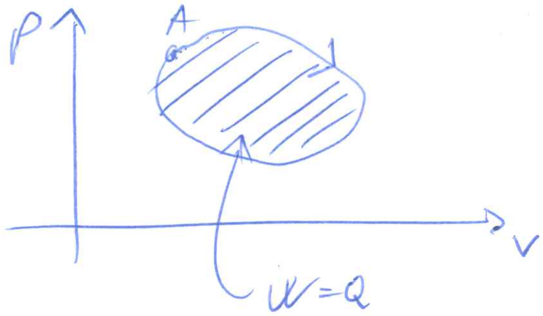
Trasformazioni cicliche

"Banalmente" primo principio si applica anche se stato iniziale = stato finale



$\Rightarrow \boxed{\Delta U = 0}$

$\Rightarrow \boxed{Q = W}$

curva chiusa PV

Senso orario → W positivo (<P> più alta in espansione, più bassa compressione)

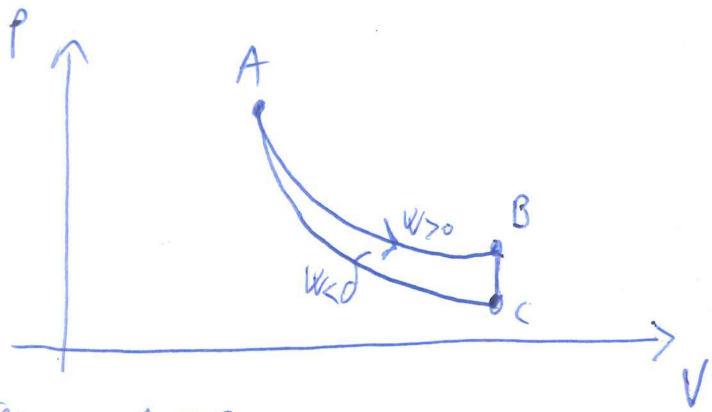
Senso antiorario → W negativo

Esempio 1: IT-IC-AD

$P_A, V_A, T_A \xrightarrow{\text{isoterma quasistatica}} P_B, V_B, T_B = T_A$

$P_B, V_B, T_B \xrightarrow{\text{isocora quasistatica}} P_C, V_C = V_B, T_C$

$P_C, V_C = V_B, T_C \xrightarrow{\text{adiabatica}} P_A, V_A, T_A$



Isoterma $A \to B$

$\Delta U_{AB} = 0$ [dato che $T_A = T_B$ e $U = U(T)$]

$W_{AB} = nR\ln\left(\frac{P_A}{P_B}\right)T_A \qquad Q_{AB} = W_{AB}$ $\qquad Q_{AB}, W_{AB} > 0$

Isocora $B \to C$

$\Delta U_{BC} = nc_V(T_C - T_B) = nc_V(T_C - T_A)$

$W_{BC} = 0$

$Q_{BC} = \Delta U_{BC}$

$T_C = \frac{P_C V_C}{nR} < T_A = \frac{P_A V_A}{nR}$

$T_B = \frac{P_B V_B}{nR}$

$T_C < T_A, T_B$

Adiabatica $C \to A$

$\Delta U_{CA} = nc_V(T_A - T_C)$

$W_{CA} = -\Delta U_{CA}$ $\quad Q_{CA} = 0$ $\qquad W<0\ ,\ \Delta U>0$

$\to$ nota: serve scelta particolare di R affinché $P_A V_A^\gamma = P_C V_C^\gamma$

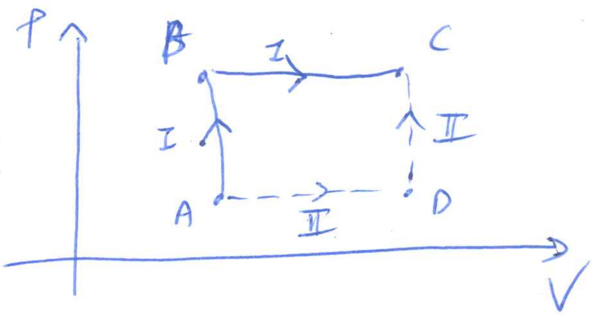
Lungo il ciclo

$\Delta U = 0 + nc_V(T_C - T_A) + nc_V(T_A - T_C) = 0$! Come dovrebbe essere

$W = nRT_A \ln\left(\frac{P_A}{P_B}\right) + \cancel{0}\, nc_V(T_A - T_C)$

$Q = nRT_A \ln\left(\frac{P_A}{P_B}\right) + nc_V(T_C - T_A) + 0 \quad = W$! Come dovrebbe essere

Esempio 2: IB-IC/IC-IB



Consideriamo prima $A \to B \to C$

Isocora $A \to B$

~~Isobara A B~~

$\frac{P_B}{P_A} = \alpha > 1$ $\qquad T_A = \frac{P_A V_A}{nR} \to T_B = \frac{P_B V_B}{nR} = \alpha T_A$

$\Delta U_{AB} = nc_V \Delta T_{AB} = nc_V T_A(\alpha - 1)$

$W_{AB} = 0$ (in quanto $\Delta V = 0$) $\qquad Q = nc_V \Delta T_{AB} = nc_V T_A(\alpha-1) = \Delta U_{AB} > 0$

~~Isocora~~ Isobara $B \to C$

$\frac{V_C}{V_B} = \beta > 1$ $\qquad P_C = \frac{nRT_C}{V_C}$ $\qquad P_B = \frac{nRT_B}{V_B} \to$ $T_C = \beta T_B$

$Q_{BC} = nc_P(T_C - T_B) = nc_P T_B(\beta - 1) = nc_P T_A \alpha(\beta - 1)$

$W_{BC} = P_B(V_C - V_B) = nR(T_C - T_B) = nRT_B(\beta-1) = nRT_A\alpha(\beta-1)$

$\Delta U_{BC} = nc_V(T_C - T_B) = nc_V T_B(\beta - 1) = nc_V T_A \alpha(\beta-1) = Q_{BC} - W_{BC}$ in quanto $c_V = c_P - R$

Complessivamente

$$\Delta U_{AC}^{I} = \Delta U_{AB} + \Delta U_{BC} = nc_v T_A(\alpha-1) + nc_v T_A \alpha(\beta-1) = \cancel{nc_v T_A \alpha(\beta-1)}$$

$$= nc_v T_A(\alpha\beta - 1)$$

$$Q_{AC}^{I} = nc_v T_A(\alpha-1) + nc_p T_A \alpha(\beta-1) = nT_A\left[c_v(\alpha-1) + c_p\alpha(\beta-1)\right]$$

$$W_{AC}^{I} = 0 + nRT_A\alpha(\beta-1) = nRT_A\alpha(\beta-1)$$

Ora consideriamo $A \to D \to C$

~~Isobara $A \to D$~~

$$\cancel{\Delta U_{AD} = nc_v(T_D - T_A) = nc_v T_A(\alpha-1)} \qquad \cancel{T_D = \frac{p_D V_D}{nR} = \frac{p_B V_D}{nR} = \frac{p_B}{p}} \qquad \cancel{T_D = \frac{p_D V_D}{nR} \frac{p_A}{p_B}}$$

Isobara $A \to D$

$$\Delta U_{AD} = nc_v(T_D - T_A) = \qquad T_D = \frac{p_D V_D}{nR} = \frac{p_A \beta V_A}{nR} = \beta T_A$$

$$= nc_v T_A(\beta - 1)$$

$$Q_{AD} = nc_p(T_D - T_A) = nc_p T_A(\beta - 1) \qquad c_p = c_v + R$$

$$W_{AD} = p_A(V_D - V_A) = nR(T_D - T_A) = nRT_A(\beta-1) = Q_{AD} - \Delta U_{AD}$$

Isocora $D \to C$

$$T_C = \frac{p_C V_C}{nR} = \frac{\alpha p_D V_D}{nR} = \alpha T_D$$

$$\Delta U_{DC} = nc_v(T_C - T_D) = nc_v T_D(\alpha - 1) = nc_v T_A \beta(\alpha-1)$$

$$W_{DC} = 0$$

$$Q_{DC} = \Delta U_{DC} = nc_v T_A \beta(\alpha - 1)$$

Complessivamente

$$\Delta U_{AC}^{II} = \Delta U_{AD}^{II} + \Delta U_{DC} = nc_v T_A(\beta-1) + nc_v T_A\beta(\alpha-1) = nc_v T_A(\alpha\beta - 1) = \Delta U_{AC}^{I}!$$

$$Q_{AC}^{II} = nc_p T_A(\beta-1) + nc_v T_A\beta(\alpha-1) = nT_A\left[c_p(\beta-1) + c_v\beta(\alpha-1)\right] \neq Q_{AC}^{I}!$$

$$W_{AC}^{II} = W_{AD} + W_{DC} = nRT_A(\beta - 1) + 0 = nRT_A(\beta-1) \neq W_{AC}^{I} \,!$$

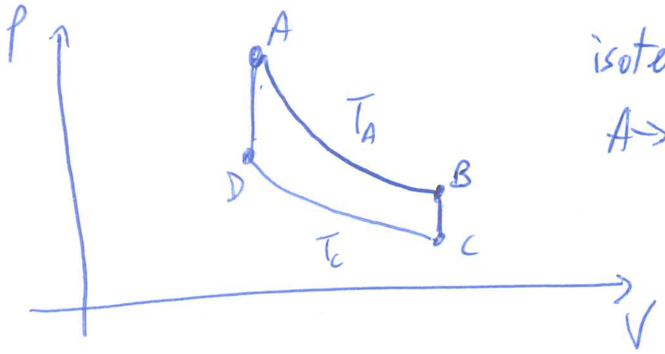
$\Delta U_{AC}^{I} = \Delta U_{AC}^{II}$ come dovrebbe essere in quanto U funzione di stato (dipende solo ~~dal percorso~~ dai punti iniziale e finale)

mentre $Q_{AC}^{I} \neq Q_{AC}^{II}$, $W_{AC}^{I} \neq W_{AC}^{II}$, confermando che Q e W non sono funzioni di stato, ma dipendono dal percorso seguito

Non si può parlare di Q, W posseduti, ma solo scambiati dal sistema

3
Esempio: Ciclo di Stirling

Brevettato nel 1816 dal reverendo Stirling



isoterma → isocora → isoterma → isocora

$A \to B$ $B \to C$ raffreddamento $C \to D$ $D \to A$ riscaldamento

Isoterma $A \to B$

$\Delta U_{AB} = 0$ $Q_{AB} = nRT_A \ln\left(\frac{V_B}{V_A}\right) = nRT_A \ln\left(\frac{P_A}{P_B}\right) = W_{AB}$

Isocora $B \to C$

$W_{BC} = 0$ $\Delta U_{BC} = nc_V(T_C - T_A) = Q_{BC}$

Isoterma $C \to D$

$\Delta U_{CD} = 0$ $Q_{CD} = nRT_C \ln\left(\frac{V_D}{V_C}\right) = nRT_C \ln\left(\frac{P_C}{P_D}\right) = W_{CD}$

Isocora $D \to A$

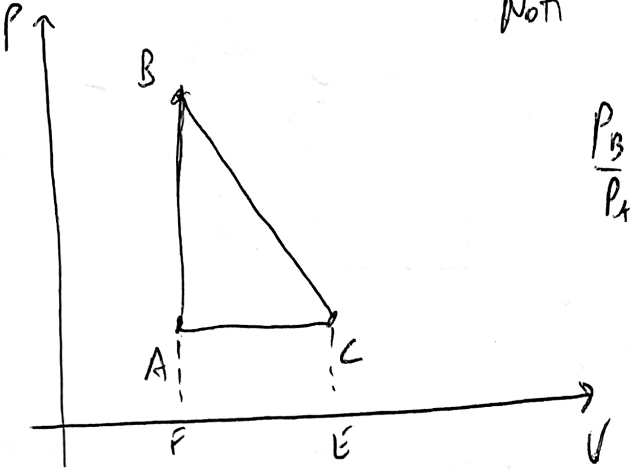
$W_{DA} = 0$ $\Delta U_{DA} = nc_V(T_A - T_C) = Q_{DA}$

In totale: $\Delta U_{A\to A} = 0 + nc_V(T_C - T_A) + 0 + nc_V(T_A - T_C) = 0$ $W_{A\to A} = nRT_A \ln\left(\frac{P_A}{P_B}\right) \cancel{+0} + nRT_C \ln\left(\frac{P_C}{P_D}\right) \cancel{+0}$

$$Q_{A\to A} = nRT_A \ln\left(\frac{P_A}{P_B}\right) + nc_V(\cancel{T_C - T_A}) + nRT_C \ln\left(\frac{P_C}{P_D}\right) + nc_V(\cancel{T_A - T_C}) = nRT_A \ln\left(\frac{P_A}{P_B}\right) + nRT_A \ln\left(\frac{P_C}{P_D}\right) = W_{A\to A}\,!$$

④ Ciclo "triangolare" (monoatomico)

Noti $P_A V_A T_A$



$$\frac{P_B}{P_A} = \alpha = 3 \qquad \frac{V_C}{V_A} = \beta = 2$$

AB isocora

$$Q_{AB} = nC_V(T_B - T_A) = \qquad T_B = \frac{P_B V_B}{nR} = \alpha\frac{P_A V_A}{nR} = \alpha T_A$$

$$= nC_V(\alpha-1)T_A = \frac{3}{\cancel{2}}nR\cancel{2}T_A = 3nRT_A$$

$$\Delta U_{AB} = nC_V(T_B - T_A) = 3nRT_A$$

$$W_{AB} = \int_A^B dV\, p(V) = 0$$

BC "lineare"

$$W_{BC} = \text{area trapezio } BCEF = \frac{(P_B+P_A)(V_C-V_A)}{2} =$$

$$= \frac{(\alpha+1)P_A(\beta-1)V_A}{2} = \frac{(\alpha+1)(\beta-1)}{2}P_A V_A = \frac{(\alpha+1)(\beta-1)}{2}nRT_A = 2nRT_A$$

$$\Delta U_{BC} = nC_V(T_C - T_B) = \qquad T_C = \frac{P_C V_C}{nR} = \beta\frac{P_A V_A}{nR} = \beta T_A$$

$$= nC_V(\beta-\alpha)T_A = -nC_V T_A = -\frac{3}{2}nRT_A$$

$$Q_{BC} = \Delta U_{BC} + W_{BC} = 2nRT_A - \frac{3}{2}nRT_A = \frac{1}{2}nRT_A$$

CA isobara

$$Q_{CA} = nC_p(T_A - T_C) = nC_p(1-\beta)T_A = -\frac{5}{2}nRT_A$$

$$W_{CA} = P_A\Delta V = P_A(V_A - V_C) = P_A(1-\beta)V_A = (1-\beta)nRT_A = -nRT_A$$

$$\Delta U_{CA} = nC_V\Delta T = nC_V(T_A - T_C) = nC_V(1-\beta)T_A = -nC_V T_A = -\frac{3}{2}nRT_A = Q_{CA} - W_{CA}$$

$$\Delta U_{tot} = 3nRT_A - \frac{3}{2}nRT_A - \frac{3}{2}nRT_A = 0$$

$$Q_{tot} = 3nRT_A + \frac{1}{2}nRT_A - \frac{5}{2}nRT_A = nRT_A \qquad W_{tot} = 0 + 2nRT_A - nRT_A = nRT_A = \text{area triangolo!}$$