

TERMODINAMICA

Teoria fisica per descrivere l'equilibrio e l'evoluzione di corpi macroscopici $\rightarrow N \approx N_A$

\rightarrow scambi energetici

> 1750: I rivoluzione industriale

> 1850: Joule calore: forma di lavoro
Clausius \rightarrow entropia

II rivoluzione industriale

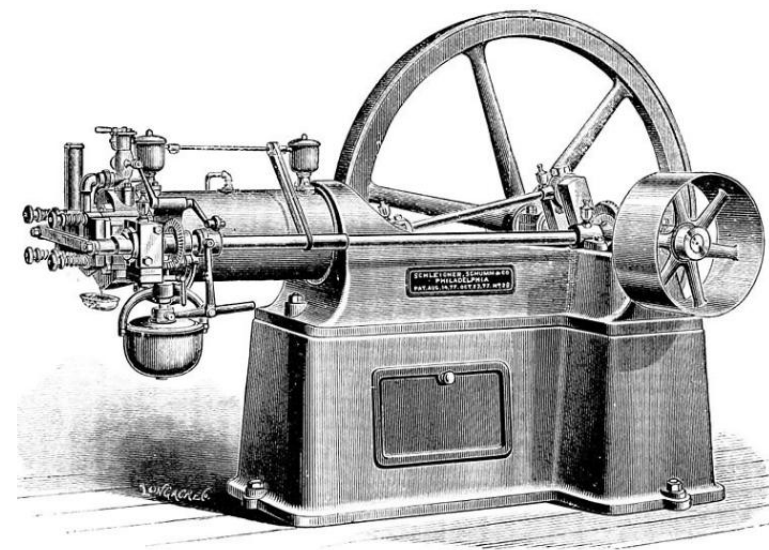
Interpretazione micro di T, S
(Maxwell, Boltzmann)

> 1900 \rightarrow fisica statistica
transizioni di fase
non-equilibrio

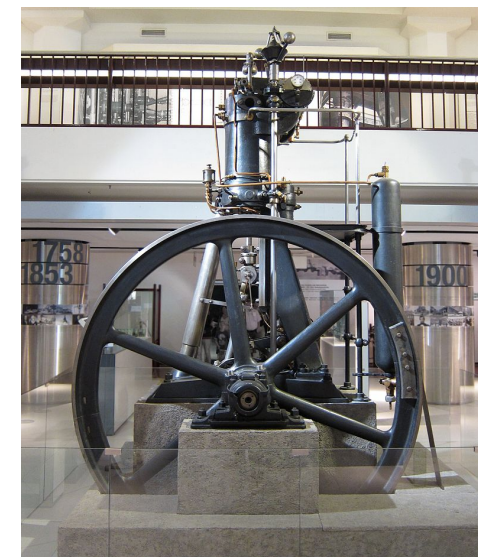
\sim 2000 termodinamica stocastica
quantistica



Macchina a vapore, Watt \sim 1770

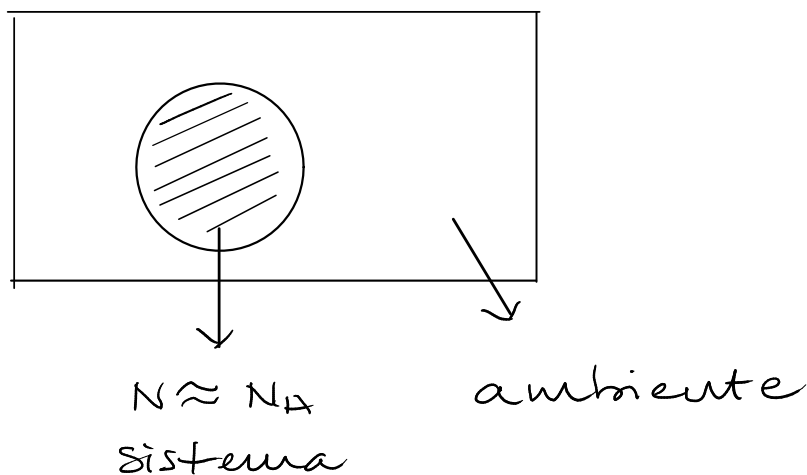


Motore Otto \sim 1880



Motore Diesel 1896

Stato di un sistema macroscopico



	scambio particelle	scambio energia
ISOLATO	$\Delta N = 0$	$\Delta E = 0$
CHIUSO	$\Delta N = 0$	$\Delta E \neq 0$
APERTO	$\Delta N \neq 0$	$\Delta E \neq 0$

universo = { sistema, ambiente } sempre isolato

Variabili di stato

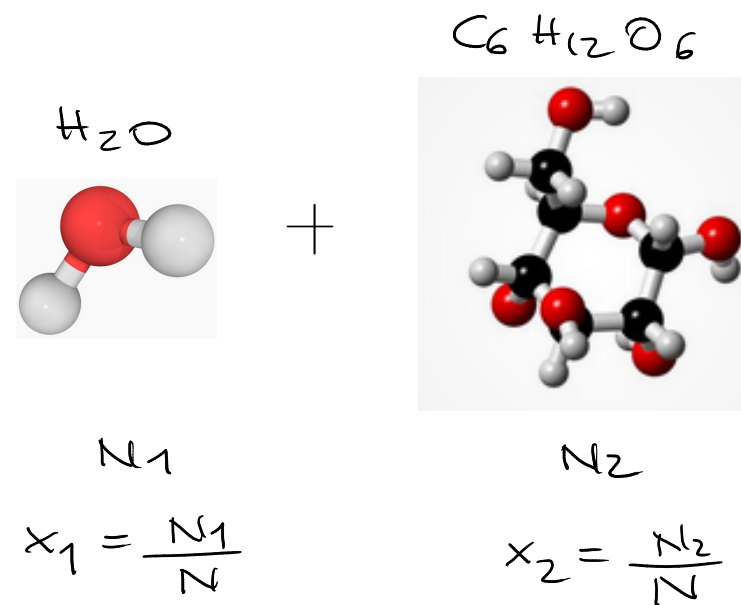
$$\{M, \vec{R}, \vec{V}\} + \{N, V, P, T\} + \{ \dots \}$$

Funzioni di stato

$$F = F(N, V, P, T, \dots)$$

↑
composizione
chimica

$$x_1, x_2 = 1 - x_1$$

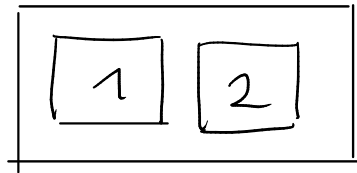


$$\left\{ \begin{array}{l} N_i \rightarrow N_f = \lambda N_i \\ V_i \rightarrow V_f = \lambda V_i \end{array} \right. \quad \lambda \in \mathbb{R} \quad X_i \rightarrow X_f = ? \quad \begin{array}{l} X_f = X_i \quad \text{INTENSIVA} \\ X_f = \lambda X_i \quad \text{ESTENSIVA} \end{array}$$

Es.: estensiva N, V, M

$$M = mN \quad M_i \rightarrow M_f = mN_f = m\lambda N_i = \lambda(mN_i) = \lambda M_i \quad \square$$

Es.: intensiva ρ, ρ_N, P, T



sistema composto
 $\{1, 2\}$

$$X_1, X_2 \quad X_{\{1,2\}} = ?$$

$$X_{\{1,2\}} = X_1 + X_2 \quad \text{ADDITIVA}$$

Es.: V, N, M, E

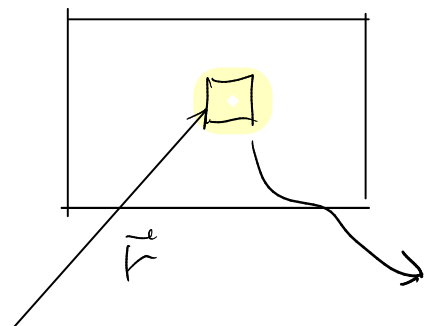
Equilibrio termodinamico

Variabili di stato hanno valori "ben definiti" indipendenti dal tempo e dallo spazio

$$\left. \begin{array}{l} \boxed{1} \mid \boxed{2} \\ \text{chiusi} \\ V_1 \neq V_2 \end{array} \right\} \begin{array}{l} T_1 = T_2 \quad \text{eq. termico} \\ P_1 = P_2 \quad \text{eq. meccanico} \end{array} \left. \vphantom{\begin{array}{l} \boxed{1} \mid \boxed{2} \\ \text{chiusi} \\ V_1 \neq V_2 \end{array}} \right\} \{1,2\} \text{ è in equilibrio}$$

→ equilibrio locale

Equilibrio locale: in ogni punto \vec{r} sistema esiste un sottosistema macroscopico che si trova in equilibrio termodinamico nell'intervallo di tempo tra t e $t + dt$

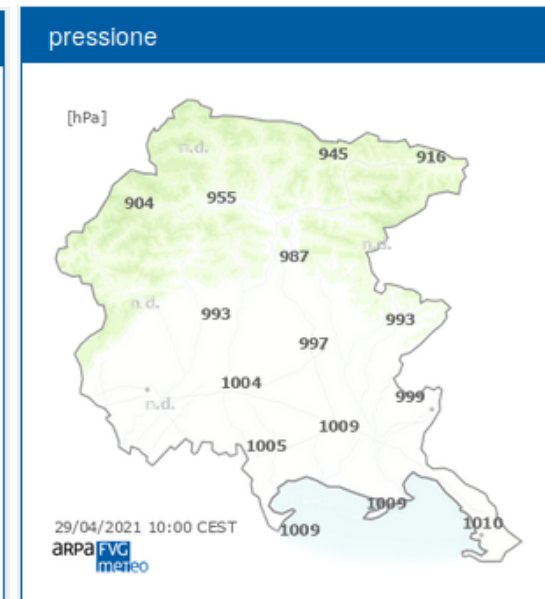
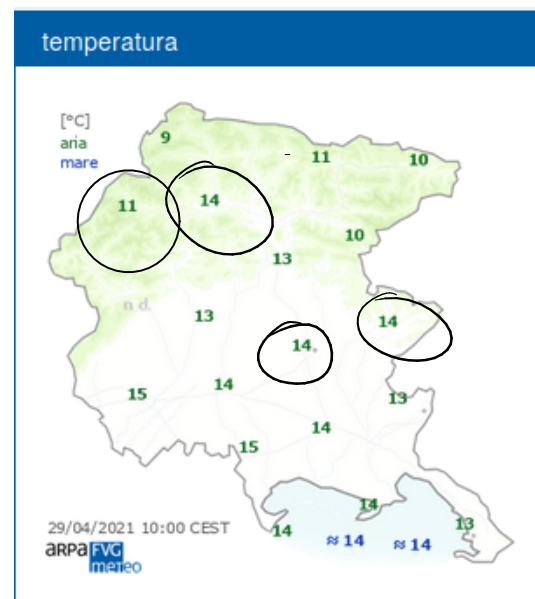
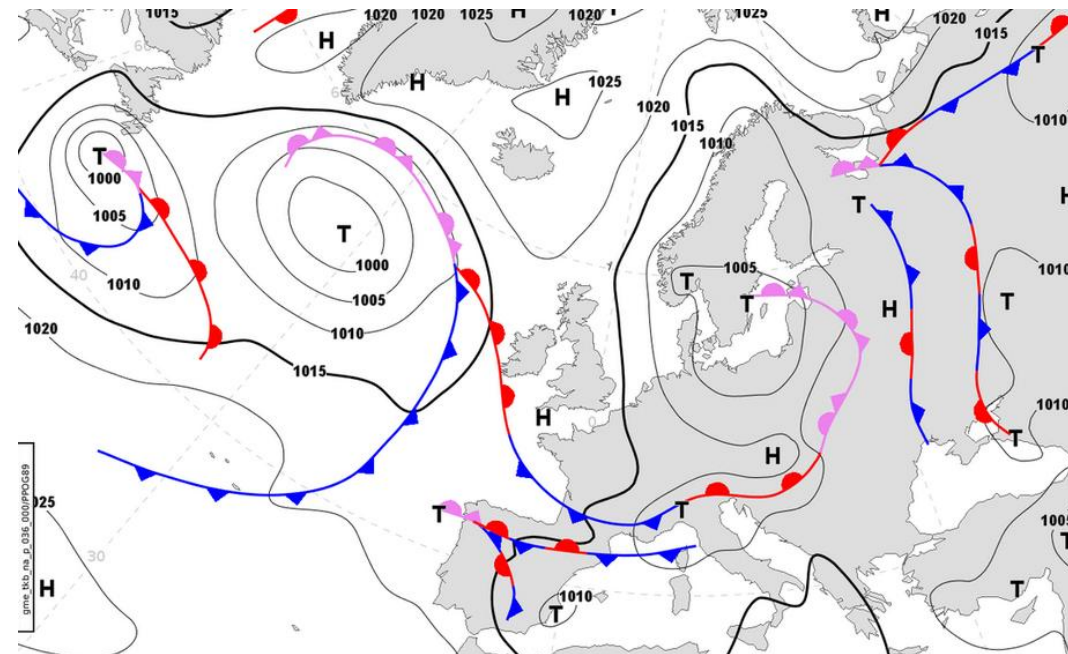


campi
 $T(\vec{r}, t)$
 $P(\vec{r}, t)$

ES.: → stazionario

$$P(z) = P(0) + \rho g z$$

$$P(z) = P(0) \exp\left(-\frac{z}{l}\right)$$



Trasformazioni termodinamiche

Trasformazione: cambiamento dello stato da i a f

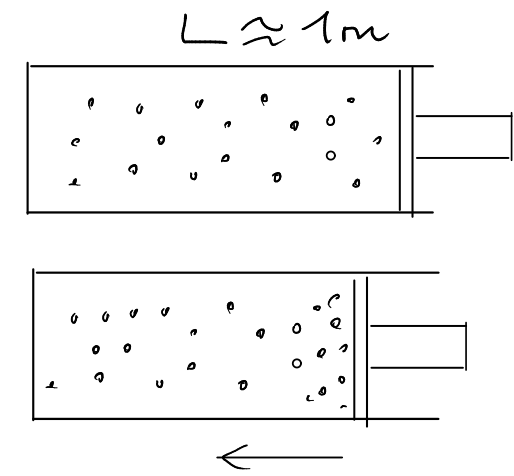
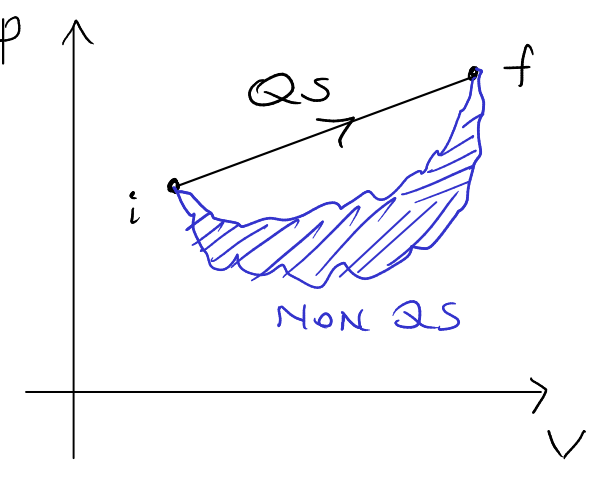
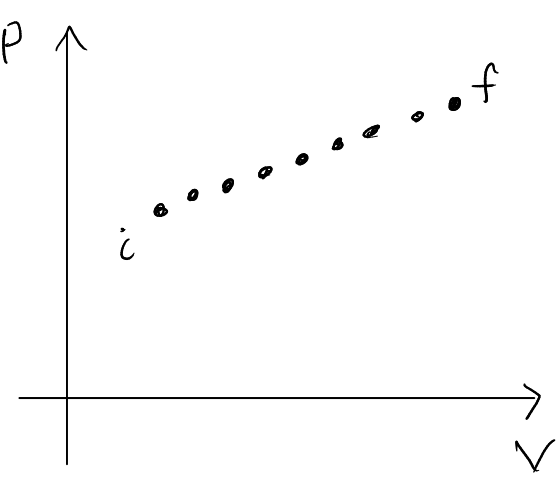
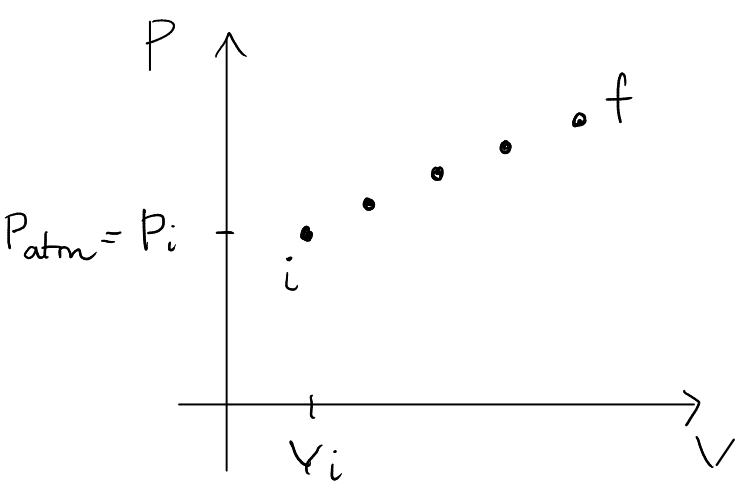
dP, dT, dV

Trasformazione elementare: tale che i e f sono "infinitamente" vicini

Casi particolari

- $T = \text{cost}$ ($dT = 0$) : ISOTERMA
- $P = \text{cost}$ ($dP = 0$) : ISOBARA
- $V = \text{cost}$ ($dV = 0$) : ISOCORA
- $i = f$: CICLO

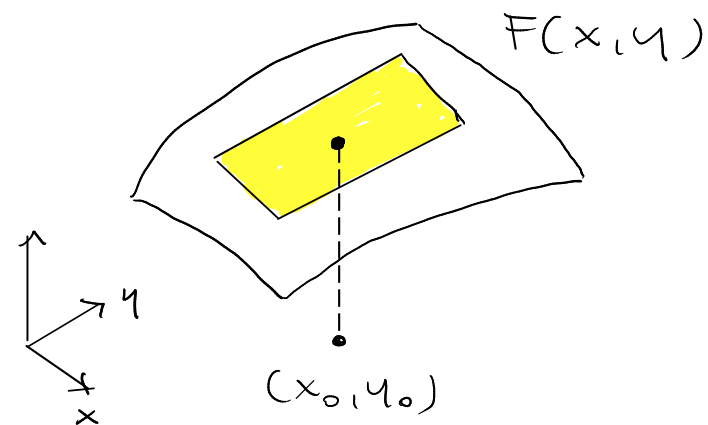
Trasformazione quasi-statica: successione di stati di equilibrio di sistema



ES:
 $L \approx c \tau$
 $\tau \approx \frac{L}{c}$
 $\approx \frac{1 \text{ m}}{300 \text{ m/s}}$
 $\approx 3 \times 10^{-3} \text{ s}$

Forme differenziali

$$F(x, y) \in \mathcal{C}^2$$



Sviluppo di Taylor al primo ordine attorno a (x_0, y_0)

$$F(x, y) = F(x_0, y_0) + \underbrace{\frac{\partial F}{\partial x}(x_0, y_0)}_{\frac{\partial F}{\partial x} \Big|_y} (x - x_0) + \underbrace{\frac{\partial F}{\partial y}(x_0, y_0)}_{\frac{\partial F}{\partial y} \Big|_x} (y - y_0) + \dots$$

$$dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy \quad (\text{differenziale totale})$$

Forma differenziale

$$\delta F = A_x(x, y) dx + A_y(x, y) dy$$

Forma differenziale esatta se $F \in \mathcal{C}^2$ tale che

$$\frac{\partial F}{\partial x} = A_x \quad \frac{\partial F}{\partial y} = A_y$$

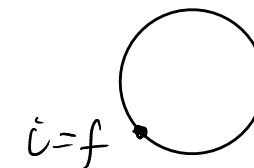
Proprietà:

$$- \frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x}$$

teor. di Schwartz

$$- dF \text{ è esatta} \Leftrightarrow \int_i^f dF \text{ non dipende dal percorso} \Leftrightarrow \oint dF = 0$$

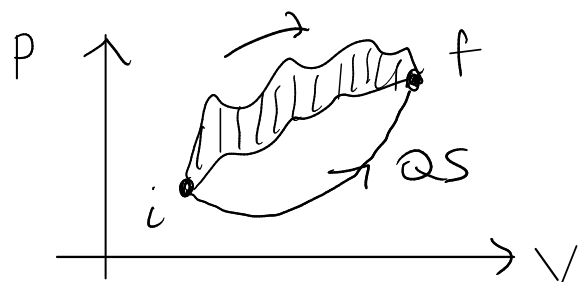
$$\delta W = \vec{F} \cdot d\vec{\ell}$$
$$dE_p = -\delta W$$



Applicazione in termodinamica

Variabili di stato \rightarrow differenziali esatti

$$\Delta F = F_f - F_i = \int_i^f dF \text{ non dipende dal percorso} \Rightarrow dF \text{ è esatto}$$



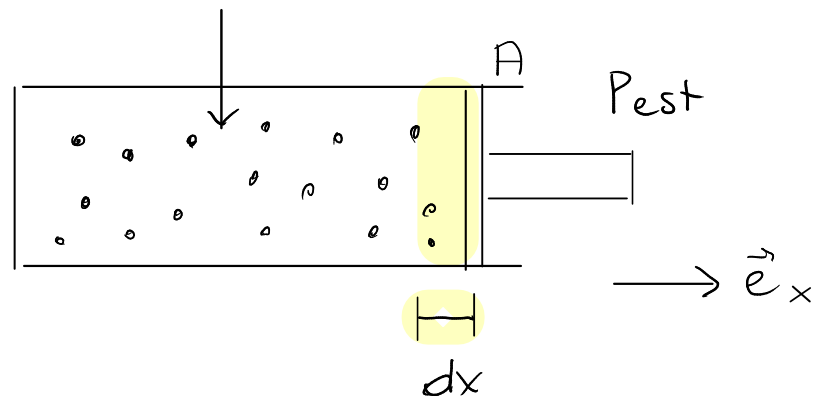
Grandezze che dipendono dalla trasformazione

$$- \delta W \rightarrow W \text{ lavoro meccanico}$$

$$- \delta Q \rightarrow Q \text{ calore}$$

Lavoro meccanico

Sistema comprimibile



Lavoro scambiato dal sistema con l'ambiente

$$\delta W = \underbrace{-P_{est} A}_{\text{forza esterna}} \cdot \underbrace{dx}_{\text{spostamento}} \vec{e}_x = -P_{est} dV = -\delta W_{est}$$

compressione : $dV < 0 \Rightarrow \delta W > 0$

espansione : $dV > 0 \Rightarrow \delta W < 0$

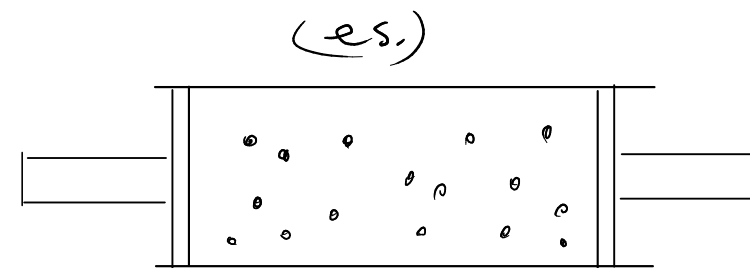
} scambio + se aumenta l'energia del sistema

Trasformazione da i a f

$$W = \int_i^f \delta W = - \int_i^f P_{est} dV$$

Trasformazione QS da i a $f \Rightarrow P = P_{est}$

$$W = - \int_i^f P dV$$



Esempi:

- **isocora**: $V = \text{cost} \Rightarrow dV = 0 \Rightarrow \delta W = 0 \Rightarrow W = 0$

- **isobara + QS**: $V_i \rightarrow V_f$

$$W = \int_i^f \delta W = \underset{QS}{\uparrow} - \int_{V_i}^{V_f} P dV = -P(V_f - V_i) = -P \Delta V$$

- **$P_{\text{est}} = \text{cost}$** :

$$W = - \int_{V_i}^{V_f} P_{\text{est}} dV = -P_{\text{est}} \Delta V$$

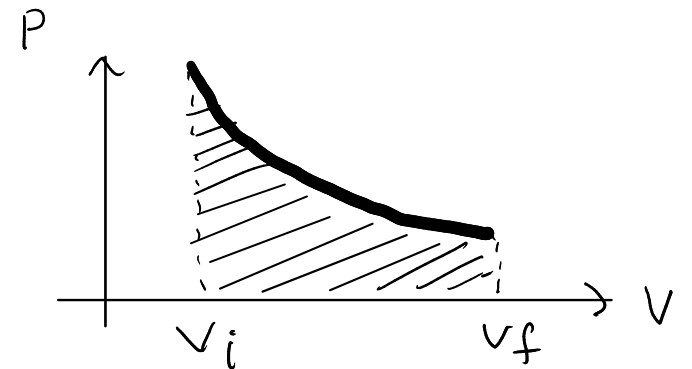
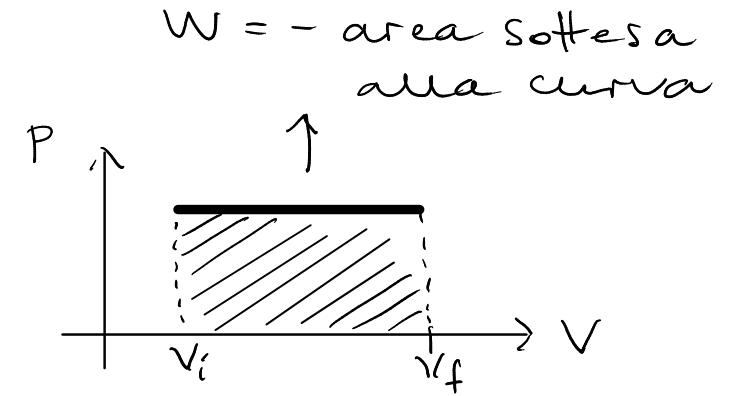
- **isoterma, gas perfetto, $V_i \rightarrow V_f$, $n = \text{cost}$, QS**

$$W = \int_i^f \delta W = - \int_{V_i}^{V_f} P dV = - \int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

$$= -nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$V_f > V_i \Rightarrow W < 0$$

$$V_f < V_i \Rightarrow W > 0$$



PRIMO PRINCIPIO DELLA TERMODINAMICA

Scambi energetici



→ lavoro meccanico

→ calore

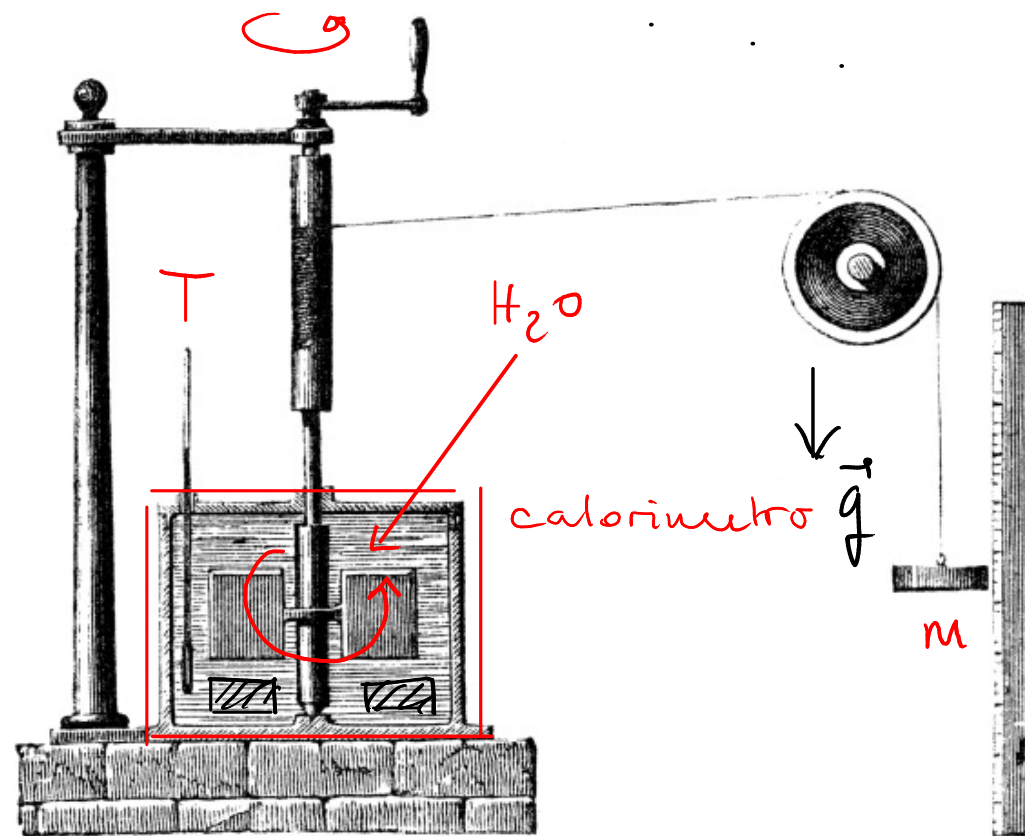
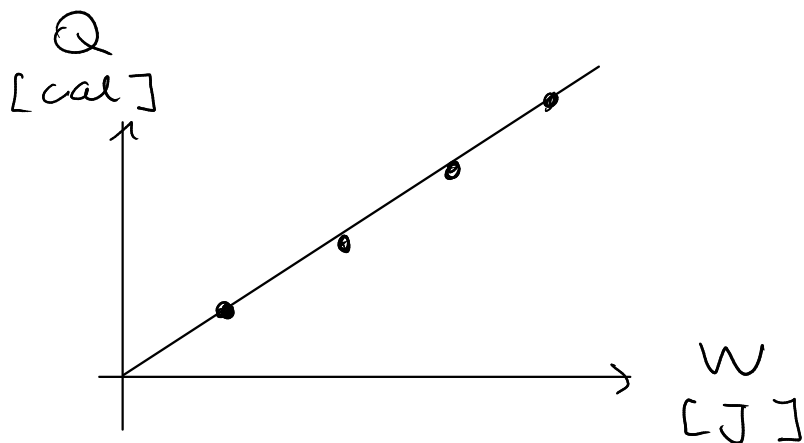
$$Q \sim \Delta T$$

1 caloria: variazione $\Delta T = 1^\circ\text{C}$
di 1g H_2O da $T = 14,5^\circ\text{C}$ a
 $T = 15,5^\circ\text{C}$ a P_{atm}

$$Q \sim W \quad W = c Q$$

$$c = 4,18 \frac{\text{J}}{\text{cal}}$$

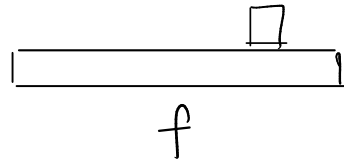
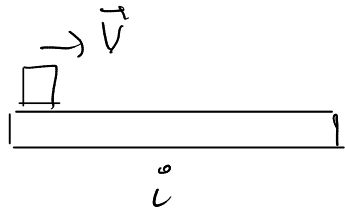
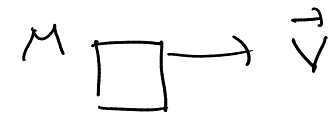
$$1 \text{ cal} = 4,18 \text{ J}$$



Esperimento di Joule 1843

Equivalenza meccanica del calore

Conservazione dell'energia in un sistema isolato



In termodinamica, postuliamo l'esistenza di una nuova variabile di stato $\Rightarrow E = \text{cost}$

I principio: ogni sistema macroscopico è caratterizzata da una variabile di stato, U , detta energia interna, additiva ed estensiva tale che

$$dE_c + dU = 0$$

se il sistema è isolato,

$$d(E_c + U) = 0$$

$$E_c + U = \text{cost}$$

Motto: energia dell'universo è costante

$$\vec{V} = \vec{0} \text{ immobile} \Rightarrow dU = 0$$

isolato

Trasf. da i a f

$$\Delta E_c + \Delta U = 0 \text{ isolato}$$

$$\Delta U = 0 \text{ isolato } \vec{V} = \vec{0}$$

Sistema non isolato: $\delta W, dU \rightarrow \delta Q$

Calore è definito come $(\vec{V} = \vec{0})$

$$\delta Q = dU - \delta W$$

$$\delta Q + \delta W = dU \quad \text{I pr.}$$

↑ ↑ ↑
calore lavoro energia
 mecc. interna

Trasf. da i a f

$$Q + W = \Delta U$$

\vec{V} variabile

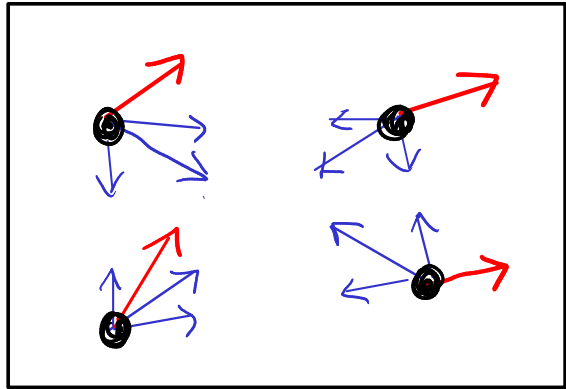
$$\delta Q = dU + dE_c - \delta W$$

$$\delta Q + \delta W = dU + dE_c$$

$$Q + W = \Delta U + \Delta E_c$$

Interpretazione microscopica di energia interna e calore

forze interne \vec{F}_{int}



forze esterne
↓
ambiente
 \vec{F}_{est}

M $\vec{V} \rightarrow$

Teor. dell'energia cinetica

$$\begin{aligned} \Delta E_c^{tot} &= W[\Sigma \vec{F}] \\ &\swarrow \quad \searrow \\ \Delta E_c + \Delta E_c^{(m)} &= W[\Sigma \vec{F}_{int}] + W[\Sigma \vec{F}_{est}] \\ \downarrow \quad \downarrow &\quad \downarrow \\ E_c = \frac{1}{2} M |\vec{V}|^2 \quad E_c^{(m)} = \sum_{i=1}^N \frac{1}{2} m_i |\vec{v}_i|^2 &\quad - \Delta E_p \end{aligned}$$

$$\Delta E_c + \Delta E_c^{(m)} + \Delta E_p^{(m)} = W[\Sigma \vec{F}_{est}]$$

Sistema isolato: $\Sigma \vec{F}_{est} = \vec{0}$

$$\Delta E_c + \Delta E_c^{(m)} + \Delta E_p^{(m)} = 0$$

$$\Delta E_c + \underbrace{\Delta(E_c^{(m)} + E_p^{(m)})}_U = 0$$

$$U = E_c^{(m)} + E_p^{(m)}$$

$$\Delta E_c + \Delta U = 0$$

energia interna:

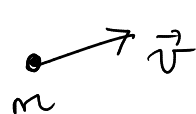
somma di energie cinetica e potenziali microscopiche

Energia interna

Teorema di equipartizione dell'energia

In un sistema macroscopico all'equilibrio a temperatura T , ogni termine di energia elementare e quadratico dà un contributo pari a $\frac{1}{2} k_B T$ all'energia interna U

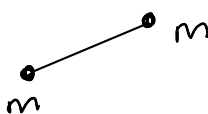
1) Gas perfetto



$$E = E_c + E_p = \frac{1}{2} m |\vec{v}|^2 = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 \rightarrow$$

3 termini di energia cinetica di traslazione

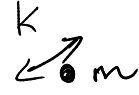
$$U = N \cdot 3 \cdot \frac{1}{2} k_B T = \frac{3}{2} N k_B T = \frac{3}{2} n R T \quad (\text{monoatomici})$$



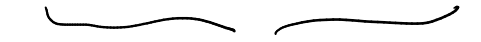
$$E = E_c = \left. \begin{array}{l} 3 \text{ termini di energia cinetica di traslazione} \\ + \\ 2 \text{ termini di energia cinetica di rotazione} \end{array} \right\} U \sim T$$

$$U = N \cdot 5 \cdot \frac{1}{2} k_B T = \frac{5}{2} N k_B T = \frac{5}{2} n R T \quad (\text{biatomici}) \quad \text{es. } H_2$$

2) Solido armonico



$$E = E_c + E_p = \frac{1}{2}mv_x^2 + \frac{1}{2}kx^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}ky^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}kz^2$$



3 termini di
energia cinetica
di **traslazione**



3 termini di
energia potenziale
elastica

$$U = N \cdot 6 \cdot \frac{1}{2}k_B T = 3Nk_B T = 3nRT$$

$$U \sim T$$

Calore

Volume costante

$$\delta Q = c_v dT$$

↑
capacità termica
a volume costante

$$\text{SI: } \frac{\text{J}}{\text{K}}$$

$$\delta Q = m c_v dT$$

↑
capacità termica
a volume cost
per unità di massa

$$\text{SI: } \frac{\text{J}}{\text{K} \cdot \text{kg}}$$

$$\delta Q = dU - \delta W$$

$$\delta Q \sim dT$$

$$\delta Q = n c_v^{(n)} dT$$

↑
capacità termica
a volume cost
molare

$$\text{SI: } \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

Pressione costante

$$\delta Q = c_p dT$$

$$\delta Q = m c_p dT$$

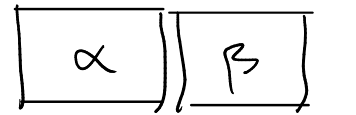
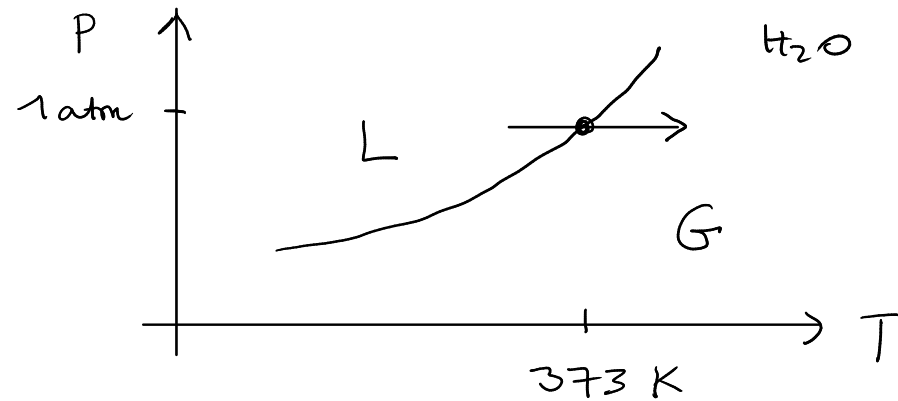
$$\delta Q = n c_p^{(n)} dT$$

Es.: H_2O liquida @ T_{amb} P_{atm}

$$c_v \approx c_p = 4,18 \text{ J/K/g} = 1 \text{ cal/K/g}$$

calore latente

Transizione di fase



coesistenza di fase

$dm \delta Q$

$\delta Q \sim dm$

$$\delta Q = L_{\alpha\beta} dm = L_{\alpha\beta}^{(m)} dn$$

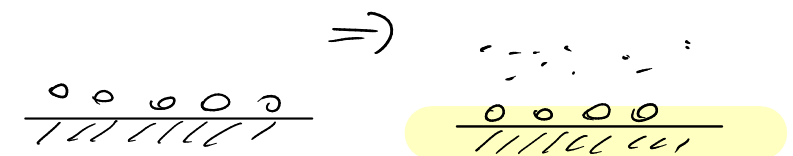
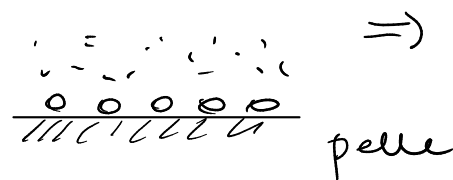
\uparrow calore latente $\alpha \rightarrow \beta$ \uparrow calore latente molare $\alpha \rightarrow \beta$
 SI: $\frac{J}{Kg}$ SI: $\frac{J}{mol}$

Es: H₂O L → G $L_{LG} = 2,26 \times 10^6 \frac{J}{Kg}$ @ Patm

$= 2,26 \frac{MJ}{Kg}$

$L_{\alpha\beta} = -L_{\beta\alpha}$

$L_{LG} > 0$



$L_{LG} > 0$



Relazione tra capacità termiche e variabili di stato

Volume costante + QS

$$\left\{ \begin{array}{l} \delta Q = c_v dT \end{array} \right.$$

$$\left\{ \begin{array}{l} \delta Q = dU - \delta W = dU + PdV = \left. \frac{\partial U}{\partial T} \right|_V dT + \frac{\partial U}{\partial V} \Big|_T dV + PdV = \frac{\partial U}{\partial T} \Big|_V dT + \left(\frac{\partial U}{\partial V} \Big|_T + P \right) dV \end{array} \right.$$

$$c_v = \left. \frac{\partial U}{\partial T} \right|_V$$

Pressione costante + QS

$$\left\{ \begin{array}{l} \delta Q = c_p dT \end{array} \right.$$

$$\left\{ \begin{array}{l} \delta Q = dU + PdV = dU + d(PV) - VdP = d(U+PV) - VdP = dH - VdP = * \end{array} \right.$$

$$d(PV) = \left. \frac{\partial(PV)}{\partial P} \right|_V dP + \left. \frac{\partial(PV)}{\partial V} \right|_P dV = VdP + PdV \Rightarrow PdV = d(PV) - VdP$$

$$* = \left. \frac{\partial H}{\partial T} \right|_P dT + (\dots) dP$$

$$c_p = \left. \frac{\partial H}{\partial T} \right|_P$$

$$H = U + PV \text{ entalpia}$$

↑

Capacità termiche dei solidi

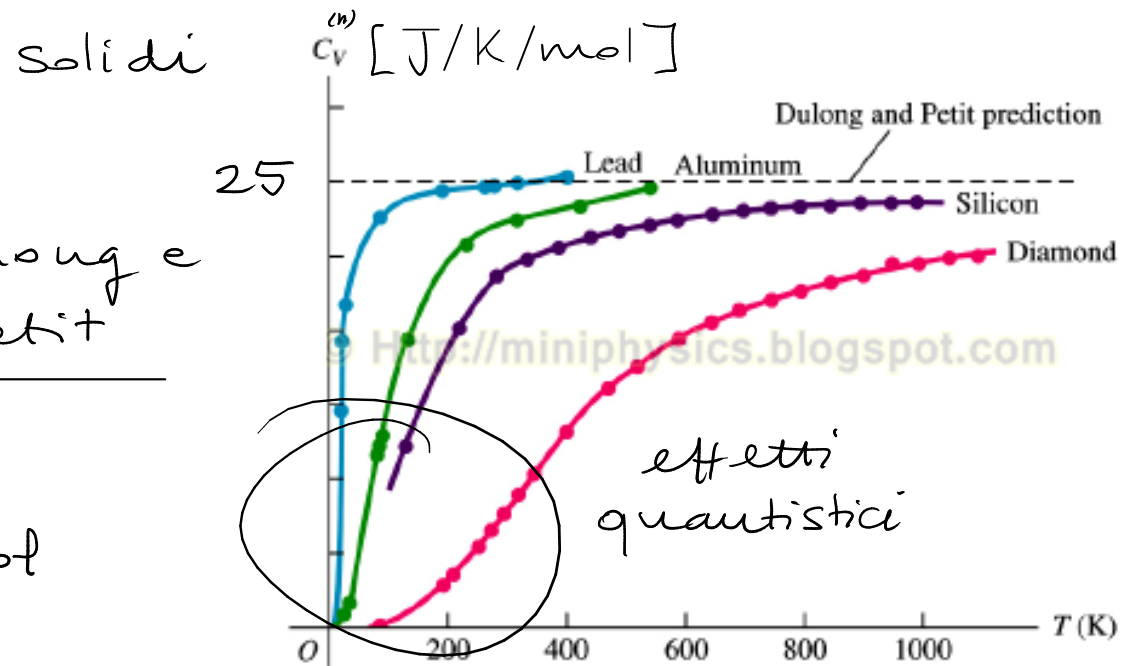
Solido armonico $n = \text{cost}$

$$U = 3nRT = C_v T$$

$$C_v = \left. \frac{\partial U}{\partial T} \right|_v = 3nR$$

$$C_v^{(m)} = 3R = 3 \times 8,314 \text{ J/K/mol} \approx 25 \text{ J/K/mol}$$

Dulong e
Petit



Capacità termiche dei gas

$$\left. \begin{array}{l} \text{Gas perfetto mono: } U = \frac{3}{2} nRT \rightarrow C_v = \left. \frac{\partial U}{\partial T} \right|_v = \frac{3}{2} nR \rightarrow C_v^{(m)} = \frac{3}{2} R \\ \text{--//--} \quad \text{bia: } U = \frac{5}{2} nRT \rightarrow C_v = \left. \frac{\partial U}{\partial T} \right|_v = \frac{5}{2} nR \rightarrow C_v^{(m)} = \frac{5}{2} R \end{array} \right\} U = C_v T$$

$$\text{(es.) } C_p = \left. \frac{\partial H}{\partial T} \right|_p \rightarrow \left. \begin{array}{l} \text{mono: } C_p = \frac{5}{2} nR \\ \text{bia: } C_p = \frac{7}{2} nR \end{array} \right\}$$

Relazione di Mayer

$$C_p = C_v + nR \quad \underline{g.p.}$$

$$C_p^{(m)} = C_v^{(m)} + R$$

Trasformazioni adiabatiche

Il sistema non scambia calore: $\delta Q = 0$



$$\Rightarrow dT = 0$$

- $\delta Q = 0$
- gas perfetto
- QS

Parametro: $\gamma = C_p / C_v$

es.: mono: $\gamma = \frac{5}{2}nR / \frac{3}{2}nR = \frac{5}{3}$

bia: $\gamma = \frac{7}{2}nR / \frac{5}{2}nR = \frac{7}{5}$

Legge delle adiabatiche: $i \rightarrow f$

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \quad \rightarrow \quad T V^{\gamma-1} = \text{cost}$$

$$PV = nRT$$

$$\Rightarrow T = \frac{PV}{nR} \sim PV$$

$$T V^{\gamma-1} \sim P V V^{\gamma-1} \sim P V^{\gamma} = \text{cost}$$

es. P, T

$$dU = \delta W + \delta Q = -P dV$$

$$dU = C_V dT$$

perché adiabatica e QS
gas perfetto

$$C_V dT = -nRT \frac{dV}{V}$$

relazione di Mayer

$$\gamma \equiv \frac{C_P}{C_V}$$

$$\text{con } \frac{nR}{C_V} \stackrel{\downarrow}{=} \frac{C_P - C_V}{C_V} = \frac{C_P}{C_V} - 1 = \gamma - 1$$

$$\frac{dT}{T} = (1-\gamma) \frac{dV}{V}$$

$$\int_{T_i}^{T_f} \frac{dT}{T} = (1-\gamma) \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\ln\left(\frac{T_f}{T_i}\right) = (1-\gamma) \ln\left(\frac{V_f}{V_i}\right) = \ln\left[\left(\frac{V_f}{V_i}\right)^{1-\gamma}\right]$$

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma} \Rightarrow T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1} \Rightarrow TV^{\gamma-1} = \text{cost} \quad \square$$

	W	Q	ΔU
ISOTERMA			
ISOBARA			
ISOCORA			
ADIBATICA		0	

$i \rightarrow f$

$g.p.$

$$W = \int_i^f \delta W$$