

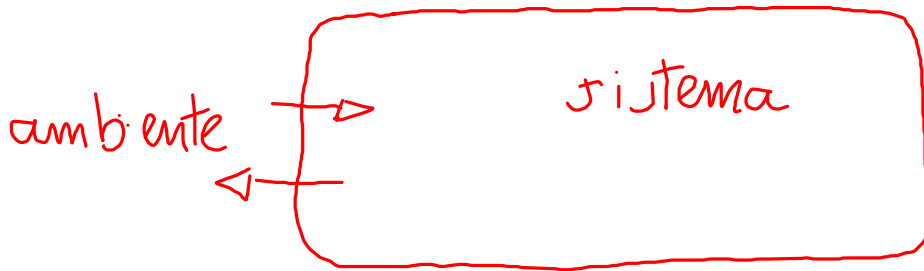
Termodinamica

Sistemi in equilibrio

Variabili di stato $p V T n$

Leggi $pV = nRT$

Sistema termodinamico

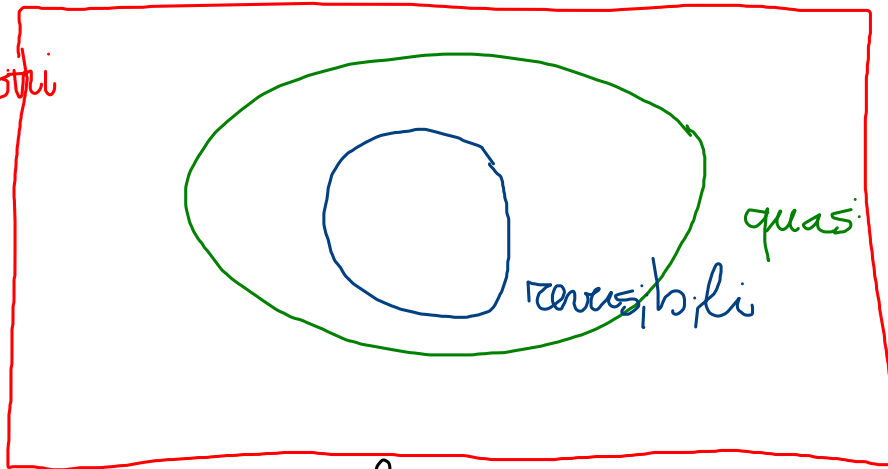


isolato
no mat. n_j km

chiuso
no mat. Si en.

Trasformazioni Termodinamiche

Trasformazioni



quasi statiche

reversibili

trasformazioni infinitesime

trasformazioni notevoli:

isoterme

T cost

isobare

p c. st

isocore

V cost

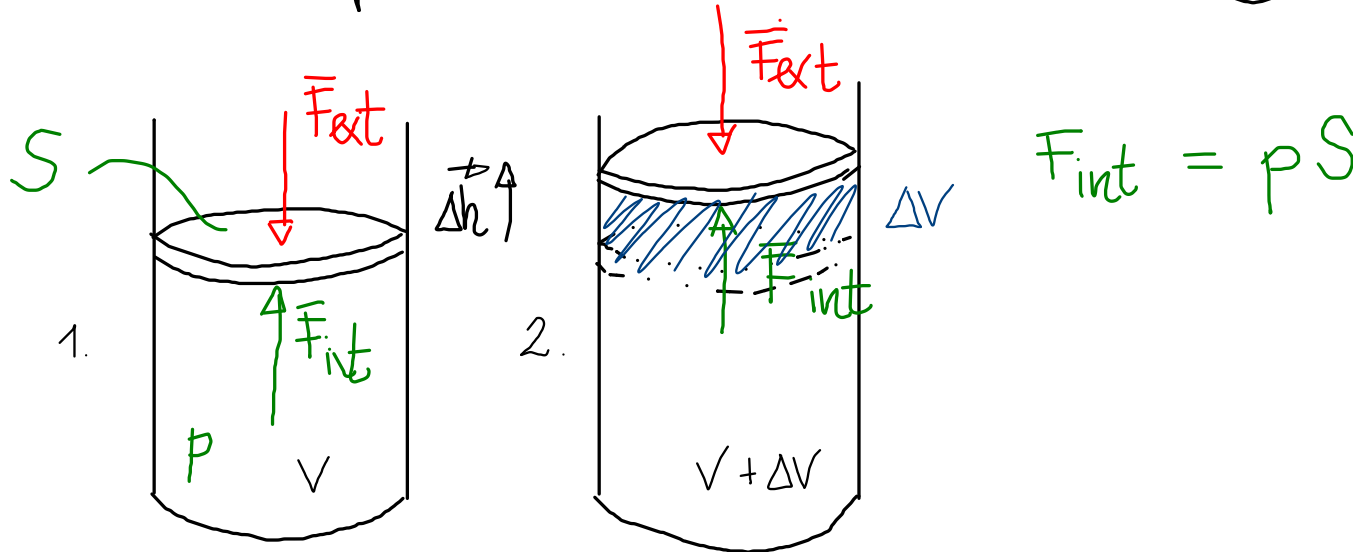
adiabatiche

senza scambio
di calore

Lavoro

A) sistema compie lavoro contro F esterne \ominus

B) F esterne compiono lavoro sul sistema \oplus



$$\begin{aligned} \mathcal{L} &= \vec{F}_{ext} \cdot \Delta \vec{h} = |\vec{F}_{ext}| |\Delta \vec{h}| \cos \pi = - |\vec{F}_{ext}| |\Delta \vec{h}| \\ &\stackrel{!}{=} - pS |\Delta \vec{h}| = - p \Delta V \end{aligned}$$

Se p non è costante

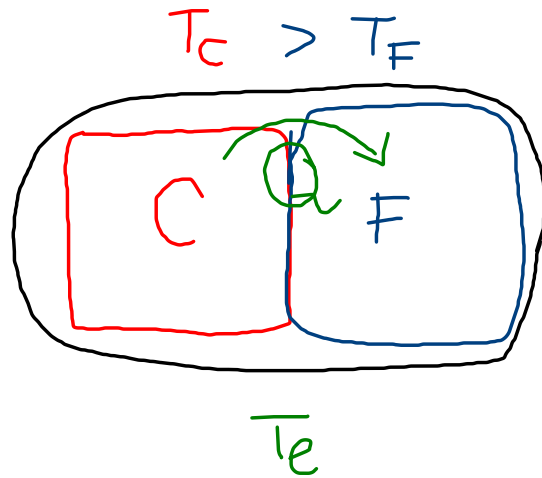
$$d\mathcal{L} = -p dV$$

(trasf. infinitesima)
 $V \rightarrow V + dV$

In generale $1 \rightarrow 2$ con p variabile

$$\mathcal{L} = - \int_1^2 p dV = - \int_{V_1}^{V_2} p dV$$

Temperatura e Calore



Q calore
 $1 \text{ cal} = 4,186 \text{ J}$
 $1 \text{ Kcal} = 4186 \text{ J}$
equilibrio tecnico

PRINCIPIO ZERO

A in eq. con C
e
B in eq. con C } A in eq. con B

I PRINCIPIO DELLA TERMODINAMICA

Per tutte le trasformazioni $1 \rightarrow 2$

$$Q + \mathcal{L} = \text{cost}$$

\swarrow \downarrow
+ ceduto al sist. + sul sistema
- ceduto dal sist. - dal sistema

\exists funzione di stato E_{int} tale che

$$Q + \mathcal{L} = \Delta E_{\text{int}} = E_{\text{int}2} - E_{\text{int}1}$$

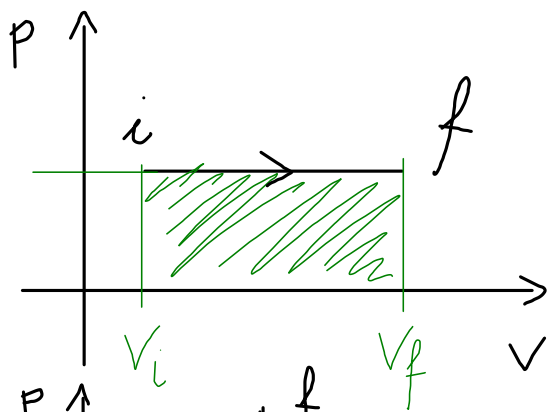
I principio della Termodinamica

$$dQ + dL = dE_{int}$$

↑
differenziale esatto

$$\Delta E_{int} = \int_1^2 dE_{int}$$

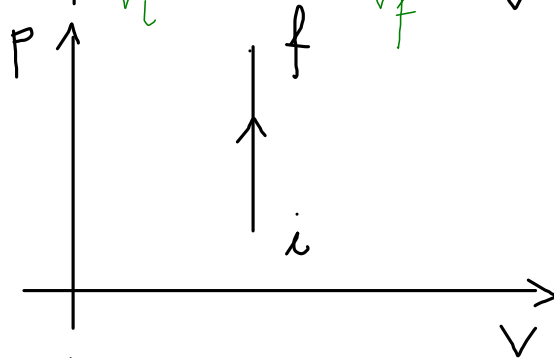
→ isobara



$$L = -p \Delta V$$

$$\Delta E_{\text{int}} = Q + L$$
$$= Q - p \Delta V$$

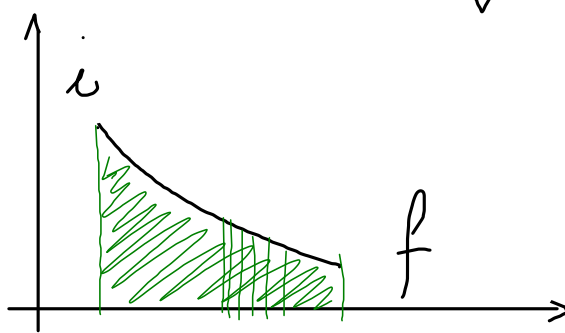
→ isocora



$$L = 0$$

$$\Delta E_{\text{int}} = Q$$

→ isoterma
 $T = \text{const}$
 \Downarrow
 $E_{\text{int}} = \text{const}$

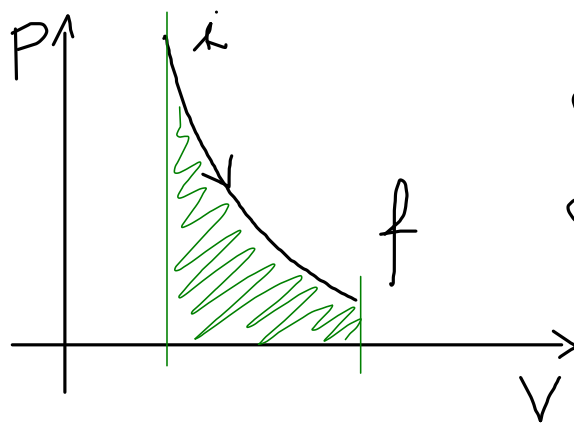


$$Q + L = 0$$

$$Q = -L$$

$$L = - \int_i^f p dV$$

→ (isentroponica)
 → adiabatica
 $Q = 0$
 $pV^\gamma = \text{const}$
 γ ---
 (a torneremo)



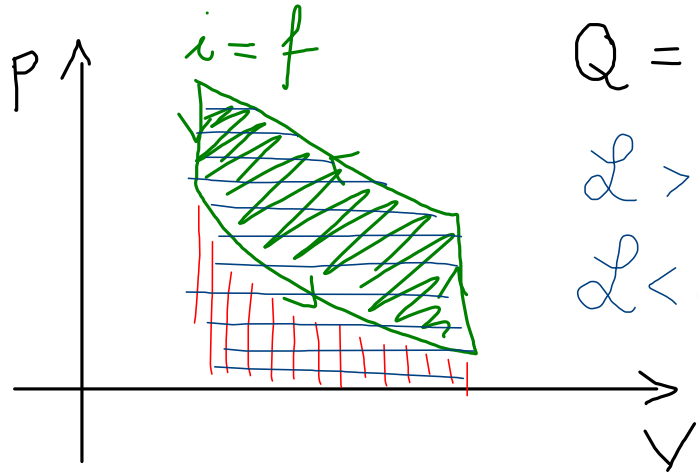
$$Q = \Delta E_{\text{int}}$$

$$Q = - \int_i^f p dV$$

→ cicliche

$$\Delta E_{\text{int}} = 0$$

$$E_{\text{int}f} - E_{\text{int}i} = 0$$



$$Q = -L$$

$$L > 0 \quad \curvearrowright$$

$$L < 0 \quad \curvearrowleft$$

CAPACITÀ TERMICA C_T

$$Q = C_T (T_2 - T_1)$$

CALORE SPECIFICO C

$$Q = C \cdot m \cdot (T_2 - T_1)$$

$$C_T = C \cdot m$$

$$C = \frac{Q}{m (T_2 - T_1)}$$

$$C_{H_2O} = \frac{1 \text{ cal}}{\text{g} \cdot \text{K}}$$

CALORE SPECIFICO MOLARE C_m

$$C_m = C \cdot PM$$

solidi $C_m = \frac{6 \text{ cal}}{\text{mol} \cdot \text{K}}$

$$C_m = \frac{Q}{m (T_2 - T_1)} = C \frac{m}{n}$$

$$C_{mH_2O} = \frac{18 \text{ cal}}{\text{mol} \cdot \text{K}}$$

CALORE SPECIFICO MOLARE GAS PERFETTI

C_p

C_v

$$C_p > C_v$$

$$C_p - C_v = R$$

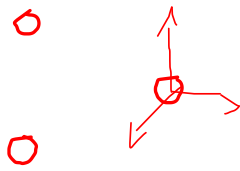
$$R = 8,314 \frac{\text{J}}{\text{mol K}}$$

	C_v	C_p
mono	$\frac{3}{2} R$	$\frac{5}{2} R$
bi	$\frac{5}{2} R$	$\frac{7}{2} R$
tri	$3 R$	$4 R$

$$Q = n c_v \Delta T \quad V \text{ cost}$$

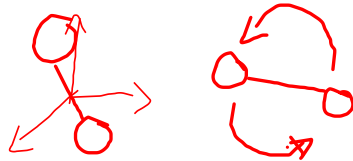
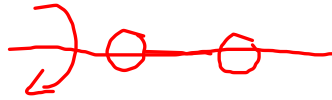
$$Q = n c_p \Delta T \quad p \text{ cost}$$

monoatomic



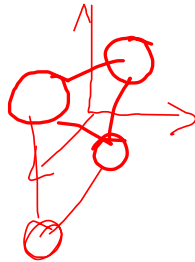
$$3 \rightarrow \frac{3}{2} \text{CV}$$

biatomic

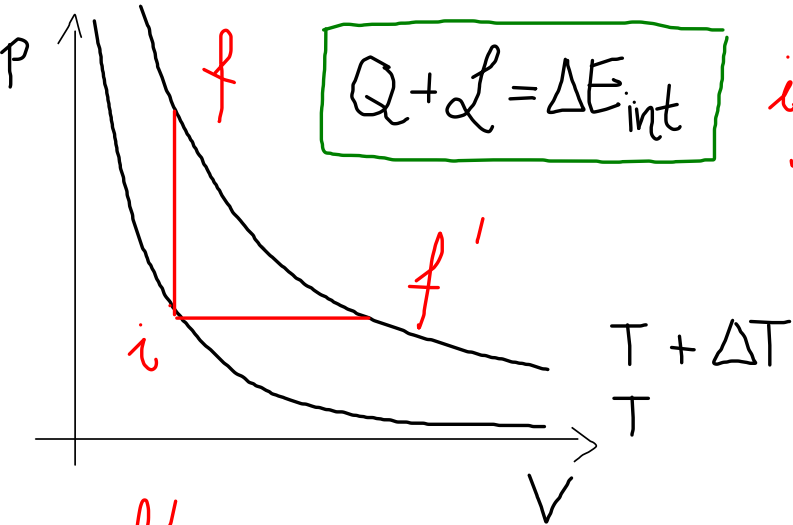


$$3 + 2 \rightarrow \frac{5}{2}$$

polyatomic



$$3 + 3 \rightarrow \frac{6}{2} = 3$$



$$Q + Q' = \Delta E_{int}$$

if

$$Q = n c_v \Delta T$$

$$Q' = 0$$

$$\Delta E_{int} = n c_v \Delta T$$

$$E_{int} = n c_v T$$

if'

$$Q = n c_p \Delta T$$

$$Q - p \Delta V = \Delta E_{int}$$

$$pV = nRT$$

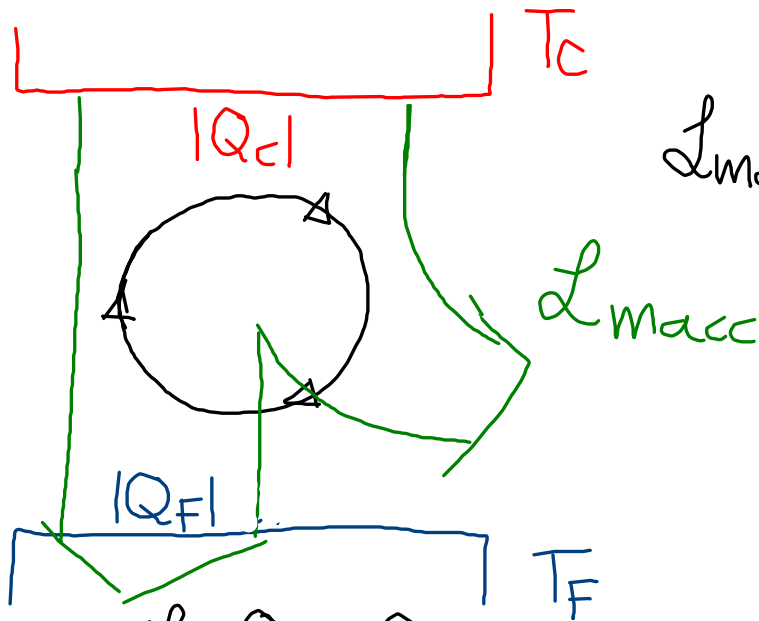
$$p \Delta V = nR \Delta T$$

$$\cancel{n c_p \Delta T} - \cancel{nR \Delta T} = n c_v \Delta T$$

$$c_p - R = c_v$$

$$c_p = c_v + R$$

MACHINE TERMICHE



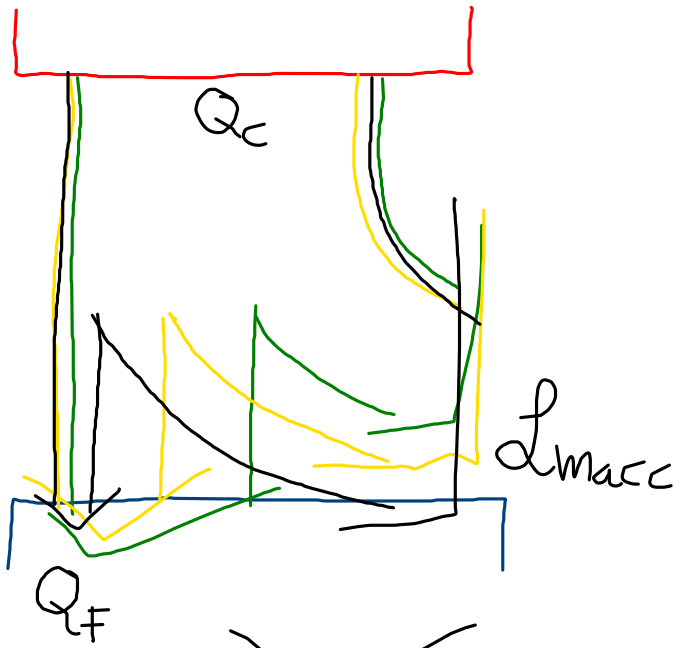
$$L_{\text{macc}} = -L$$

$$\eta = \frac{L_{\text{macc}}}{|Q_C|} = \frac{|Q_C| - |Q_F|}{|Q_C|} = 1 - \frac{|Q_F|}{|Q_C|}$$

$$L + Q = 0$$

$$L + |Q_C| - |Q_F| = 0$$

$$|Q_C| - |Q_F| = -L = L_{\text{macc}} > 0$$

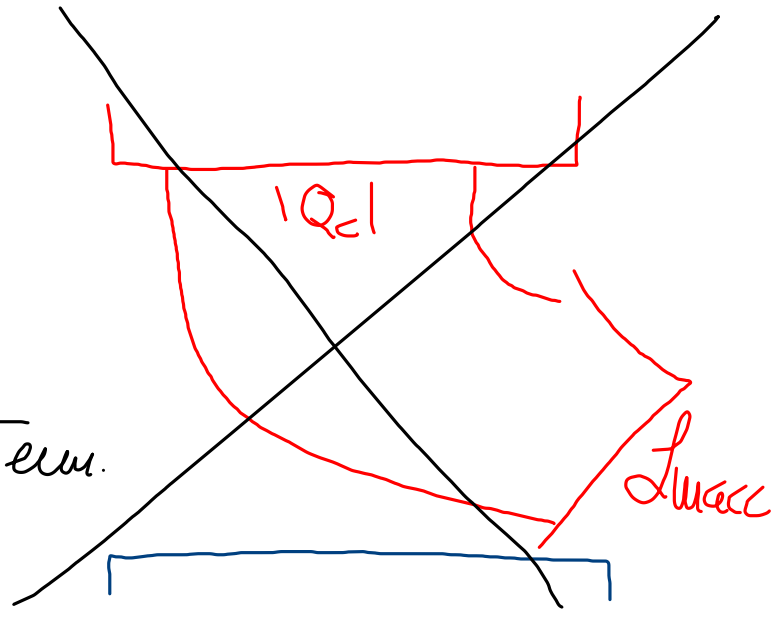


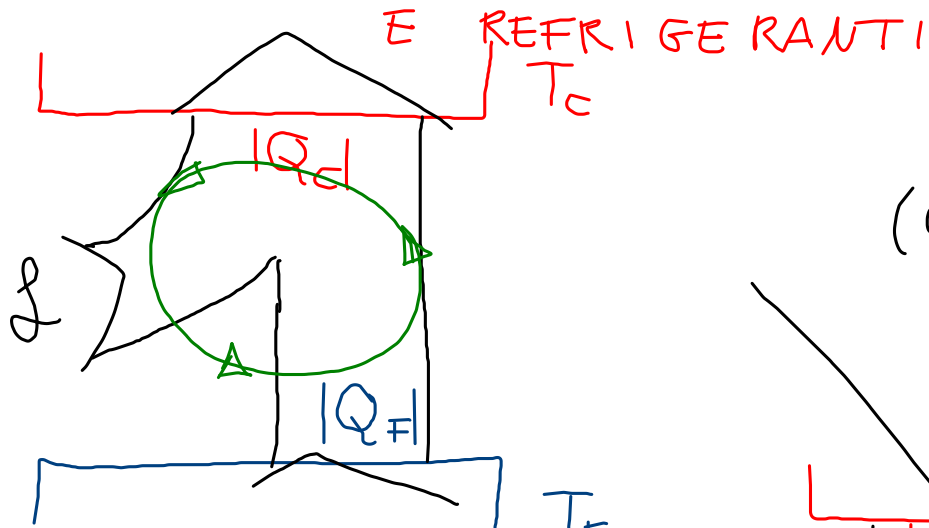
$$\eta < \eta < \eta$$

~~$$\eta = 1$$~~

II principio della
(Kelvin - Planck)

Term.

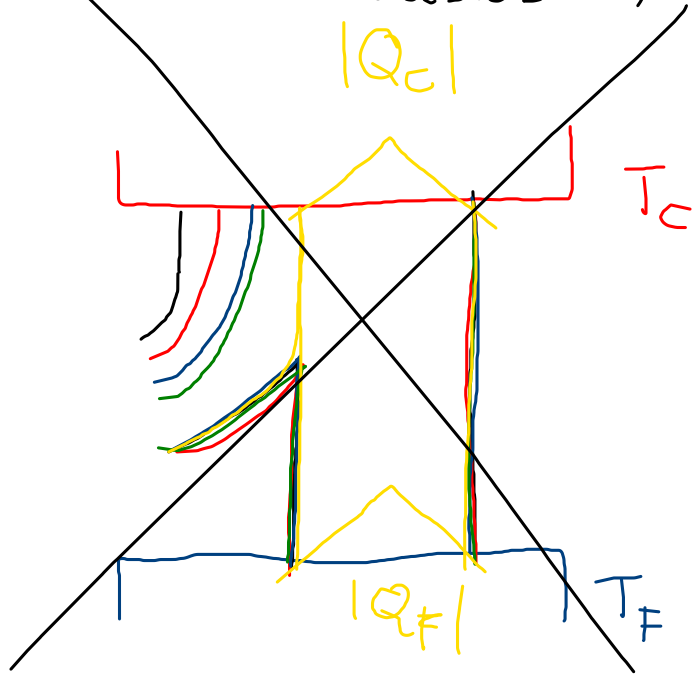




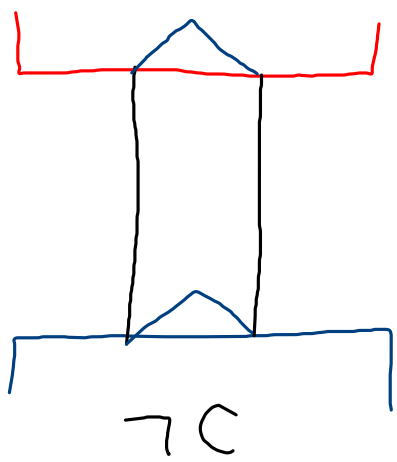
$$|Q_F| - |Q_c| = -\mathcal{L}$$

$$\mathcal{L} = |Q_c| - |Q_F| > 0$$

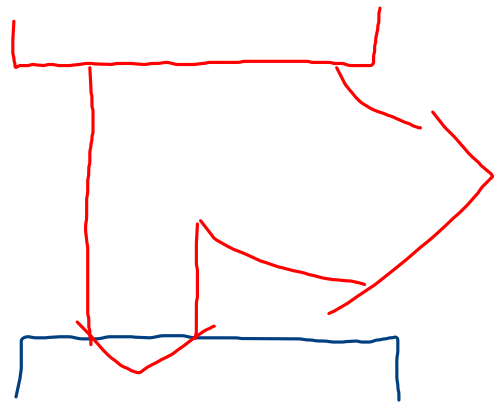
Il principio
(enunciato di)
Clausius



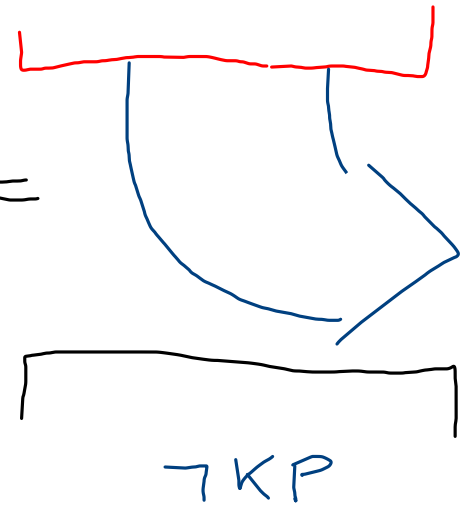
$KP \Rightarrow C$
 $\neg C \Rightarrow \neg KP$



+



=



$\neg KP \Rightarrow \neg C$

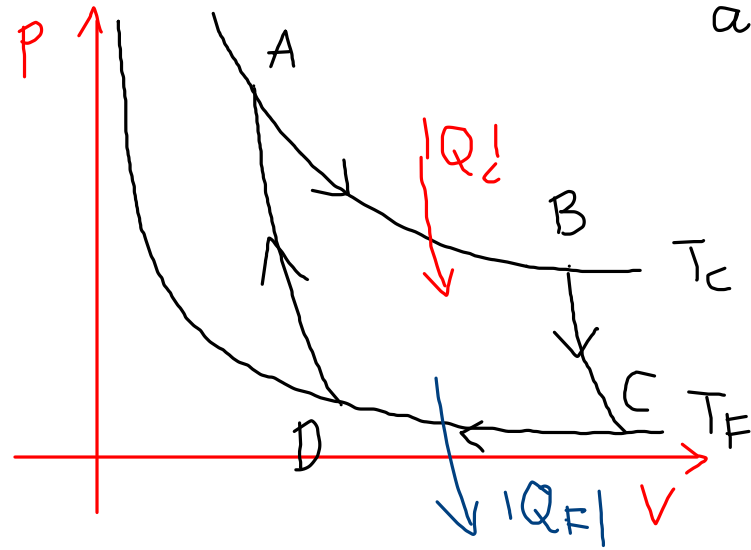
CICLO DI CARNOT

adiabatica $pV^\gamma = \text{cost}$

$$\gamma > 1$$

$$\gamma = \frac{C_p}{C_v}$$

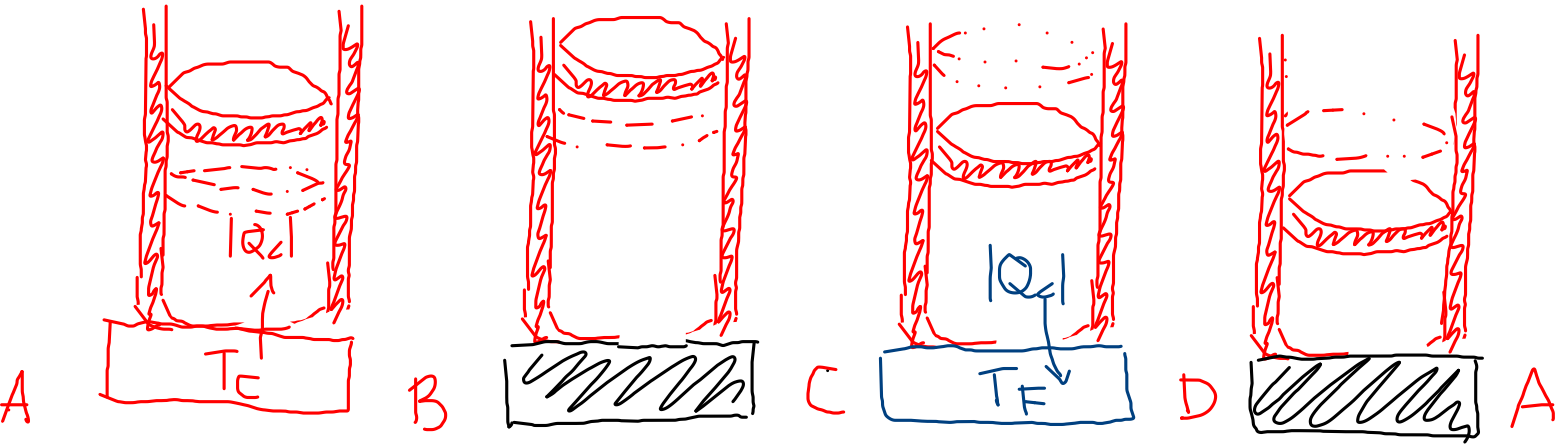
$$L < 0 \Rightarrow L_{\text{max}} > 0$$



2 isoterme, 2 adiabatiche, tutte reversibili

$$\eta = \frac{|Q_C| - |Q_F|}{|Q_C|} = 1 - \frac{|Q_F|}{|Q_C|} = 1 - \frac{T_F}{T_C}$$

Teorema di Carnot $\frac{|Q_F|}{|Q_C|} = \frac{T_F}{T_C}$

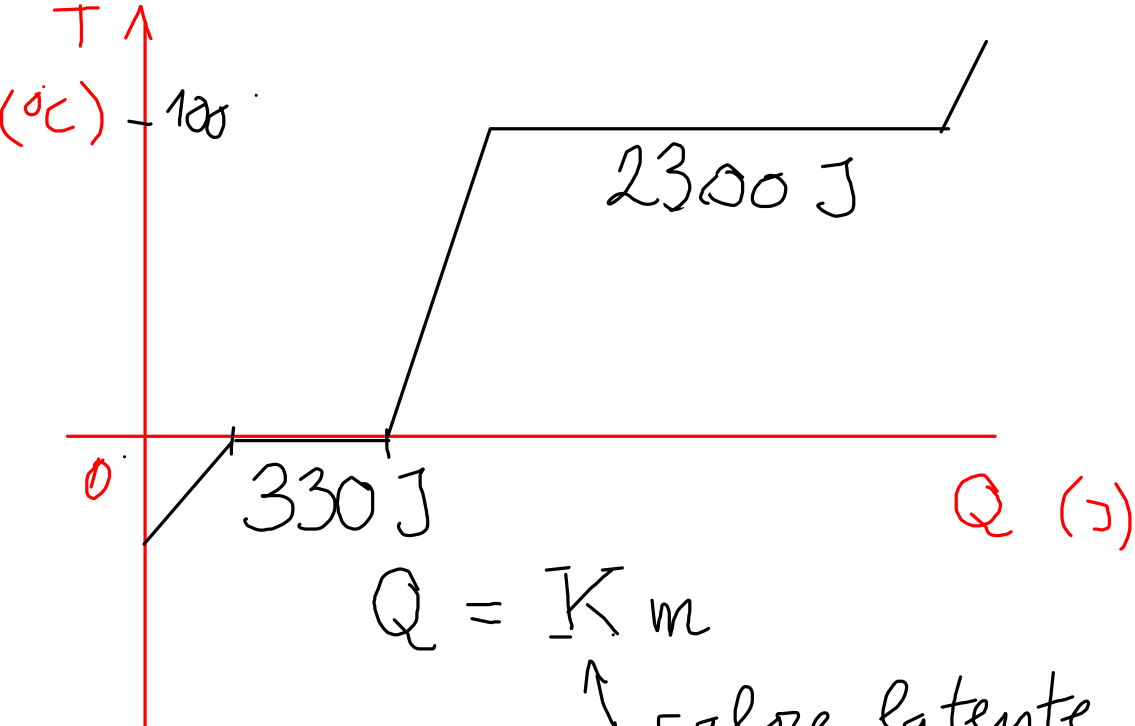


$$\eta = 1 - \frac{T_F}{T_C}$$

$$T_F > 0 \Rightarrow \eta < 1$$

Teorema di
Nernst

TRASFORMAZIONI DI FASE



1 g H_2O

$$Q = \underline{K} m$$

↑ calore latente
fusione

vaporizzazione

ENTROPIA

Isoterma Reversibile

$$S_2 - S_1 = \Delta S = \left(\frac{Q}{T} \right)_{\text{rev}}$$

disuguaglianza
di Clausius

$$\left(\frac{Q}{T} \right)_{\text{irr}} < \left(\frac{Q}{T} \right)_{\text{rev}} = \Delta S$$

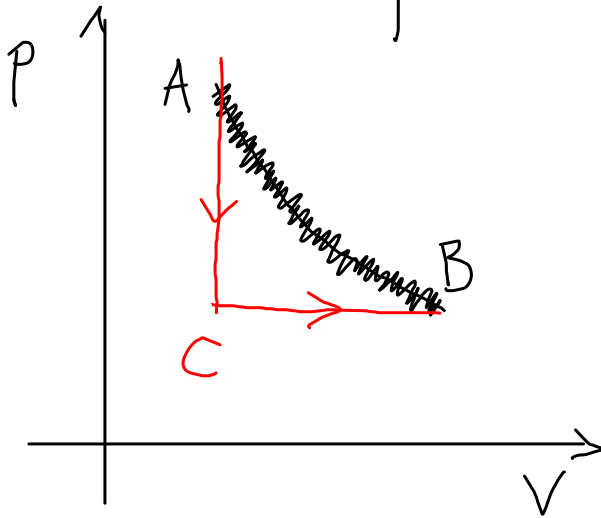
Trasformazione Reversibile Infinitesima

$$dS = \left(\frac{dQ}{T} \right)_{\text{rev}}$$

Trasformazione Arbitraria Reversibile

$$\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{\text{rev}}$$

→ E per una trasformazione NON reversibile?



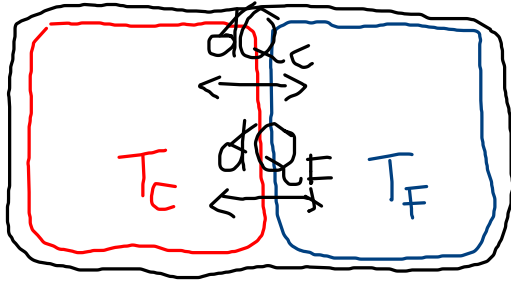
ΔS calcolata
sulle tr.
reversibili

è la stessa

ΔS della trasf.
irreversibile

ENUNCIATO ALTERNATIVO II PRINCIPIO

$$\Delta S \geq 0$$



$$dQ_C + dQ_F = 0$$

$$dQ_F = -dQ_C$$

$$dS_C = \frac{dQ_C}{T_C}$$

$$dS_F = \frac{dQ_F}{T_F}$$

$$dS = dS_C + dS_F = \frac{dQ_C}{T_C} + \frac{dQ_F}{T_F}$$

$$= \frac{dQ_C}{T_C} - \frac{dQ_C}{T_F} = dQ_C \underbrace{\left(\frac{1}{T_C} - \frac{1}{T_F} \right)}_{< 0} > 0$$

$$\Rightarrow dQ_C < 0$$

ENTALPIA

$$H = E_{int} + pV$$

p costante

$$\begin{aligned}\Delta H &= \Delta E_{int} + p \Delta V \\ &\stackrel{!}{=} Q - \cancel{p \Delta V} + p \Delta V\end{aligned}$$

$$\begin{aligned}\Delta E_{int} &= Q + L \\ &\stackrel{!}{=} Q - p \Delta V\end{aligned}$$

$\Delta H < 0$ esotermiche

$\Delta H > 0$ endotermiche

$$\Delta H = \Delta E_{int} + p \Delta V$$

$$\Delta V \rightarrow 0$$

$$\Delta H = \Delta E_{int}$$

per trasformazioni: solta
fase gassosa

ENERGIA LIBERA DI GIBBS / DI HELMHOLTZ

$$G = H - TS$$

$$F = E_{int} - TS$$

$\Delta G \sim \Delta F$ quando $\Delta H \sim \Delta E_{int}$
(fase gas trascurabile)

sistema chiuso a p e T costanti

$$\Rightarrow \Delta G < 0$$

$\Delta G < 0$ esergonica

$\Delta G > 0$ endergonica

Riepilogo delle funzioni di stato

$E_{int} = E_{int}(V, S)$ utile V e S sono costanti

$H = E_{int} + pV = H(p, S)$ " p e S " "

$G = H - TS = G(p, T)$ " p e T " "

$F = E_{int} - TS = F(V, T)$ " V e T " "

$$S = k_B \log W$$

$$k_B = 1,38 \cdot 10^{-23} \frac{\text{J}}{\text{K}} = \frac{R}{N_A}$$



DADI

macrostato
(somma)

μstato

2
DADI

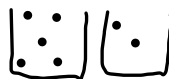
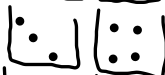
2



⋮



7



⋮



12

