

Temperatura ed energia

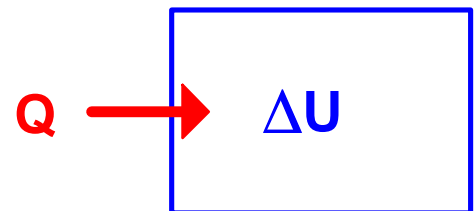
Calori specifici

- Calori specifici molari



$$Q = n c \Delta T = \Delta U + W$$

- Processi a volume costante



$$Q = n c_V \Delta T = \Delta U$$

- Informazioni sull'energia interna

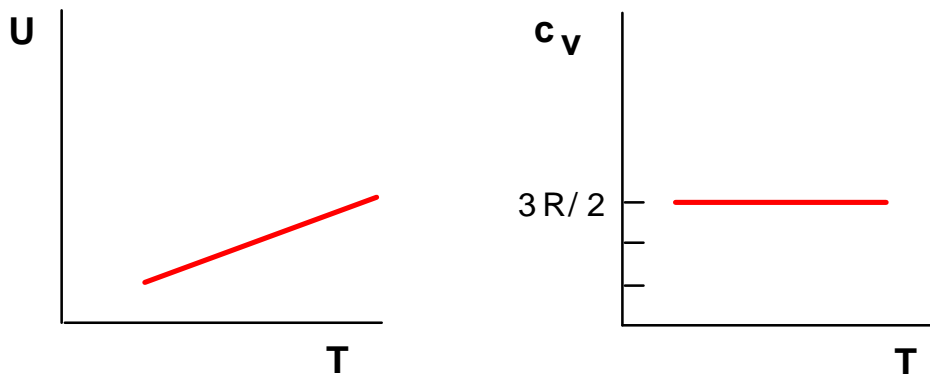
$$c_V = \frac{1}{n} \frac{dU}{dT}$$

Misure di $c_V(T) \Rightarrow$ informazioni su $U(T)$

Gas ideale monoatomico

- **Energia interna = energia cinetica traslazionale**

$$U = \sum_i E_i^{\text{tras}} = N \langle E^{\text{tras}} \rangle = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$



- **Equipartizione classica dell'energia**

3 "gradi di libertà" = 3 termini quadratici

$$\frac{1}{2} m \langle v_x^2 \rangle \quad \frac{1}{2} m \langle v_y^2 \rangle \quad \frac{1}{2} m \langle v_z^2 \rangle$$

Per ogni grado di libertà:

$$\frac{1}{2} k_B T$$

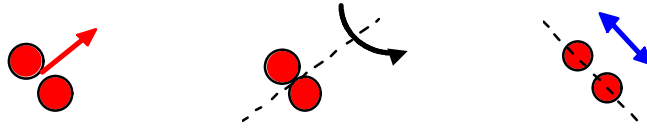
energia media / molecola

$$\frac{1}{2} R T$$

energia media / mole

Gas ideale bi-atomico

- Traslazione + rotazione + vibrazione



$$U = \sum_i E_i^{\text{tras}} + \sum_i E_i^{\text{rot}} + \sum_i E_i^{\text{vib}}$$

$$\frac{1}{2} m \langle v_x^2 \rangle + \frac{1}{2} m \langle v_y^2 \rangle + \frac{1}{2} m \langle v_z^2 \rangle$$

$$\frac{1}{2} I \langle \omega_x^2 \rangle + \frac{1}{2} I \langle \omega_y^2 \rangle$$

$$\frac{1}{2} m \langle v_{\text{rel}}^2 \rangle + \frac{1}{2} k \langle u^2 \rangle$$

3

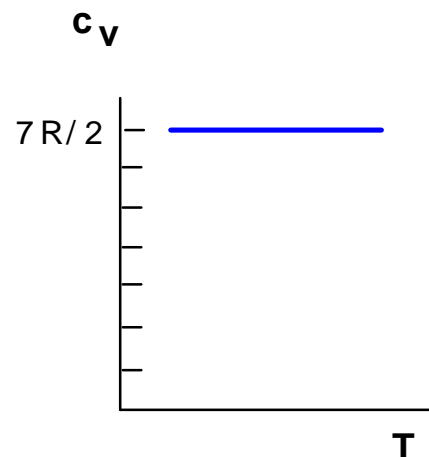
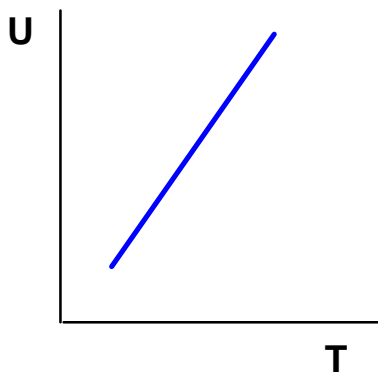
2

2

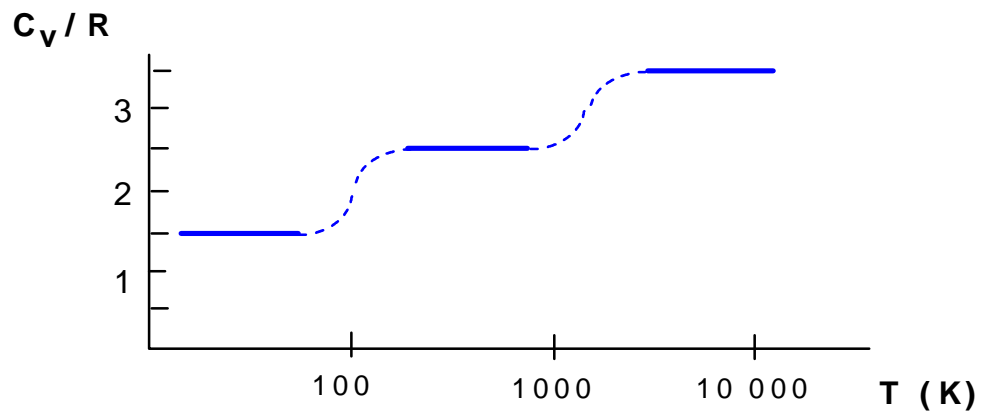
gradi di libertà

- Equipartizione classica

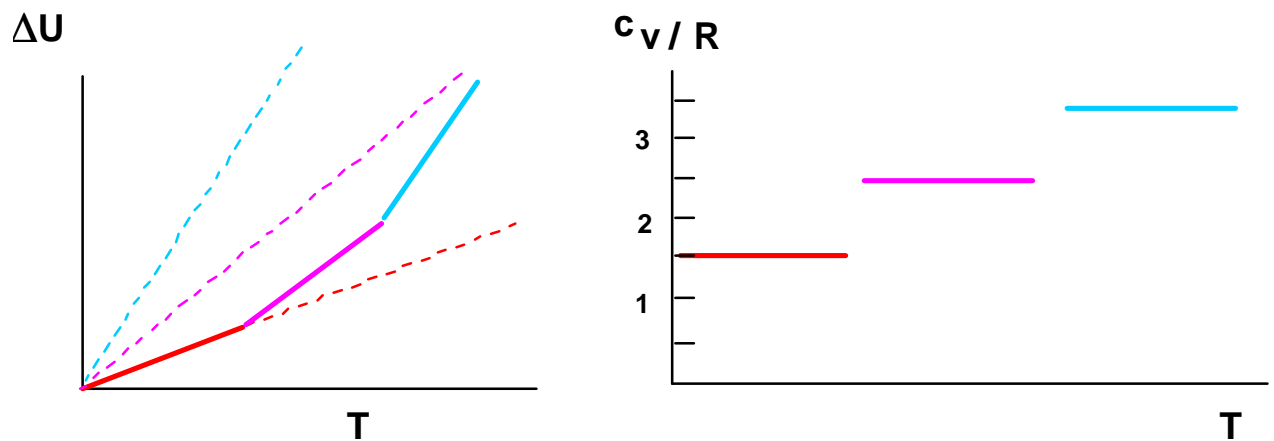
Previsioni:



- **Idrogeno H_2 : risultati sperimentali**



- **Schematicamente**

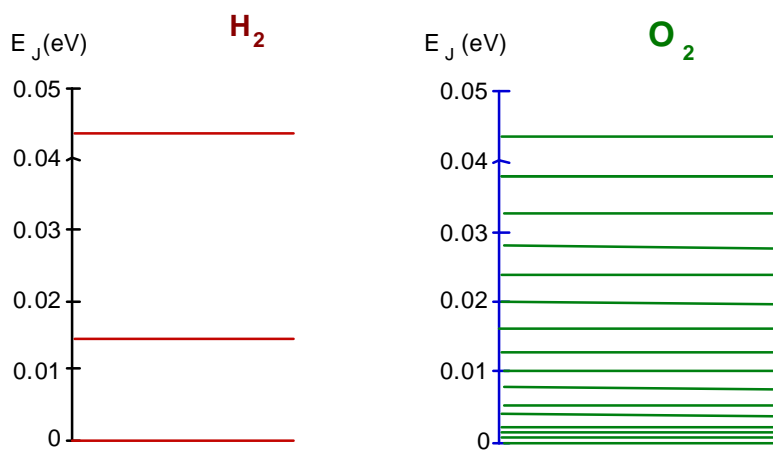
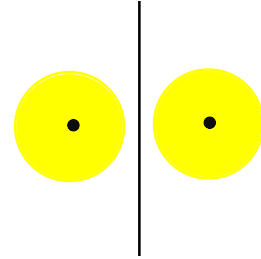


U e T non sono proporzionali

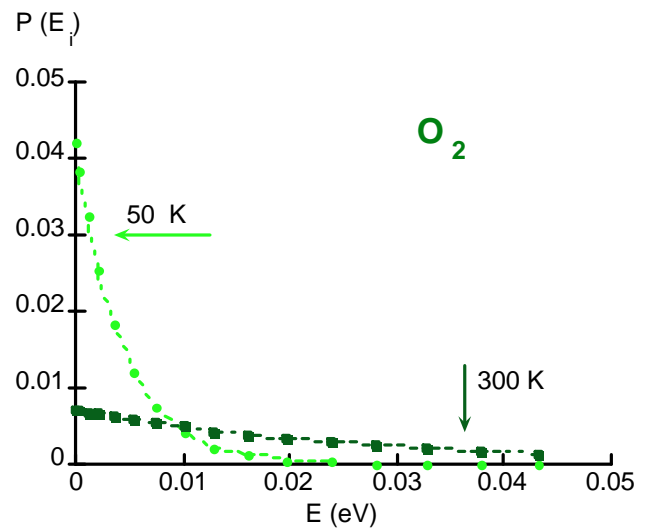
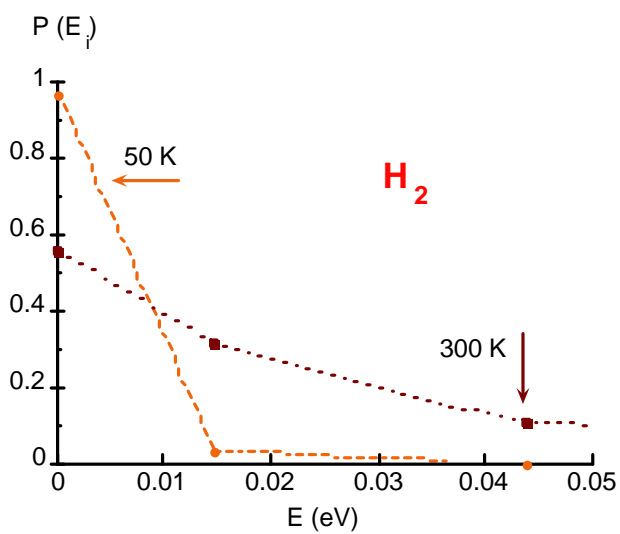
accensione progressiva dei gradi di libertà

- Quantizzazione dei livelli rotazionali

$$E_J^{\text{rot}} = \frac{L^2}{2I} = \frac{\hbar^2}{2I} J(J+1)$$

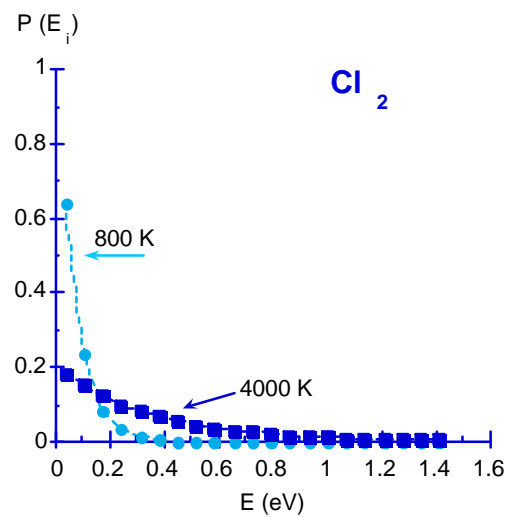
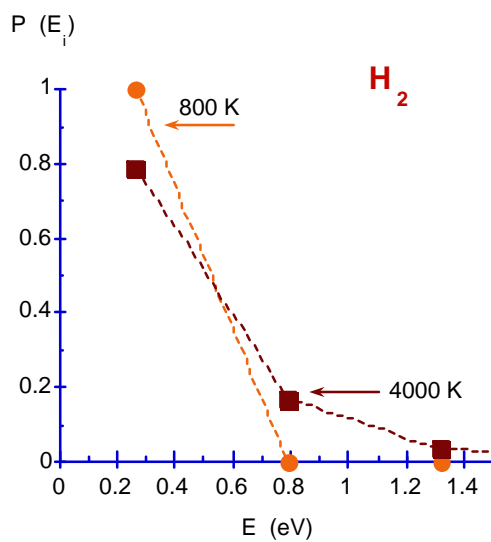
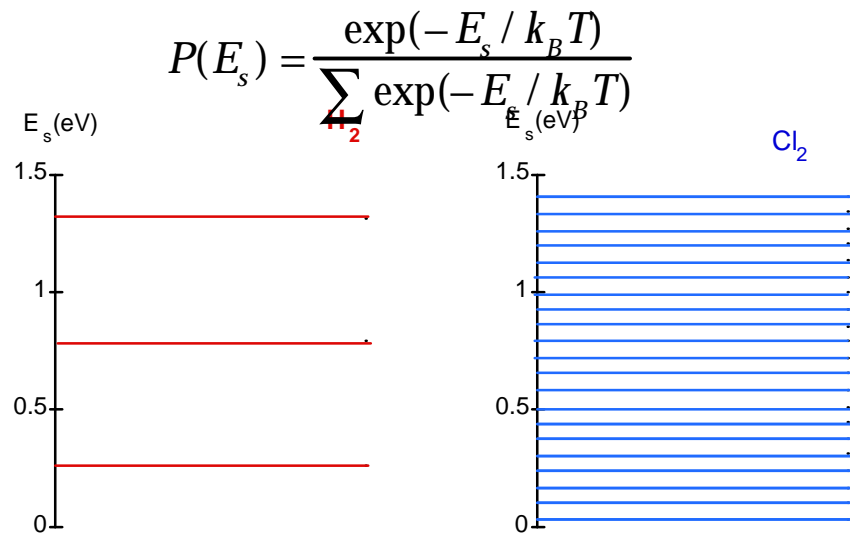
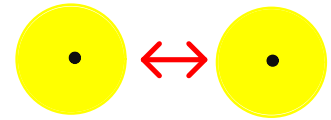


$$P(E_i) = \frac{\exp(-E_i / k_B T)}{\sum \exp(-E_i / k_B T)}$$



- Quantizzazione dei livelli vibrazionali

$$E_s = \left(s + \frac{1}{2} \right) h\nu$$



Facciamo il punto ...

• Quantizzazione dell' energia

traslazionale	$\Delta E \approx 0$	→ trattazione classica
rotazionale	$\Delta E \approx 0.001 \text{ eV}$	
vibrazionale	$\Delta E \approx 0.1 \text{ eV}$	
elettronica	$\Delta E \geq 1 \text{ eV}$	→ atomi rigidi

Possibilità di **CONTARE I MICROSTATI**

• Energia interna

$$U = E(\text{tr}) + E(\text{rot}) + E(\text{vib}) + E(\text{el}) + E(\text{str}) + E(\text{ij})$$

Termini dovuti alla struttura più interna

→ costante additiva dell'energia U_0

Interazione tra molecole: gas reali
stati condensati

• Temperatura

$T \propto U$ solo per gas ideale mono-atomico

$T \propto U(\text{tr})$ solo per gas ideale

$T \leftrightarrow$ "agitazione termica" sempre vero ?

$T \leftrightarrow$ **distribuzione** sempre vero !

• Entropia

$S \leftrightarrow$ numero di microstati

$S \leftrightarrow$ **distribuzione** come ??