. an unknown system undergoes an arbitrary quasistatic cyclic process.



show: The heat capacity is not constant.

[Proof]: If $C = \text{const}$.

$$Q = \oint C\,dT = C \cdot \oint dT = 0.$$

But: $\Delta U = 0$.

$W \neq 0$. (W = area enclosed $\neq 0$)

Then. $\Delta U \neq W + Q$.

Vialates the first Law! — impossible.