ENTROPIA

→ Variabili di stato $(p, V, T, U \dots) \Longleftrightarrow$ $\forall$ ciclo $i \to f$

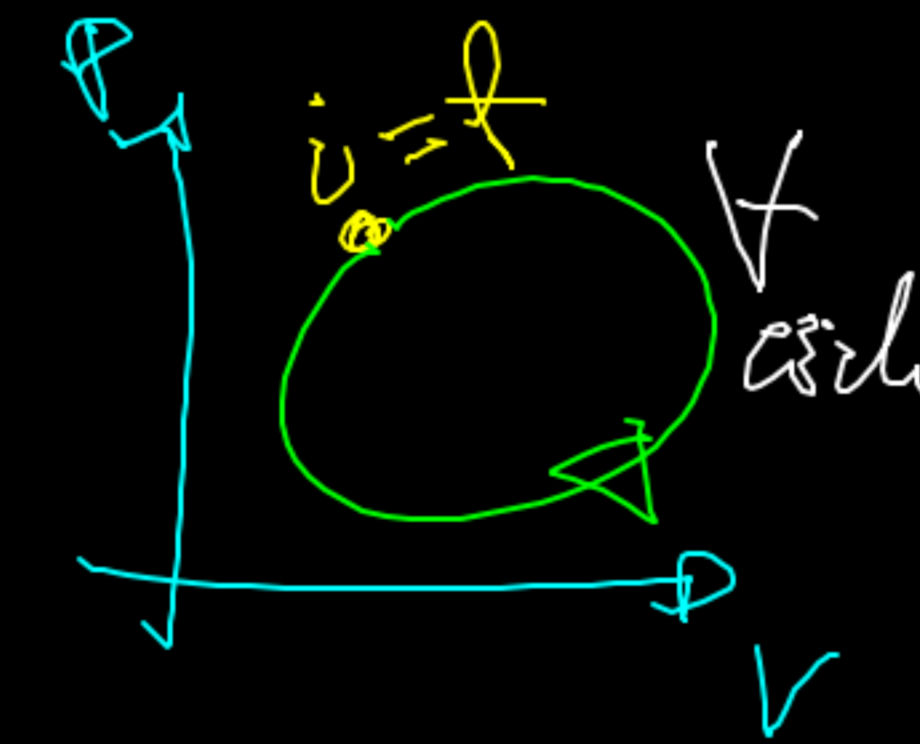
$\Delta p = 0$

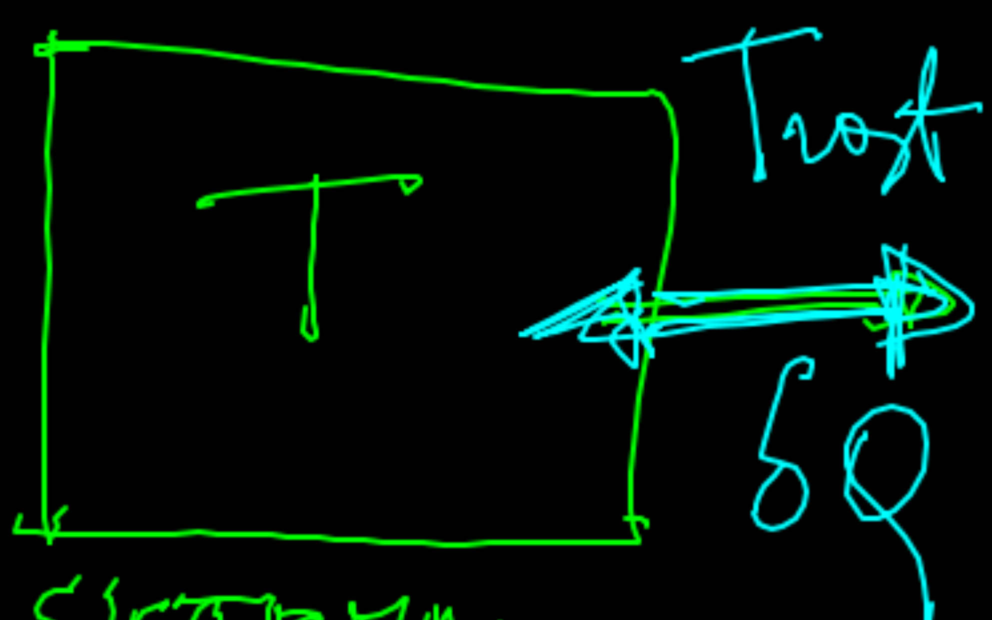
$\Delta U = 0$

$\Delta T = 0$

$\Delta V = 0$

$\vdots$





$$\boxed{dS = \frac{\delta Q}{T}}$$

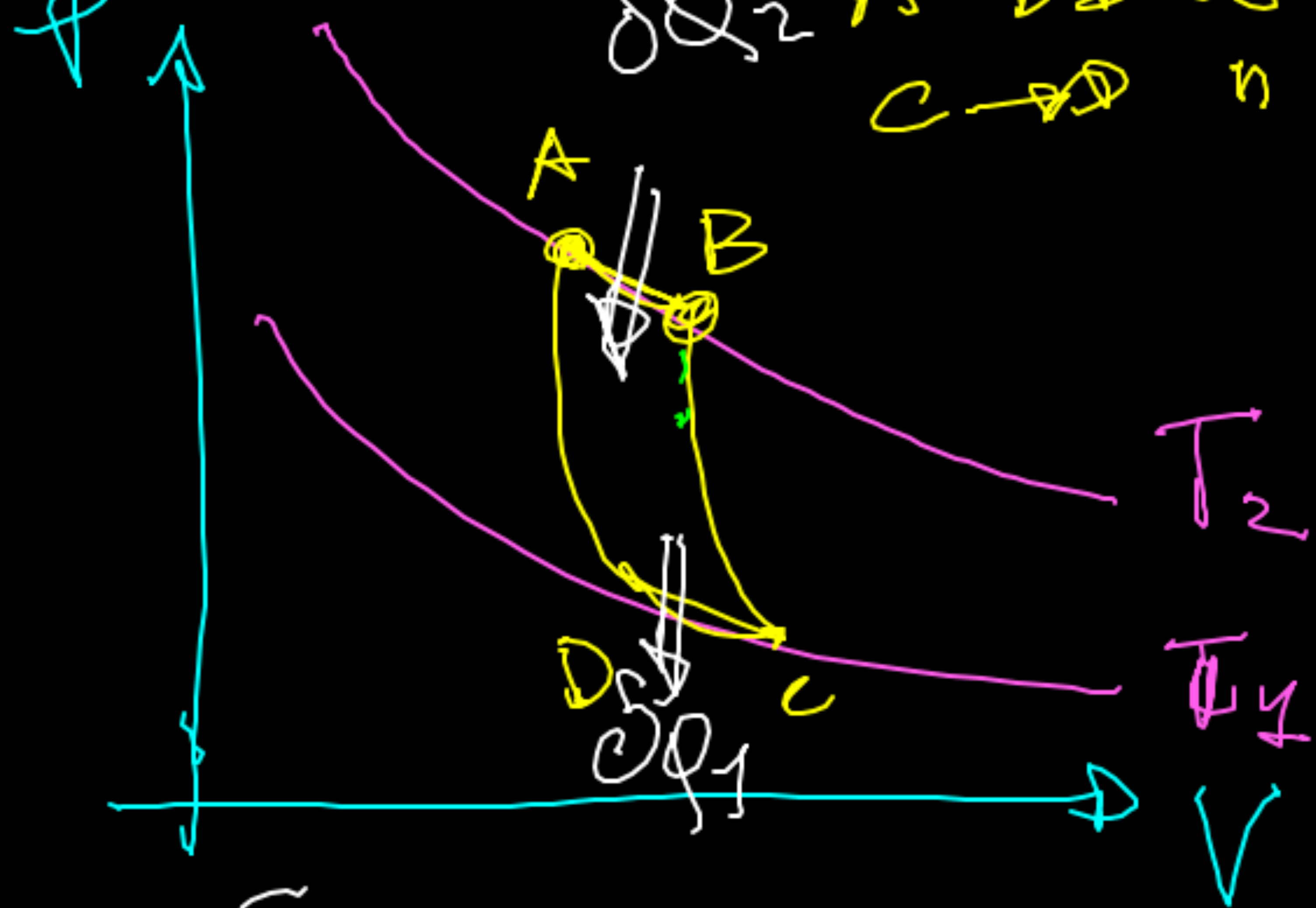
VARIAZIONE DI ENTROPIA

$\Delta S = 0$ SU UN CICLO?

PER UNA TRASF. FINITA REV.

$$\Delta S = \int_i^f \frac{\delta Q}{T} = S_f - S_i$$

δQ_2 $A \to B$ è isoterma.
$C \to D$ " "



$\delta Q_1 < 0$

$\delta Q_2 > 0$

$dS_{AD} = 0$

perché $\delta Q = 0$

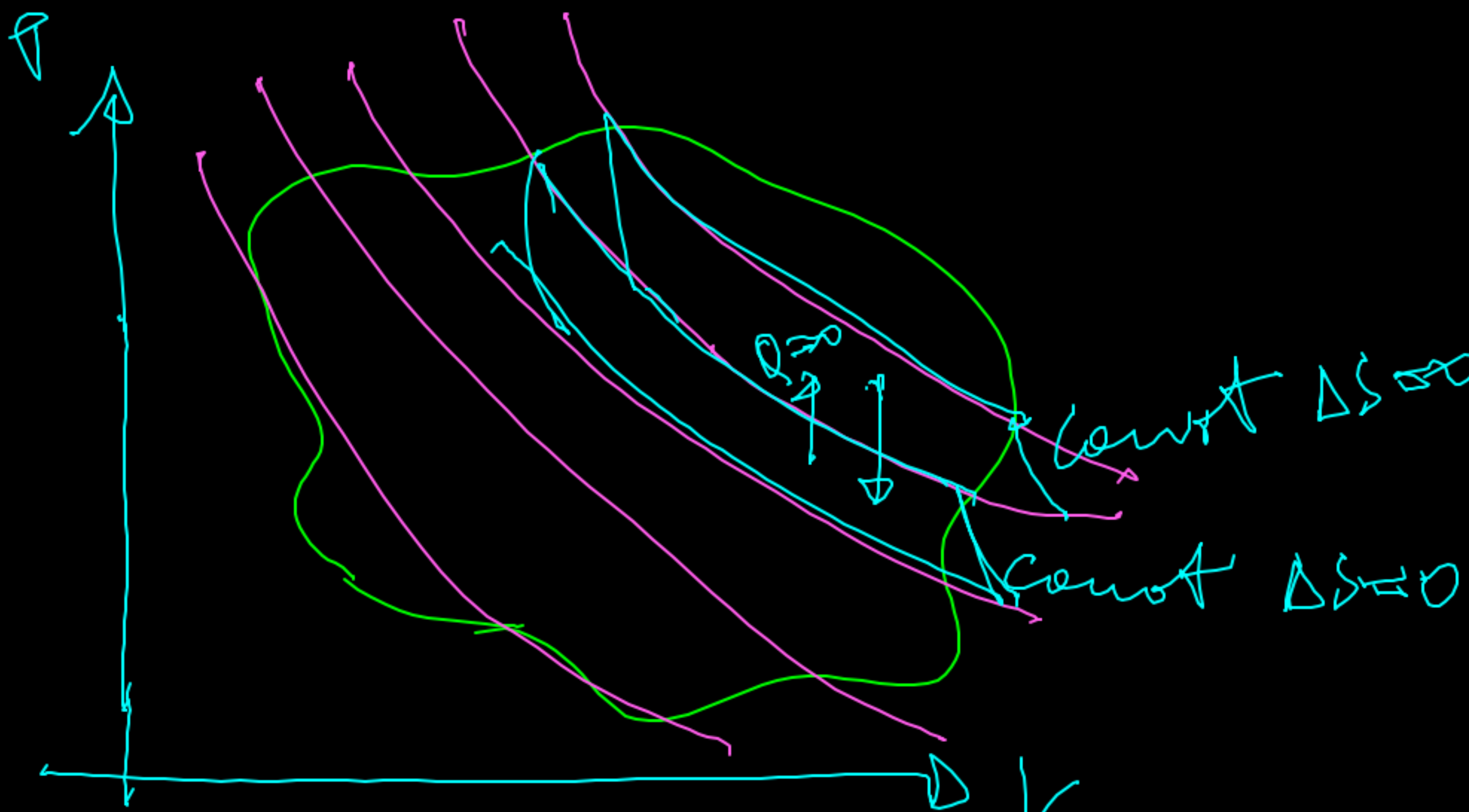
$$\frac{\delta Q_2}{|\delta Q_1|} = \frac{T_2}{T_1} \Rightarrow \frac{\delta Q_2}{T_2} = \frac{|\delta Q_1|}{T_1}$$

$$\frac{\delta Q_2}{T_2} - \frac{|\delta Q_1|}{T_1} = \boxed{0 = \underbrace{\frac{\delta Q_2}{T_2}}_{dS_2} + \underbrace{\frac{\delta Q_1}{T_1}}_{dS_1}}$$

PER UN CICLO DI CARNOT REV.

$$\boxed{0 = dS_2 + dS_1}$$

$$\Delta S = 0$$



L'ENTROPIA È UNA FUNZIONE DI STATO

$\forall$ CICLO REV. → SOMMA DI CICLI DI CARNOT REV.

$\Delta S = 0$

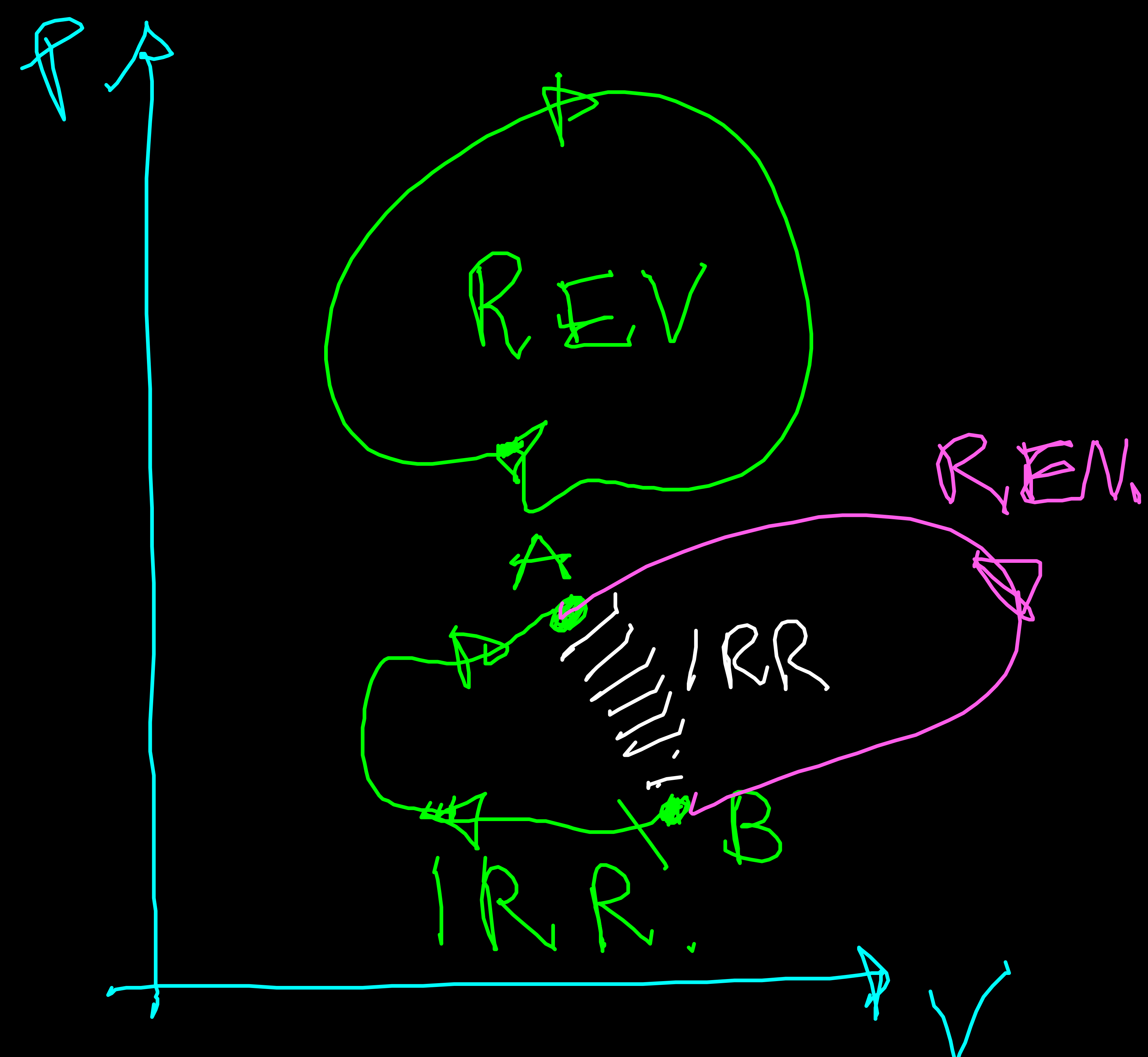
$\Delta S = 0$ →

$$\Delta S_{ciclo} = 0 \qquad (\text{ciclo qualsiasi})$$

$$\Delta S_{ciclo} = \int_{\substack{\text{CICLO}\\\text{REV.}}} \frac{\delta Q}{T} = \boxed{\oint_{\text{REV.}} \frac{\delta Q}{T} = 0}$$

S è una funzione di stato

Variabili di stato: $p, V, n, T, U, S \ldots$



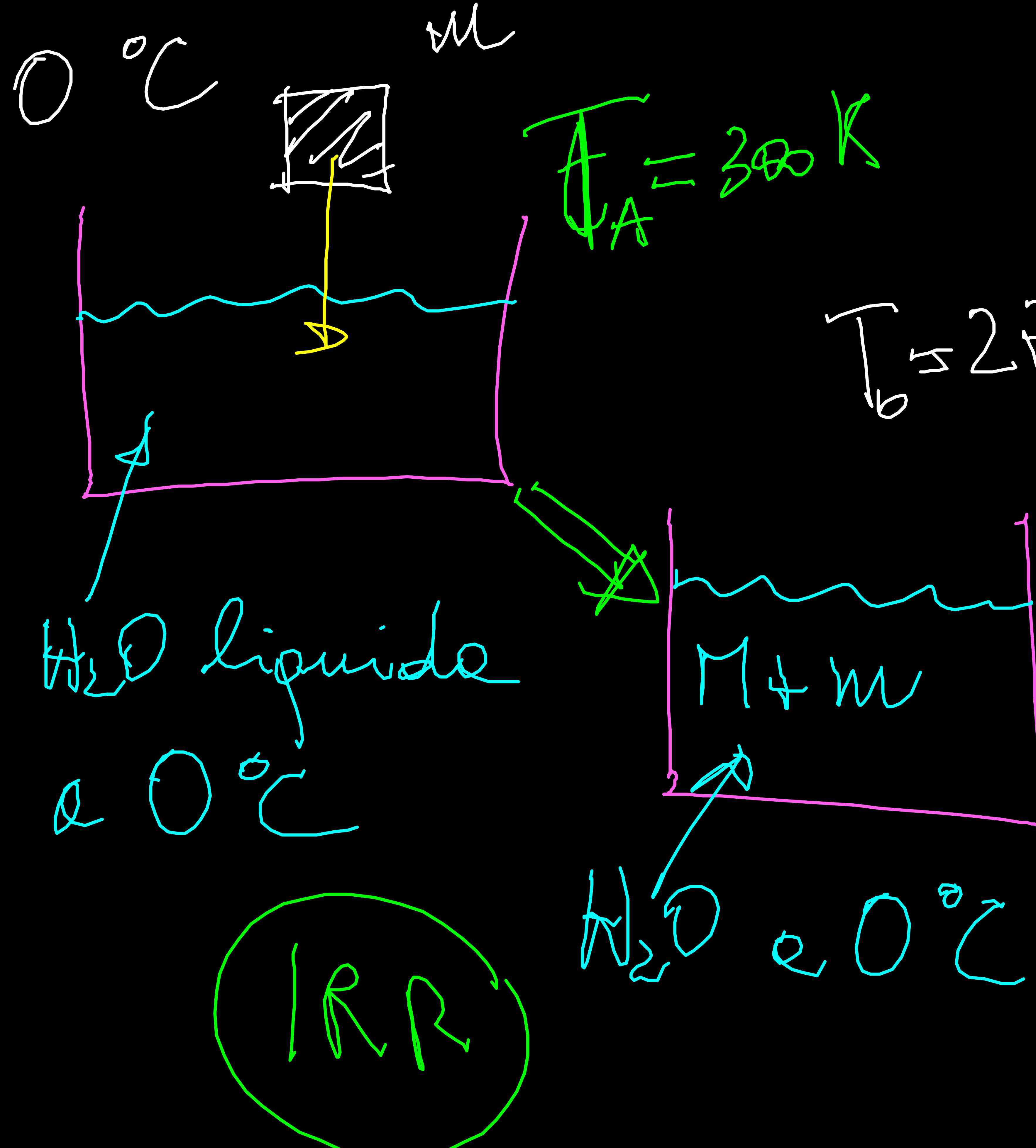
$$\oint \frac{\delta Q}{T} \begin{cases} = 0 & \text{REV.} \\ < 0 & \text{IRR.} \end{cases}$$

INTEGRALE DI CLAUSIUS

$A \to B$ TRASF. REALE IRR, si può comunque calcolare $\Delta S_{AB} = S_B - S_A$ usando una qualunque trasformazione REV. da $A \to B$

ESEMPI DI CALCOLO DI ΔS

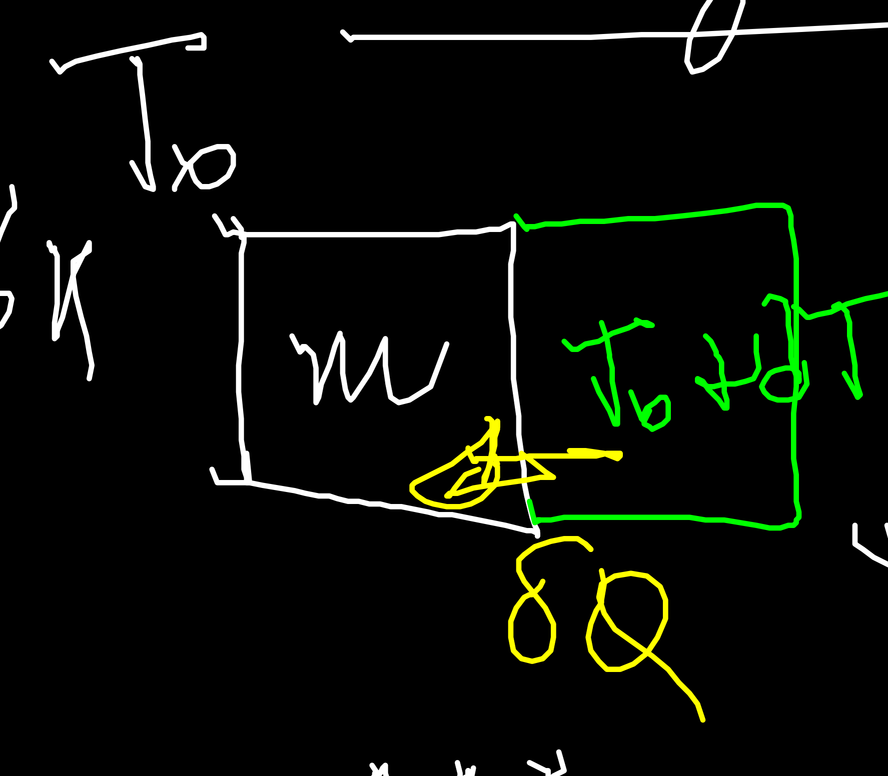
• Cambiamento di fase



$T_0 = 273.16$ K

Per calcolare $\Delta S_{fusione}$

immagino una trasf. rev.



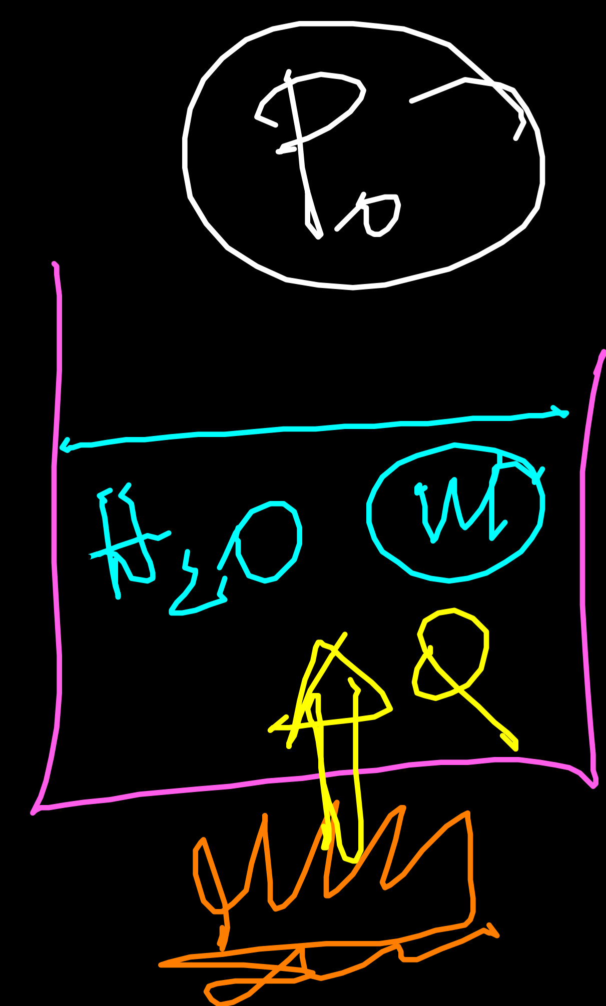
INFINITE QUASI-STATICHE REV.

$$Q_{TOT} = m\lambda_f$$

$$\Delta S_{fusione} = S_{LIQ} - S_{SOLIDO} = \int_i^f \frac{\delta Q}{T} = \frac{1}{T_0}\int_i^f \delta Q = \frac{Q_{TOT}}{T_0}$$

$$\Delta S_{fus} = \frac{Q_{TOT}}{T_0} = \frac{m\lambda_f}{T_0} > 0 \quad \left[\frac{J}{K}\right]$$

- riscaldamento



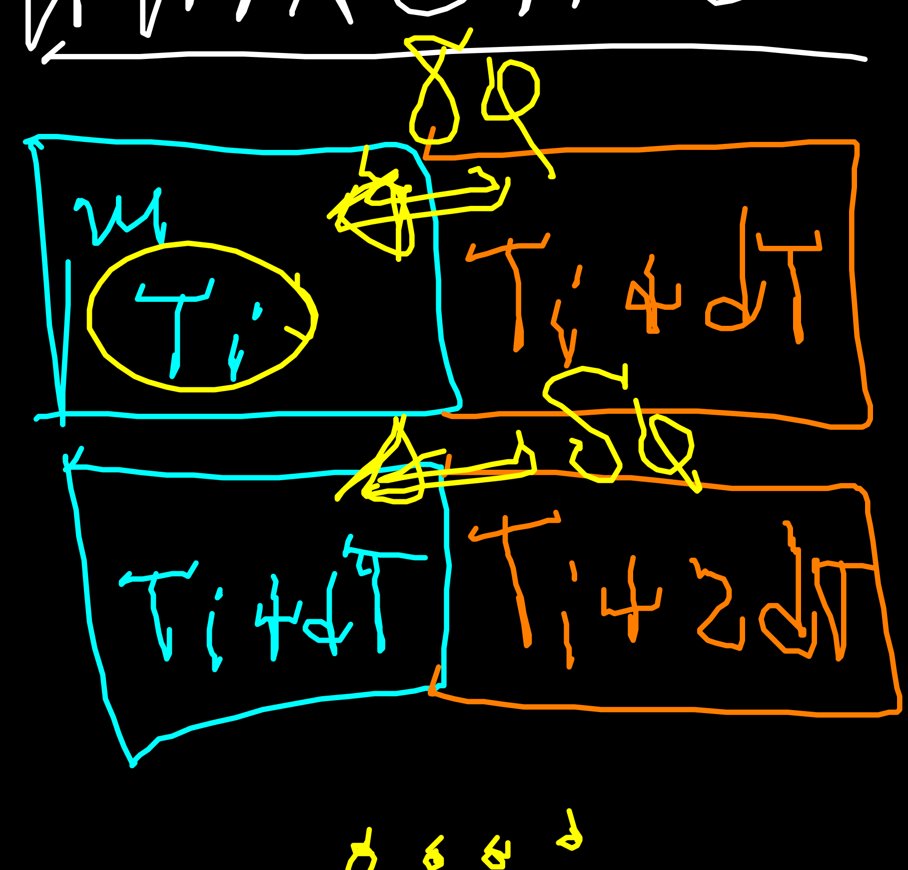
H_2O

$t_i \to t_f < 100°C$

$T_i \to T_f < 373.16$ K

IRR.

IMMAGINO



quasi-statico rev.

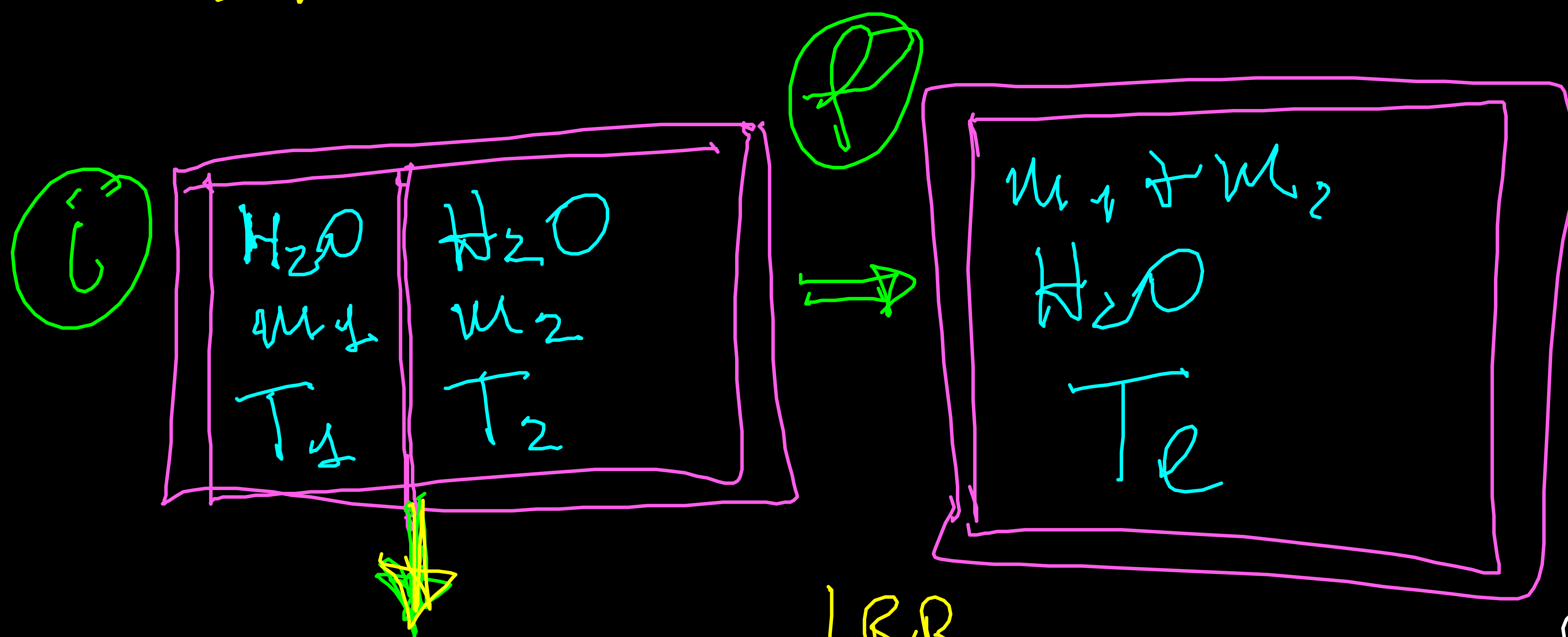
T_f

$$\Delta S = \int_{T_i}^{T_f} \frac{\delta Q}{T} = \int_{T_i}^{T_f} \frac{\overbrace{m c_p \, dT}^{\delta Q}}{T}$$

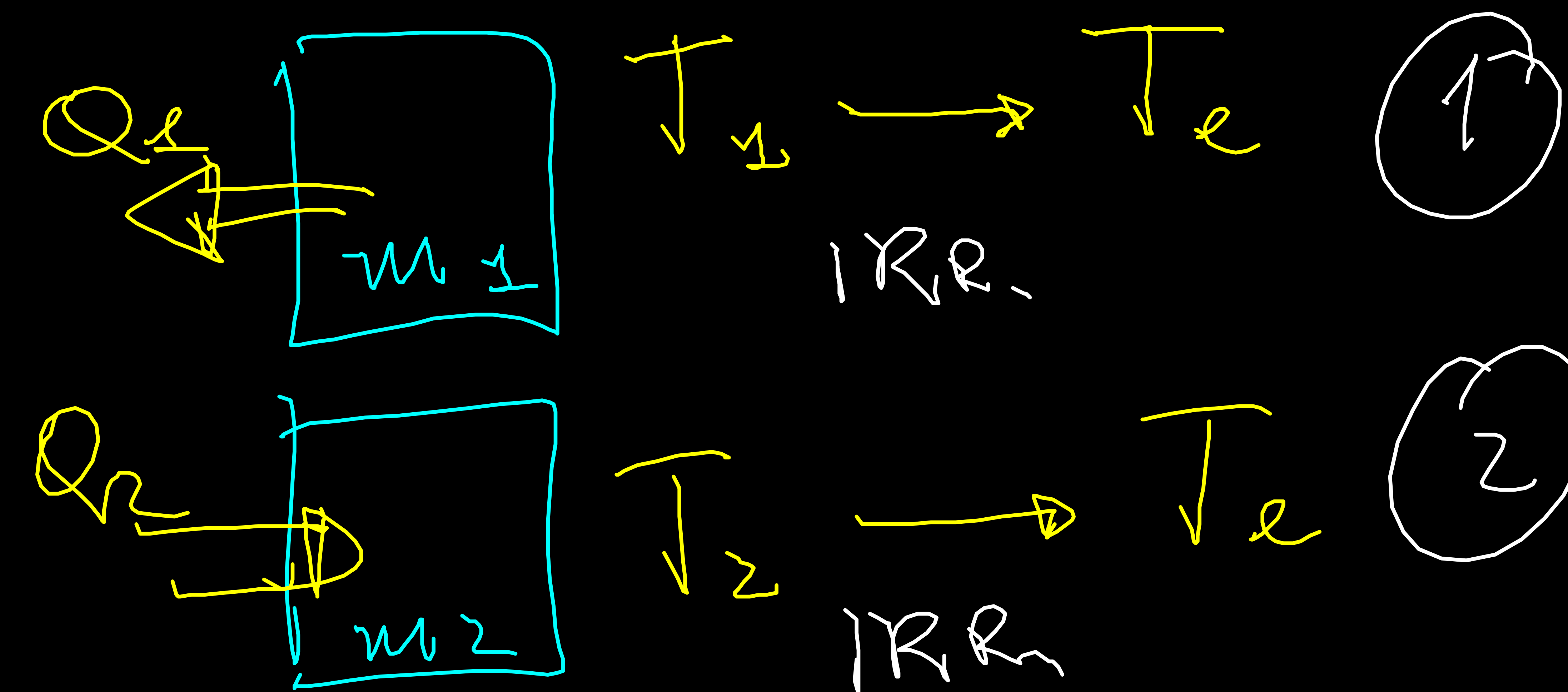
$$= m c_p \int_{T_i}^{T_f} \frac{dT}{T} = m c_p \ln \frac{T_f}{T_i} > 0$$

$T_f > T_i$

• mescolamento



IRR



• $T_1 = 363\ K$

$T_2 = 283\ K$

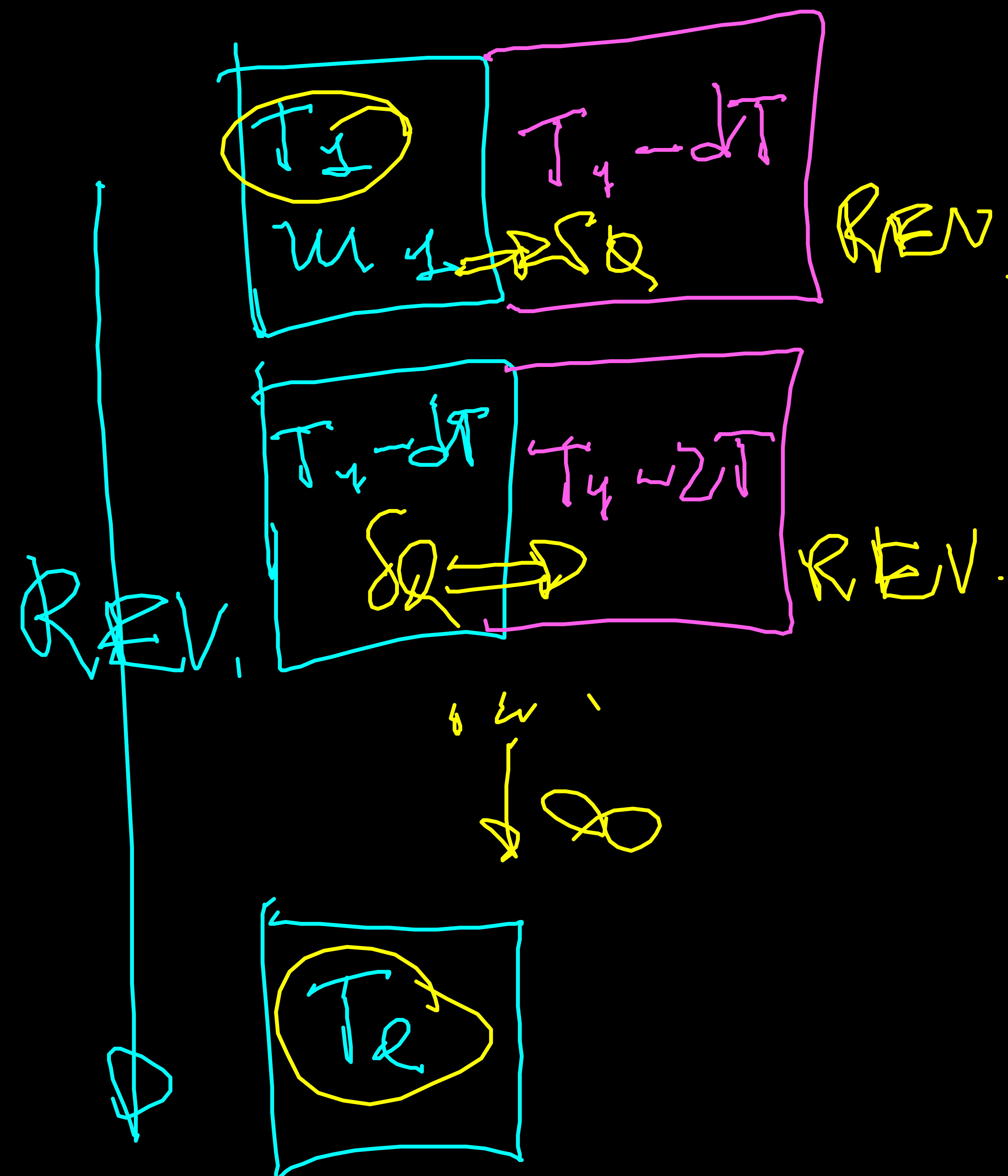
$m_2 > m_1$

$$-m_1 c_p (T_e - T_1) = m_2 c_p (T_e - T_2)$$

$$T_2 < T_e < T_1$$

S è additiva

$$\Delta S_{sist} = \Delta S_1 + \Delta S_2$$



$$\delta Q = m_1 c_p \, dT$$

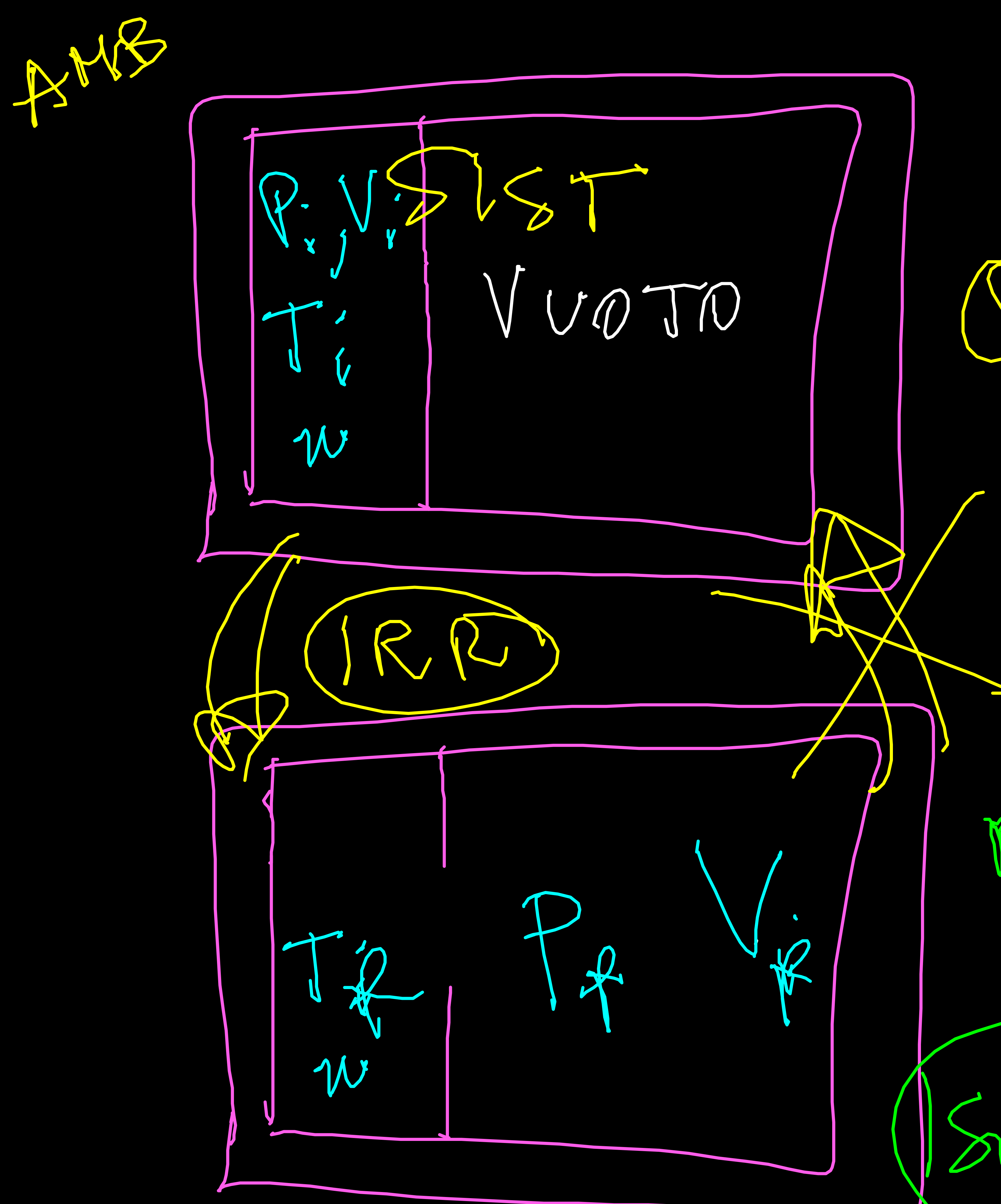
$$T_1 > T_e > T_2$$

$$\Delta S_1 = \int_{T_1}^{T_e} \frac{m_1 c_p \, dT}{T} = m_1 c_p \ln \frac{T_e}{T_1} < 0$$

ANALOGAMENTE $\Delta S_2 = m_2 c_p \ln \frac{T_e}{T_2} > 0$

$$\underset{?}{\Delta S_{SIST}} = \underbrace{\Delta S_1 + \Delta S_2}_{} = \underbrace{m_1 c_p \ln \frac{T_e}{T_1}}_{<0} + \underbrace{m_2 c_p \ln \frac{T_e}{T_2}}_{>0}$$

• espansione libera di un gas perfetto



$T_f = T_i$

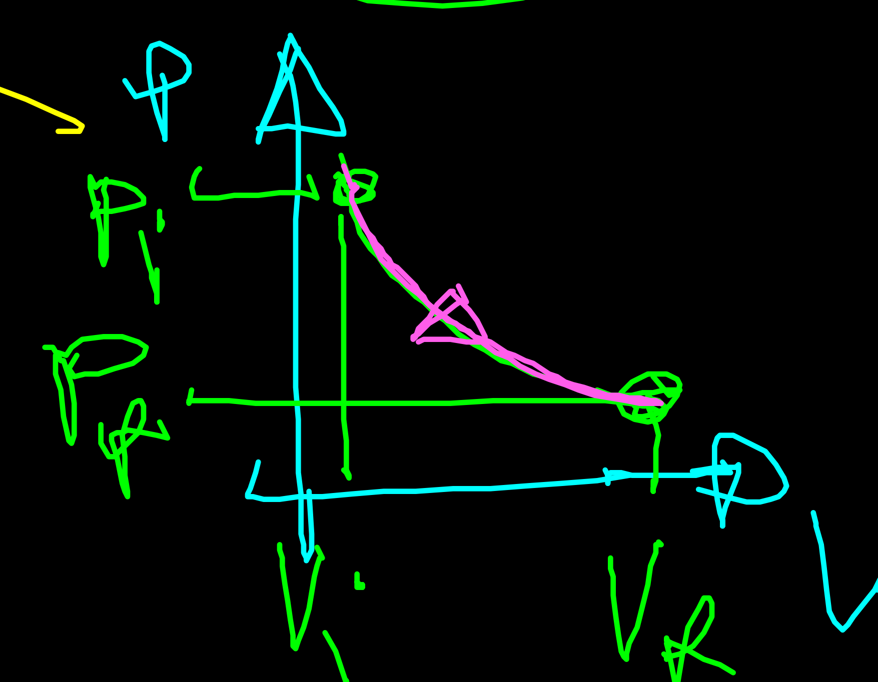
$Q = 0$

$\Delta U = 0 \quad (T_f = T_i)$

$\mathcal{L} = 0$

$\Delta S \; ? \geq 0$ → uso una ISOT. REV. che va da $p_i, V_i \to p_f, V_f$

ISOLATO



$$dS = \frac{\delta Q}{T} = \frac{\cancel{dU} + \delta \mathcal{L}}{T} = \frac{p\,dV}{T} \qquad \delta \mathcal{L}$$

$$\Delta S = \int_{V_i}^{V_f} \frac{p\,dV}{T} = \int_{V_i}^{V_f} \frac{nR\,dV}{V} = nR \ln \frac{V_f}{V_i}$$

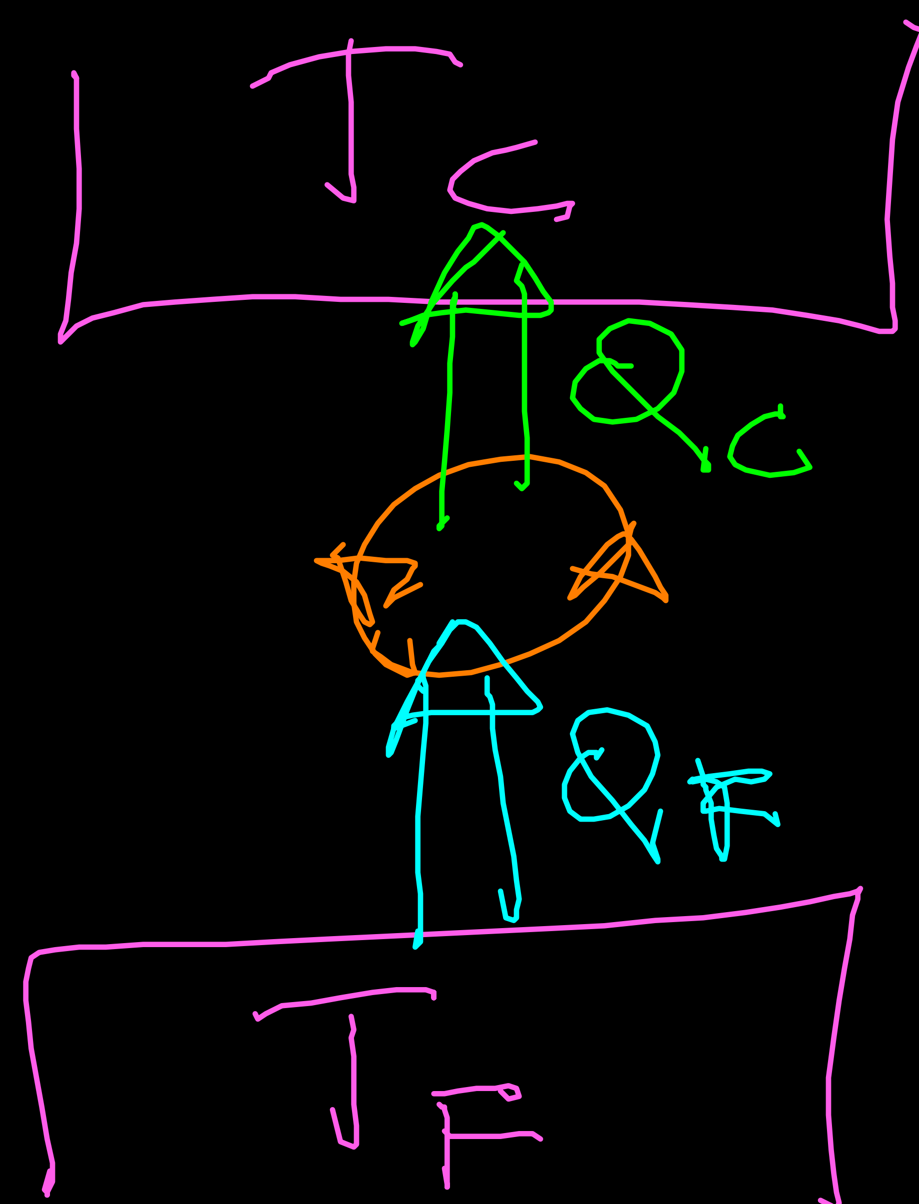
> 0 $\qquad$ > 0

$$\Delta S_{UNIV} = \Delta S_{AMB} + \Delta S_{SIST}$$

$$\boxed{\Delta S_{UNIV} \underset{\text{REV.}}{\overset{\text{IRR.}}{\geq}} 0}$$

II PRINCIPIO DELLA TERMODINAMICA

Il verso naturale delle trasformazioni è <u>S in aumento</u>



CLAUSIUS

NO

$T_C > T_F$

Supponiamo che

~~CLAUSIUS~~

$Q_F = Q_C = Q$

$$\Delta S_F = \frac{Q_F}{T_F} = \frac{-|Q|}{T_F}$$

$$\Delta S_C = \frac{Q_C}{T_C} = \frac{|Q|}{T_C}$$

$$\Delta S_T = -\frac{|Q|}{T_F} + \frac{|Q|}{T_C} = |Q|\left(\frac{1}{T_C} - \frac{1}{T_F}\right) < 0$$

BOLTZMANN

$$S_s = K \ln W_s$$

costante di Boltzmann

"probabilità" di realizzare lo stato S