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

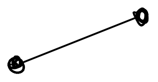
1) Gas perfetto

$$E = E_c + \underbrace{E_p}_{=0} = \frac{1}{2} m |\vec{v}|^2 = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2$$

3 termini energia cinetica traslazione

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

monoatomico



$$E = E_c$$

3 termini energia cinetica traslazione + 2 termini energia cinetica rotazione

$$U = N \cdot 5 \cdot \frac{1}{2} k_B T = \frac{5}{2} N k_B T = \frac{5}{2} nRT$$

diatomico

2) Solido armonico

$$E = E_c + E_p = \frac{1}{2} m v_x^2 + \frac{1}{2} k x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} k y^2 + \frac{1}{2} m v_z^2 + \frac{1}{2} k z^2$$

3 termini energia cinetica traslazione + 3 termini energia potenziale elastica

$$U = N \cdot 6 \cdot \frac{1}{2} k_B T = 3 N k_B T = 3 n R T$$ solido armonico

Calore

$dU = \delta W + \delta Q$

$\delta Q \sim dT$

Volume costante

$\delta Q = C_v \, dT$

capacità termica volume costante

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

$\delta Q = m c_v \, dT$

capacità termica volume costante per unità di massa

SI : $\frac{J}{K \, kg}$

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

capacità termica volume costante molare

SI : $\frac{J}{K \, mol}$

H_2O : $c_v = 4.18 \frac{J}{g K} = 1 \frac{cal}{g K}$

Pressione costante

$\delta Q = C_p \, dT$

$\delta Q = m c_p \, dT$

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

pressione sistema costante

Transizioni di fase

$\boxed{\alpha}\ \boxed{\beta}$

coesistenza

$$\delta Q = dm\, L_{\alpha\beta}$$

calore latente
per unità di massa

SI : $\frac{J}{kg}$

$$\delta Q = dn\, L^{(n)}_{\alpha\beta}$$

calore latente
molare

SI : $\frac{J}{mol}$

Es: $L_{LG} = 2.26 \times 10^{6} \frac{J}{kg}$

H_2O

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

Relazione tra capacità termiche e variabili di stato

Volume costante QS

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

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

Pressione costante QS

$$\delta Q = dU + P\,dV = dU + d(PV) - V\,dP = d(U + PV) - V\,dP = dH - V\,dP$$

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

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dx \qquad f(x,y) = xy$$

$$\delta Q = C_p\, dT \qquad \Rightarrow \qquad C_p = \left.\frac{\partial H}{\partial T}\right|_P$$

Entalpia: $H \equiv U + PV$ variabile di stato

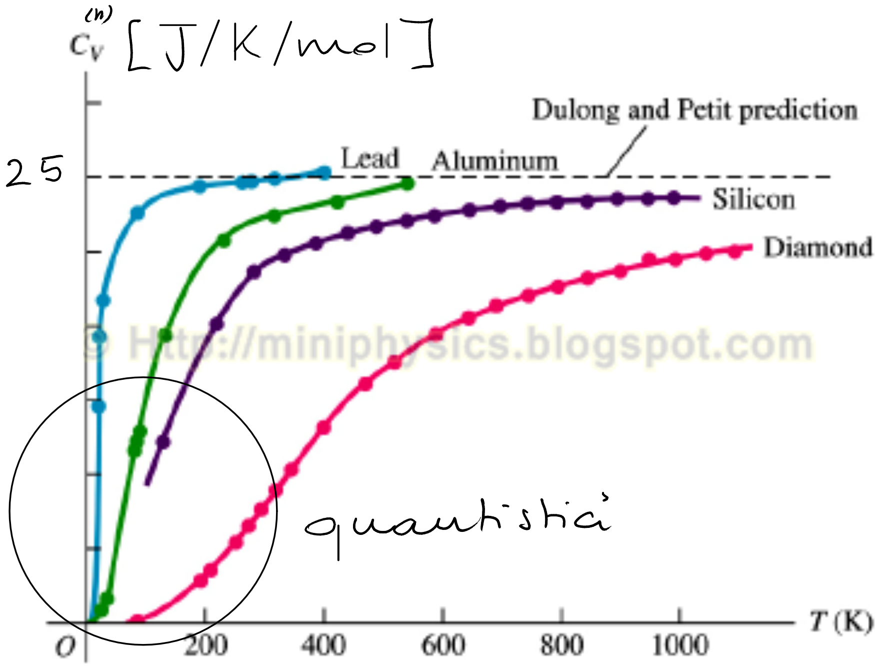
Capacità termiche dei solidi

Solido armonico : $U = 3nRT \longrightarrow U = C_v T$

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = 3nR$$

$$c_V^{(n)} = \frac{C_V}{n} = 3R \approx 25 \frac{J}{K\,mol}$$

Legge di DULONG e PETIT



Capacità termiche dei gas

g.p. mono : $U = \frac{3}{2} nRT$ $\quad C_V = \left.\frac{\partial U}{\partial T}\right|_V = \frac{3}{2} nR$ $\quad c_V^{(n)} = \frac{3}{2} R$

g.p. diato : $U = \frac{5}{2} nRT$ $\quad C_V = \quad = \frac{5}{2} nR$ $\quad c_V^{(n)} = \frac{5}{2} R$

$\Big\} \; U = C_V T$

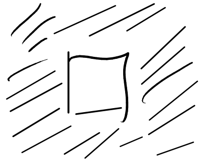
ES: $C_p = \left.\frac{\partial H}{\partial T}\right|_p$ $\qquad H = U + PV$

Relazione di Mayer : $C_p = C_V + nR$ $\qquad c_p^{(n)} = c_V^{(n)} + R$

Trasformazioni adiabatiche

	W	Q	ΔU
isocora			
isobara			
isoterma			
adiab.		0	

$\delta Q = 0$ (no scambio calore)



⚠ $\not\Rightarrow dT = 0$

$$\begin{cases} \delta Q = 0 \\ \text{g.p.} \\ \text{QS} \end{cases} \qquad \gamma \equiv \frac{C_p}{C_v} \qquad \begin{cases} \text{mono} & \gamma = \frac{5/2}{3/2} = \frac{5}{3} \\ \text{diato} & \gamma = \frac{7/2}{5/2} = \frac{7}{5} \end{cases}$$

$U = C_v T$

$\Delta U = C_v \Delta T$ g.p. / solidi

$Q = C_v \Delta T$ $V = \text{cost}$

$$T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1} \Rightarrow \boxed{TV^{\gamma-1} = \text{cost}}$$

$$\text{g.p.}: \quad PV \sim T \quad \Rightarrow \quad P\cancel{V} V^{\gamma \cancel{-1}} = \text{cost} \quad \Rightarrow \quad \boxed{PV^{\gamma} = \text{cost}}$$

Es.: P, T

$dU = \delta W + \delta Q = - P\,dV$ perchè adiabatica e QS

$dU = C_v\,dT$ gas perfetto

$C_v\,dT = - nRT \dfrac{dV}{V}$

$\gamma \equiv \dfrac{C_p}{C_v}$

relazione di Mayer

$\dfrac{dT}{T} = - \dfrac{nR}{C_v} \dfrac{dV}{V}$ con $\dfrac{nR}{C_v} = \dfrac{C_p - C_v}{C_v} = \dfrac{C_p}{C_v} - 1 = \gamma - 1$

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

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

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

$\dfrac{T_f}{T_i} = \left(\dfrac{V_f}{V_i}\right)^{1-\gamma} \Rightarrow T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1} \Rightarrow T V^{\gamma-1} = \text{cost}$ $\square$