

## Lezione 7 - Reazioni e Coefficienti Misurabili

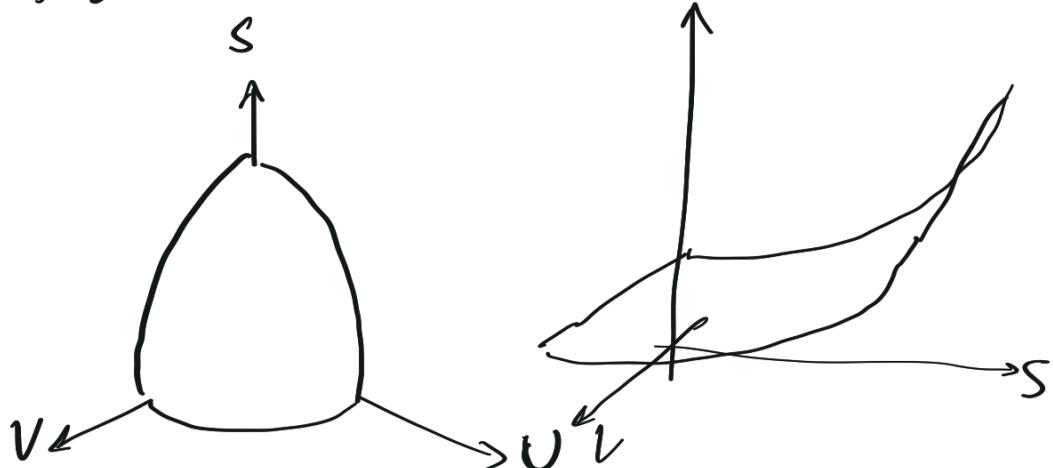
sistema chiuso, semplificato e semplice

<sup>misura</sup>  
Scopo Veli coefficienti: Cve Cp

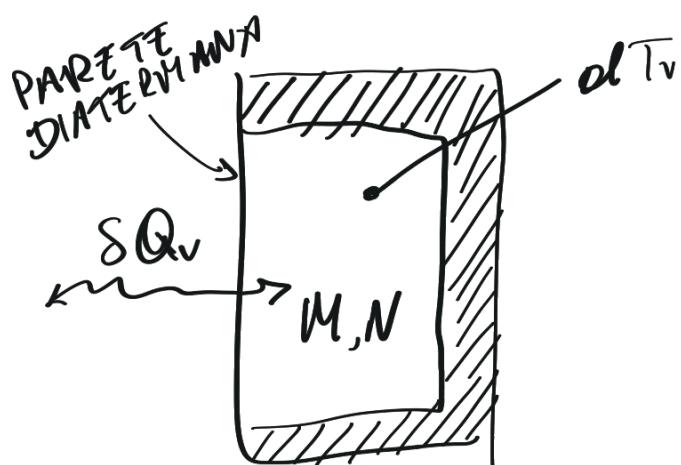
Per relazioni fondamentali

$$U = U(S, V, N_i) \rightarrow U = U(S, V)$$

$$S = S(U, V, N_i) \rightarrow S = S(U, V)$$



Sistema chiuso, rigido, tutte tiranne 1 parete adiabatica



calore specifico a volume costante

$$\dot{E}_v = \frac{1}{N} \left( \frac{\delta Q}{\alpha l} \right)_v \left[ \frac{J}{mole K} \right]$$

$$C_v^{\text{massimo}} = \frac{1}{M} \left( \frac{\delta Q}{\alpha l} \right)_v \left[ \frac{J}{kg K} \right]$$

$$c_v = c_v(T, p)$$

$\hookrightarrow$   $p$  può cambiare per temperatura e pressione

1<sup>a</sup> principio termodinamico

$$dV = T dS - P dV + \mu dN$$

$\delta Q$

diiso e non  
reagente

processo  
impreciso  
perché dipende  
dal percorso

costante quinoli = 0

$$dV = T dS = \delta Q$$

$$c_v = \frac{1}{N} \left( \frac{dV}{dT} \right)_V \rightarrow dV = N c_v dT$$

$$dV = M c_v^* dT$$

$$dS = \frac{\delta Q_v}{T}$$

$$c_v = \frac{1}{N} \left( \frac{T dS}{dT} \right)_V \rightarrow dS = N c_v \frac{dT}{T} \left[ \frac{J}{k} \right]$$

$$dS = M c_v^* \frac{dT}{T} \left[ \frac{J}{k} \right]$$

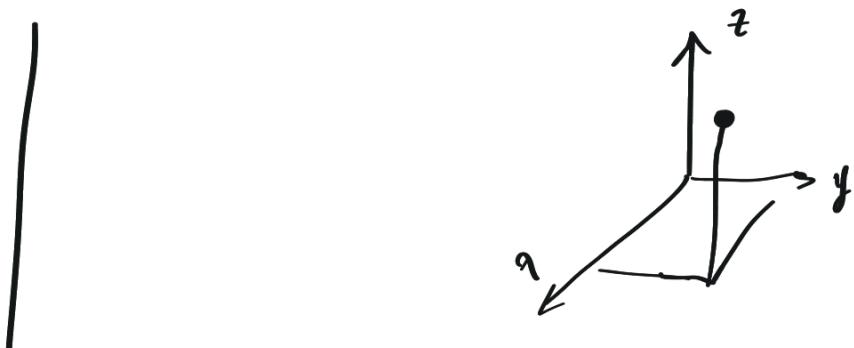
Per gas ideali:

$\hookrightarrow$  dipende solo da come è fatta la molecola di gas

$$c_v = \frac{1}{2} (\# \text{golli roto-traslatoriali}) R$$

$\hookrightarrow$  COORDINATE GEOMETRICHE  
che occorre fissare  
per DETERMINARSI

## - GAS MONOATOMICO (He, Ne, Ar)



$$C_V = \frac{3}{2} R \quad C_P = \frac{5}{2} R$$

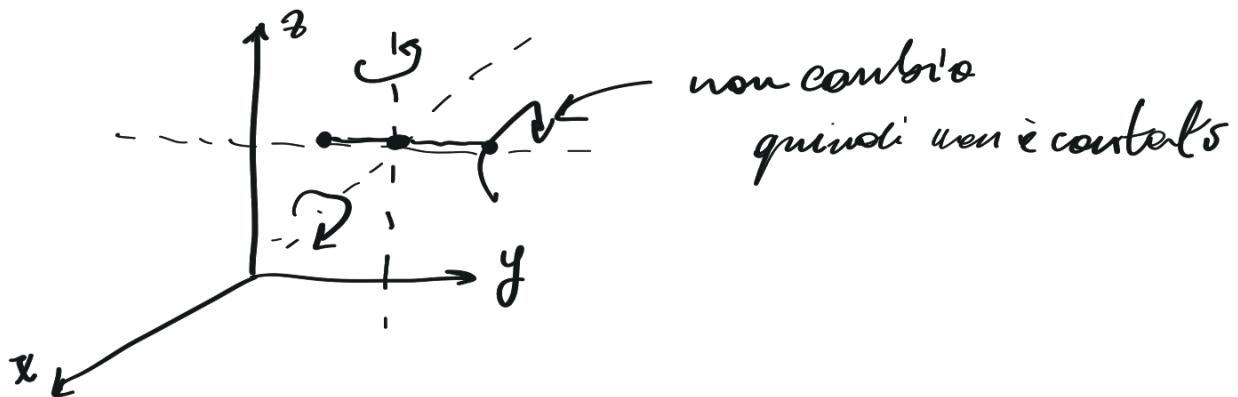
Legge di Mayer

$$C_V^* = \frac{3}{2} R^* \left[ \frac{1}{\frac{1}{2} - \frac{1}{k_B T}} \right]$$

$$C_P^* = \frac{5}{2} R^*$$

$$C_P = C_V + R$$

## - BIATOMICO o poliatomico allineati ( $H_2, O_2, N_2, CO_2$ )



$$C_V = \frac{5}{2} R$$

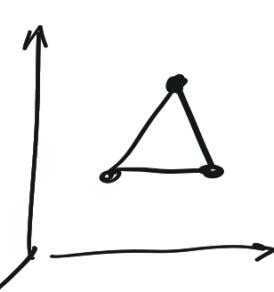
$$C_V^* = \frac{5}{2} R^*$$

Legge di Mayer

$$C_P = \frac{7}{2} R$$

$$C_P^* = \frac{7}{2} R^*$$

## POLIATOMICI NON ALLINEATI, $NH_3$

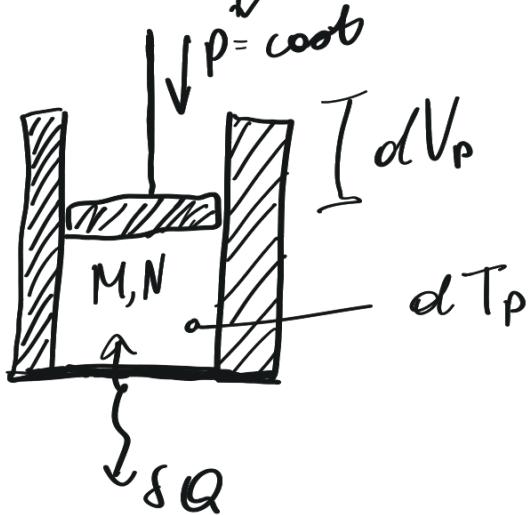


$$C_P = \frac{6}{2} R = 3R \quad C_V^* = 3R^*$$

$$C_P = 4R \quad C_P^* = 4R^*$$

$\leftarrow$  invece di  $V$  costante

Cilindrino adiabatico su tutte le penali altre una



$$C_p = \frac{1}{N} \left( \frac{\delta Q_p}{dT} \right)_p$$

$$C_p^* = \frac{1}{M} \left( \frac{\delta Q}{dT} \right)_p$$

Entalpia  $H = U + PV$

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

$$C_p = \frac{1}{N} \left( \frac{\partial H}{\partial T} \right)_p$$

$$\rightarrow dH = N C_p dT$$

$$dH = M C_p^* dT$$

$$C_p = C_p(P, T)$$

$$dH = dU + PdV + VdP$$

$$= \underbrace{TdS}_{dU} - \cancel{PdV} + \cancel{PdV} + \cancel{VdP}$$

Per  
stiamo  
facendo  
a pressione  
costante

$$dH = TdS = \delta Q$$

$$C_p = \frac{1}{N} \left( \frac{TdS}{dT} \right)_p \rightarrow dS = N C_p \frac{dT}{T} \quad dS = M C_p^* \frac{dT}{T}$$

COEFFICIENTE DI

DILATAZIONE ISOBARICA

$$\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \left[ \text{m}^{-1} \right]$$

volume massico /  
specifico

$$v = \frac{V}{N} \left[ \frac{m^3}{mol} \right] \quad \alpha_p = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p \quad v^* = \frac{1}{p} = p^{-1}$$

$$v^* = \frac{V}{M} \left[ \frac{m^3}{kg} \right] \quad \alpha_p = \frac{1}{v^*} \left( \frac{\partial v^*}{\partial T} \right)_p = p \left( \frac{\partial p^{-1}}{\partial T} \right)$$

$$= -p p^{-2} \left( \frac{\partial p}{\partial T} \right)_p = -\frac{1}{p} \left( \frac{\partial p}{\partial T} \right)_p$$

aumenta  
 con  $\partial T$   
 quindi segue  
 è giusto

$p$  diminuisce  
 con  $\partial T$ ,  
 quindi serve  
 $(-)$

per gas ideali

$$PV = nRT$$

$$P_V = RT \rightarrow v = \frac{RT}{P} \quad \frac{\partial v}{\partial T} = \frac{R}{P}$$

$$\frac{1}{v} = \frac{P}{RT}$$

$$\alpha_p = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p = \frac{P}{RT} \cdot \frac{R}{P} = \frac{1}{T} [h^{-1}]$$

$\hookrightarrow$  per gas ideali è dipendente  
solo da  $T$ , inverso di temperatura  
assoluta

m funzioni  $u, v, \dots, w$

n variabili  $x, y, \dots, z$

Jacobiana

Se  $m = n$

$$\frac{\partial(u, v, \dots, w)}{\partial(x, y, \dots, z)} = \begin{bmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} & \dots & \frac{\partial u}{\partial z} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} & \dots & \frac{\partial v}{\partial z} \\ \vdots & \vdots & & \vdots \\ \frac{\partial w}{\partial x} & \frac{\partial w}{\partial y} & \dots & \frac{\partial w}{\partial z} \end{bmatrix}$$

m righe  
n colonne

uso termodynamico:

2 funzioni:

$u, v$

2 variabili:

$x, y$

$$\frac{\partial(u, v)}{\partial(x, y)} = \frac{1}{\frac{\partial(x, y)}{\partial(u, v)}}$$

Proprietà 1:

$$\frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial(u, v)}{\partial(x, y)} \cdot \frac{\partial(r, s)}{\partial(r, s)}$$

Varabile auxiliarie  
e.g. Te P

Proprietà 2:

$$\frac{\partial(u, v)}{\partial(x, y)} = - \frac{\partial(v, u)}{\partial(x, y)} = - \frac{\partial(u, v)}{\partial(y, x)} = \frac{\partial(v, u)}{\partial(y, x)}$$

Proprietà 3:

$$\frac{\partial(u, y)}{\partial(x, y)} = \left( \frac{\partial u}{\partial x} \right)_y$$

Per ricavare la legge di Mayer generalizzata per 1 mole

$$c_V = \left( \frac{\partial Q}{\partial T} \right)_V = T \left( \frac{\partial s}{\partial T} \right)_V \xrightarrow{\text{prop 3}} T \frac{\partial(s, v)}{\partial(T, v)} \cdot \frac{\partial(T, p)}{\partial(T, p)} =$$

o leg  
Proprietà

$$T \frac{\partial(s, v)}{\partial(T, p)} \cdot \frac{\partial(T, p)}{\partial(T, v)} = T \frac{\partial(s, v)}{\partial(T, p)} \cdot \frac{\partial(p, T)}{\partial(v, T)}$$

$$c_V = T \frac{\partial(s, v)}{\partial(T, p)} \cdot \left( \frac{\partial p}{\partial v} \right)_T$$

$$k_T = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T$$

coefficiente di  
comprimibilità isotermica

$$c_V = -T \cdot \frac{1}{v \cdot k_T} \left( \frac{\partial(s, v)}{\partial(T, p)} \right)$$

Usando proprietà di metrica jacobiana

$$\frac{\partial(s, v)}{\partial(T, p)} = \det \begin{vmatrix} \left( \frac{\partial s}{\partial T} \right)_p & \left( \frac{\partial s}{\partial p} \right)_T \\ \left( \frac{\partial v}{\partial T} \right)_p & \left( \frac{\partial v}{\partial p} \right)_p \end{vmatrix} = \left( \frac{\partial s}{\partial T} \right)_p \cdot \left( \frac{\partial v}{\partial p} \right)_T - \left( \frac{\partial s}{\partial p} \right)_T \cdot \left( \frac{\partial v}{\partial T} \right)_p$$

$$= \frac{T}{V} \left( \frac{\partial s}{\partial T} \right)_p$$

$$\frac{V}{V} \left( \frac{\partial v}{\partial p} \right)_T$$

IV Maxwell

$$- \left[ \frac{-V}{V} \left( \frac{\partial v}{\partial T} \right)_p \cdot \frac{V}{V} \left( \frac{\partial v}{\partial T} \right)_p \right]$$

$$C_p = -\frac{c_p k_T \sigma}{T} + v^2 \alpha_p^2$$

-  $k_T$ 
 $\alpha_{10}$ 
 $\alpha_p$

$$C_V = \frac{-T}{v k_T} \left[ \frac{-c_p k_T v}{T} + v^2 \alpha_p^2 \right] = c_p - \frac{T v \alpha_p^2}{k_T}$$

Fa senso perché  $C_V < C_p$

$$C_V = c_p - \frac{v T \alpha_p^2}{k_T}$$

per gas ideale

$$\alpha_p = \frac{1}{T}$$

$$k_T = \frac{1}{P}$$

$$C_V = c_p - \frac{v \cancel{T} P}{T} = c_p - \frac{v}{P T} \cancel{P} = c_p - R$$

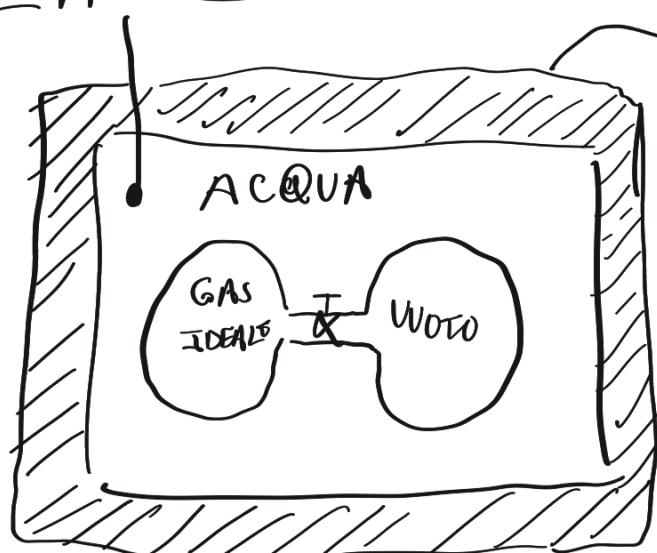
$$P_V = RT$$

$$R = \frac{P_V}{T}$$

$$\frac{V}{N}$$

V  
P  
T

### A proposito di gas ideali



lavoro fatto = 0  
perché sta lavorando  
contro nulla

$$\Delta U = Q - L = 0 \text{ perche' sistema chiuso isolato}$$

$\Delta U_{\text{gas}}$  HA VARIAZIONI

DI E VARIAZIONE DI  $V$

la  $T$  rimane costante

$$\Delta U_{\text{gas}} = 0 \Rightarrow U = \text{cost} \text{ e } T_{\text{gas}} = \text{costante}$$

$$U_{\text{gas}}^{\text{IDEALE}} = U(T)$$

$$dU = NcvdT \leftarrow \text{in ogni caso}$$

$$H = U + PV$$

$$\text{per 1 mole di gas } PV = nRT$$

$$H = U + RT$$

$$dH = dU + RT = cvdT + RT = cpdT \text{ per 1 mole}$$

$$\begin{aligned} dU &= Mc_v^* dT \\ dH &= Mc_p^* dT \end{aligned} \quad \left\{ \begin{array}{l} \text{sol per gas ideali, sempre} \\ \text{sempre} \end{array} \right.$$

Altre sostanze hanno leggi per processi isobare e isocori

$\Delta S$  di gas ideali in coordinate diverse  
 $\hookrightarrow (P, T), (P, V), (V, T)$

$$dU = TdS - PdV \rightarrow dS = \frac{PdV}{T} + \frac{P}{T} dV$$

$$dU = Nc_v dT$$

$$PV = NRT \rightarrow \frac{P}{T} = \frac{NR}{V}$$

$$\int_i^f dS = Nc_v \left[ \frac{dT}{T} + NR \left( \frac{dV}{V} \right) \right] \rightarrow \Delta S_{i-f} = Nc_v \ln \frac{T_f}{T_i} + NR \ln \frac{V_f}{V_i}$$

$$\boxed{\Delta S_{i-f} = Mc_v^* \ln \frac{T_f}{T_i} + MR^* \ln \frac{V_f}{V_i}}$$

$$dS = Mc_v^* \frac{dT}{T} + MR^* \frac{dV}{V}$$

↑ coordinate  
T, V

$$PV = MR^* T \quad (1)$$

$$PdV + VdP = MR^* dT \quad (2)$$

$$\frac{(2)}{(1)} \rightarrow \frac{dV}{V} + \frac{dP}{P} = \frac{dT}{T}$$

ci permette il  
cambio di coordinate  
attraverso cambi  
di variabili

$$dS = Mc_v^* \left( \frac{dV}{V} + \frac{dP}{P} \right) + MR^* \frac{dV}{V} =$$

$$= Mc_v^* \frac{dP}{P} + M(c_v^* + R^*) \frac{dV}{V}$$

$$\boxed{\Delta S = Mc_v^* \ln \frac{P_f}{P_i} + Mc_p^* \ln \frac{V_f}{V_i}}$$

coordinate P, V

$$\frac{dV}{V} = \frac{dT}{T} - \frac{dP}{P}$$

$$\begin{aligned}
 dS &= M C_v^* \frac{dT}{T} + M R^* \left( \frac{dT}{T} - \frac{dP}{P} \right) \\
 &= M (C_v^* + R^*) \frac{dT}{T} - M R^* \frac{dP}{P} \\
 &= M C_p^* \frac{dT}{T} - M R^* \frac{dP}{P}
 \end{aligned}$$

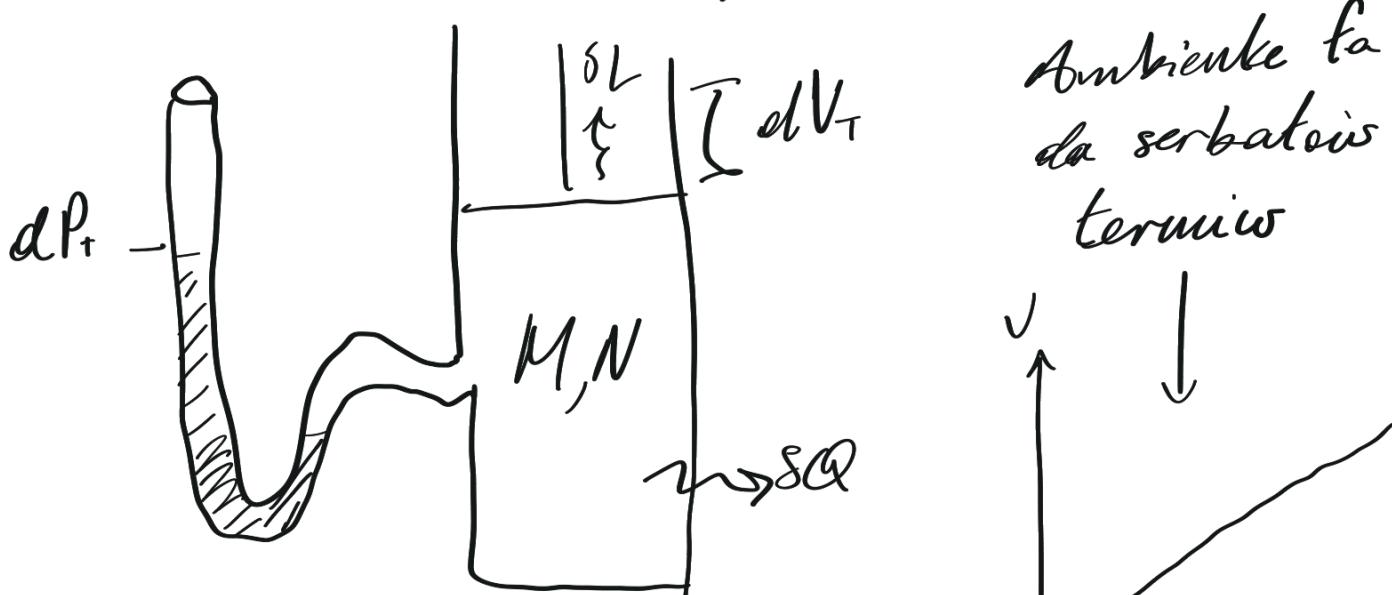
$$\Delta S = M C_p^* \ln \frac{T_f}{T_i} - M R^* \ln \frac{P_f}{P_i}$$

coordinate T, P

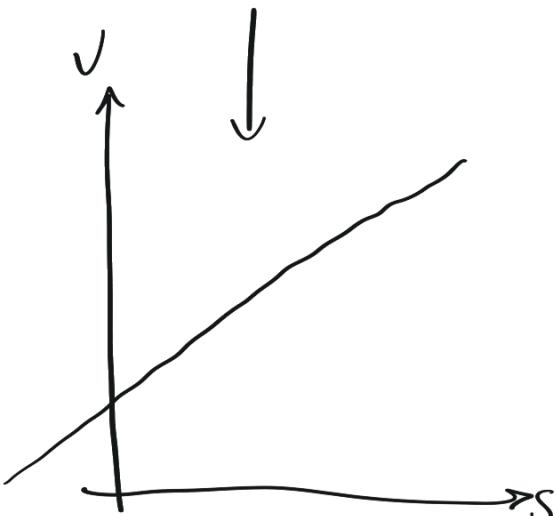
Usare quella che elimina almeno una parte

PROCESSO ISOTERMO - REVERSIBILE

contorno perfettamente diatermico



Ambiente fa da serbatoio termico



Se la serbatoio termico ha temperatura costante nel lungo termine, se  $dP_e \neq 0$   
anche

e.g. acqua che bolle

$$k_T = \frac{-1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad k_T(T, P)$$

$$P_V = RT \quad \nu = \frac{RT}{P} = RTP^{-1}$$

$$\left( \frac{\partial V}{\partial P} \right)_T = -RT P^{-2}$$

$$\frac{1}{V} \frac{RT}{P^2} = \frac{P}{P^2} = \frac{1}{P} \left[ \frac{1}{P_a} \right]$$

Solo per gas ideale

$$\alpha_p = \frac{1}{T}$$

$$k_T = \frac{1}{p}$$

$$\frac{\alpha_p}{k_T} = \cancel{\frac{1}{V}} \left( \frac{\partial v}{\partial T} \right)_p \left[ -v \left( \frac{\partial p}{\partial v} \right)_T \right] = - \frac{\partial(v, p)}{\partial(T, p)} \cdot \frac{\partial(p, T)}{\partial(v, T)}$$

$\rightarrow = \frac{\partial(p, v)}{\partial(p, T)} \quad \frac{\partial(p, T)}{\partial(T, v)}$

Scambiano variabili  
se ne va sia (-)

$$\left( \frac{\partial p}{\partial T} \right)_v = \left( \frac{\partial s}{\partial v} \right)_T$$

II Maxwell

$$v \alpha_p = v \cdot \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p = \left( \frac{\partial v}{\partial T} \right)_p = - \left( \frac{\partial s}{\partial p} \right)_T$$

IV Maxwell