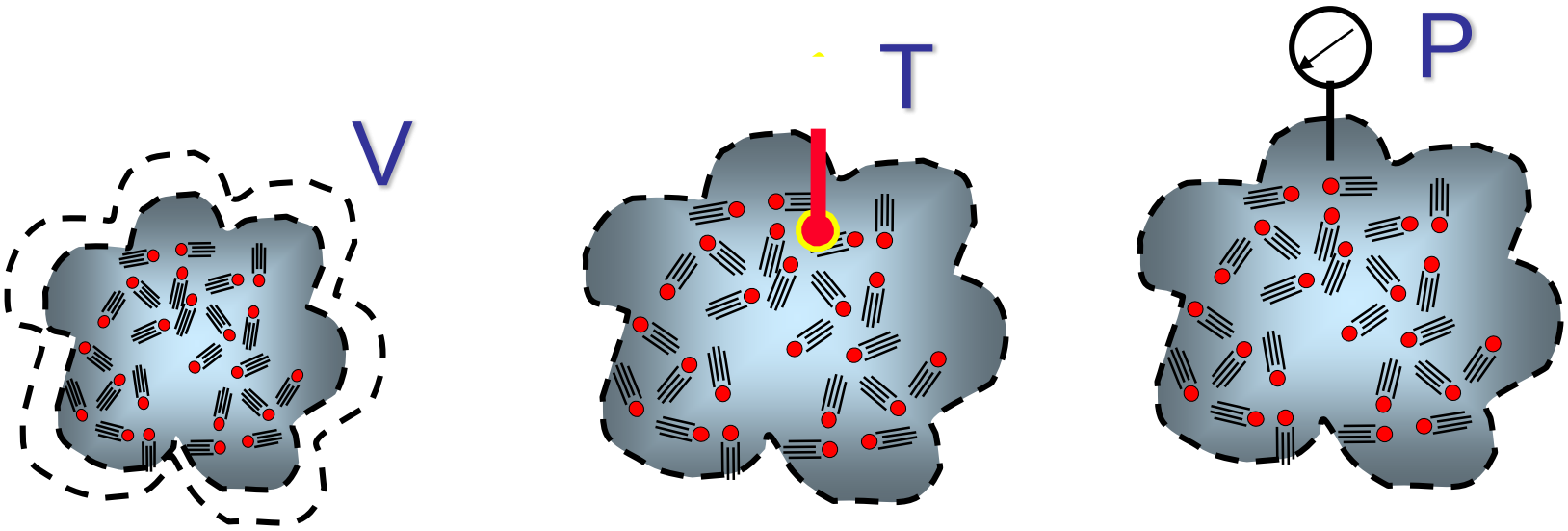
Unutarnja energija

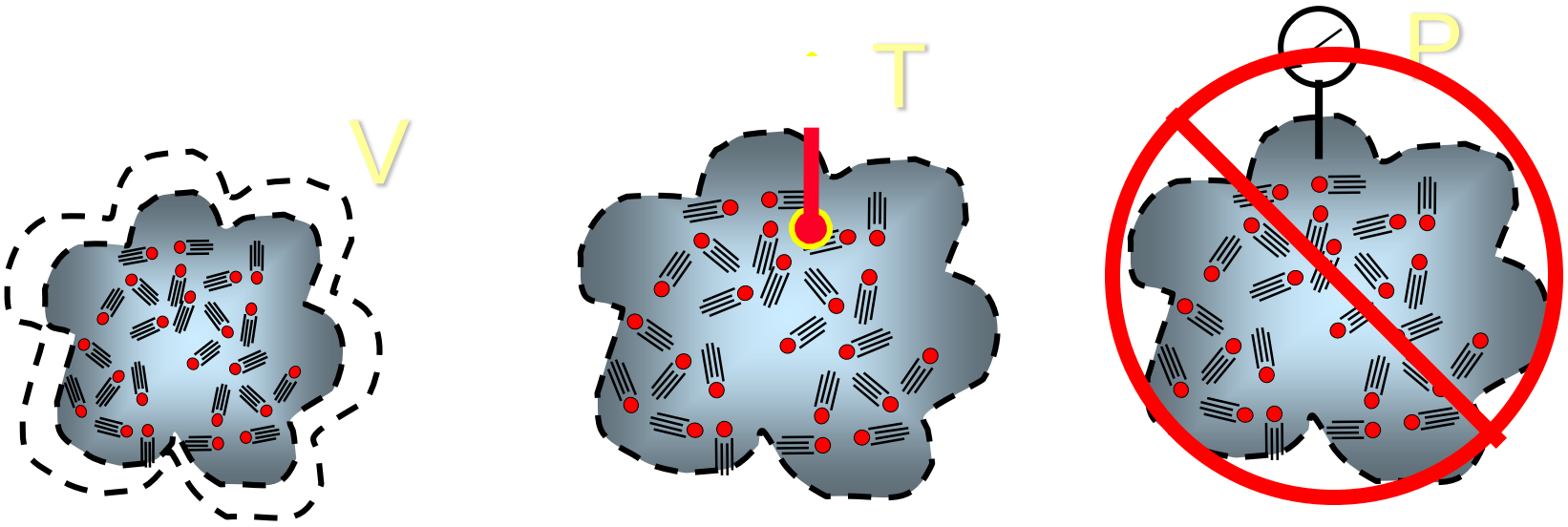
Kako ovisi o:

- Temperaturi?
- Volumenu?
- Tlaku?

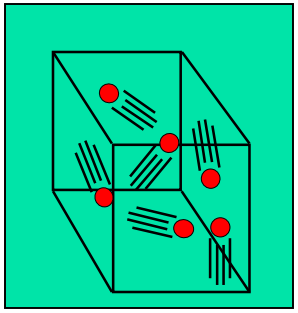


- Jednu od varijabli možemo eliminirati (jednadžba stanja!)

$$p = \frac{nRT}{V}$$

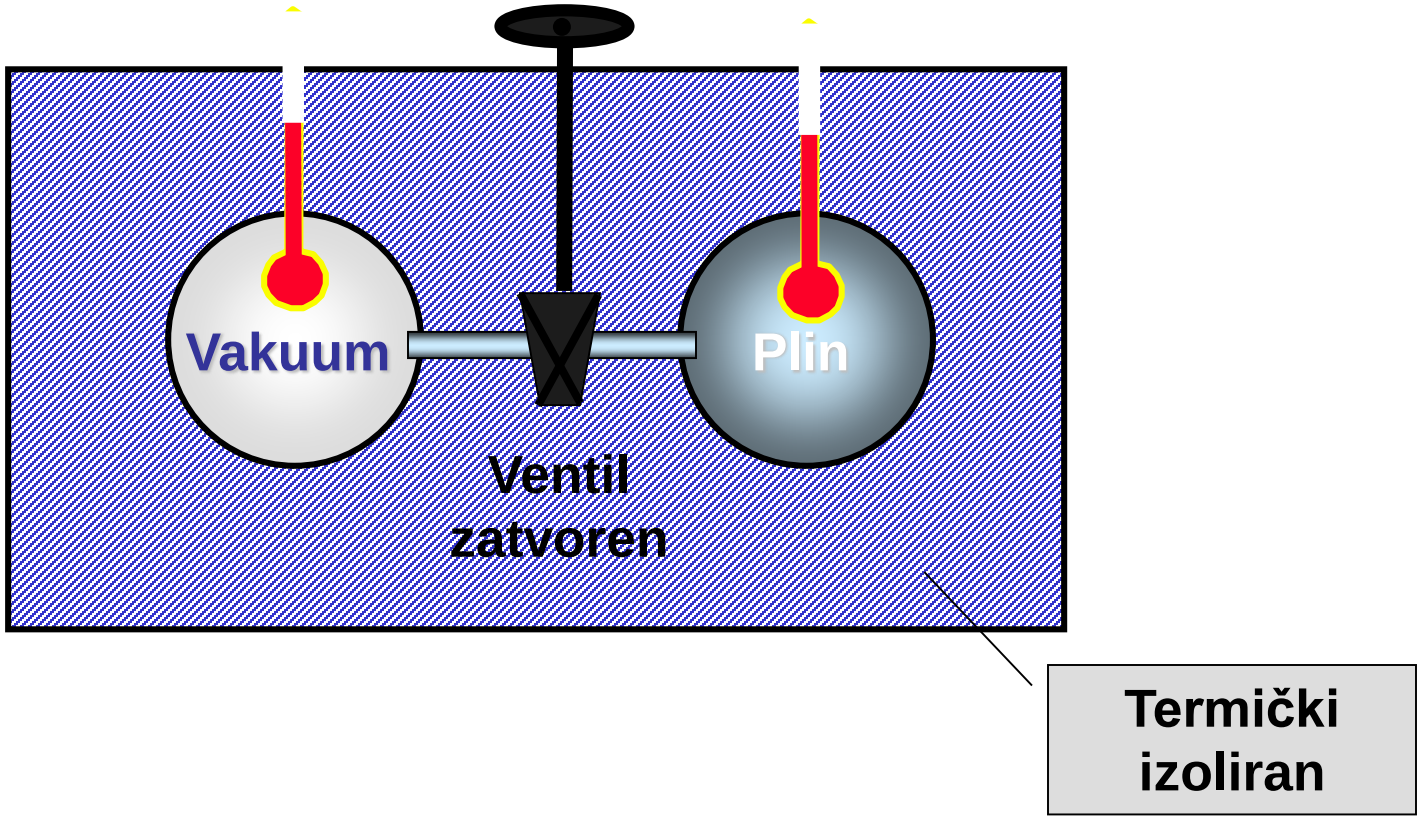


$$U = f(V,T)$$

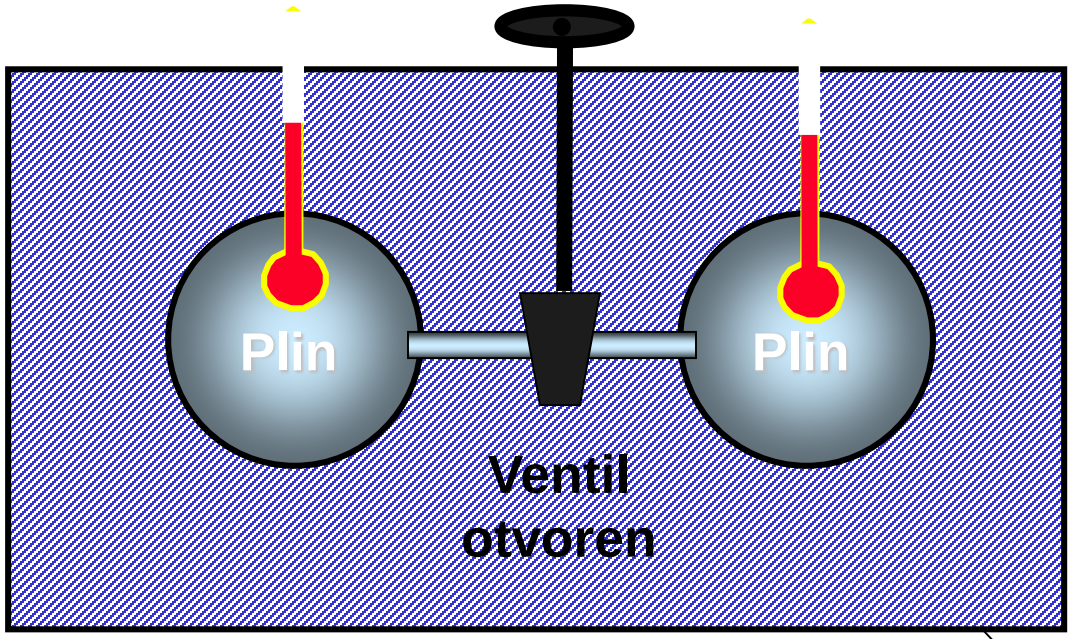


$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

- Joule-ov pokus



$$\left(\frac{\partial T}{\partial V}\right)_U$$



$$Q = 0$$

$$W = 0$$

$$\Delta U = 0$$

$$dU = 0$$

$$\left(\frac{\partial U}{\partial V}\right)_T dV = -\left(\frac{\partial U}{\partial T}\right)_V dT \qquad / \div dV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial T}\right)_V \frac{dT}{dV}$$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0}$$

Idealni plin!!!

Unutarnja energija idealnog plina je samo funkcija temperature

$$\left(\frac{\partial U}{\partial V}\right)_T <> 0$$

Realni plinovi!!!

? $$\left(\frac{\partial U}{\partial T}\right)_V$$

Konstantni volumen-IZOHORNI SUSTAV

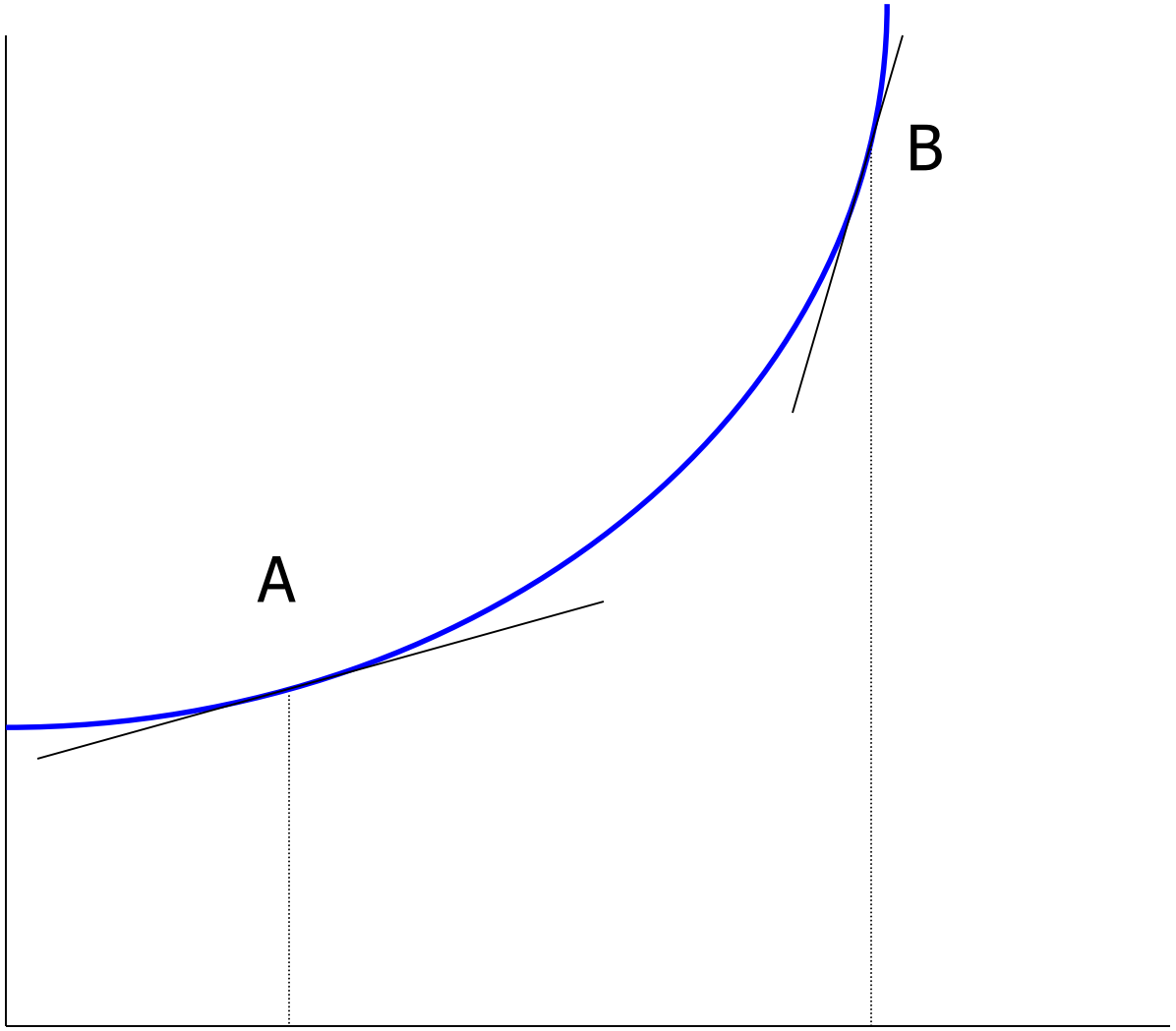
$$\Delta U = Q + W$$

$$\Delta U = Q$$

$$dU = (\delta Q)_V$$

$$\left(\frac{dU}{dT}\right)_V \equiv \left(\frac{\delta Q}{dT}\right)_V = C_V$$

Toplinski kapacitet pri konstantnom volumenu



V=konst.

Temperatura,T

Nagib tangente na krivulju je toplinski kapacitet sustava, c_v, na danoj temperaturi.

$$dU = C_V dT \qquad / \int$$

$$U_2 - U_1 = \Delta U = \int_{T_1}^{T_2} C_V dT$$

$$\Delta U_m = \int_{T_1}^{T_2} C_{V,m} dT$$

Molarni toplinski kapacitet, tablice!

IZOBARNI SUSTAVI

-konstantan tlak

(volumen se može mijenjati -moguća razmjena rada)

Promjena unutarnje energije nije jednaka dovedenoj toplini (dio energije dovedene u sustav u obliku topline vraća se u okoliš kao rad ekspanzije)

Toplina dovedena u uvjetima konstantnog tlaka jednaka je promjeni jedne druge termodinamičke veličine-entalpije

ENTALPIJA-veličina stanja, analogna unutarnjoj energiji ali u uvjetima stalnog tlaka

$$H = U + pV$$

$$H = U + pV$$

$$dH = dU + pdV + Vdp \qquad dU = \delta Q + \delta W$$

$$dU = \delta Q - pdV$$

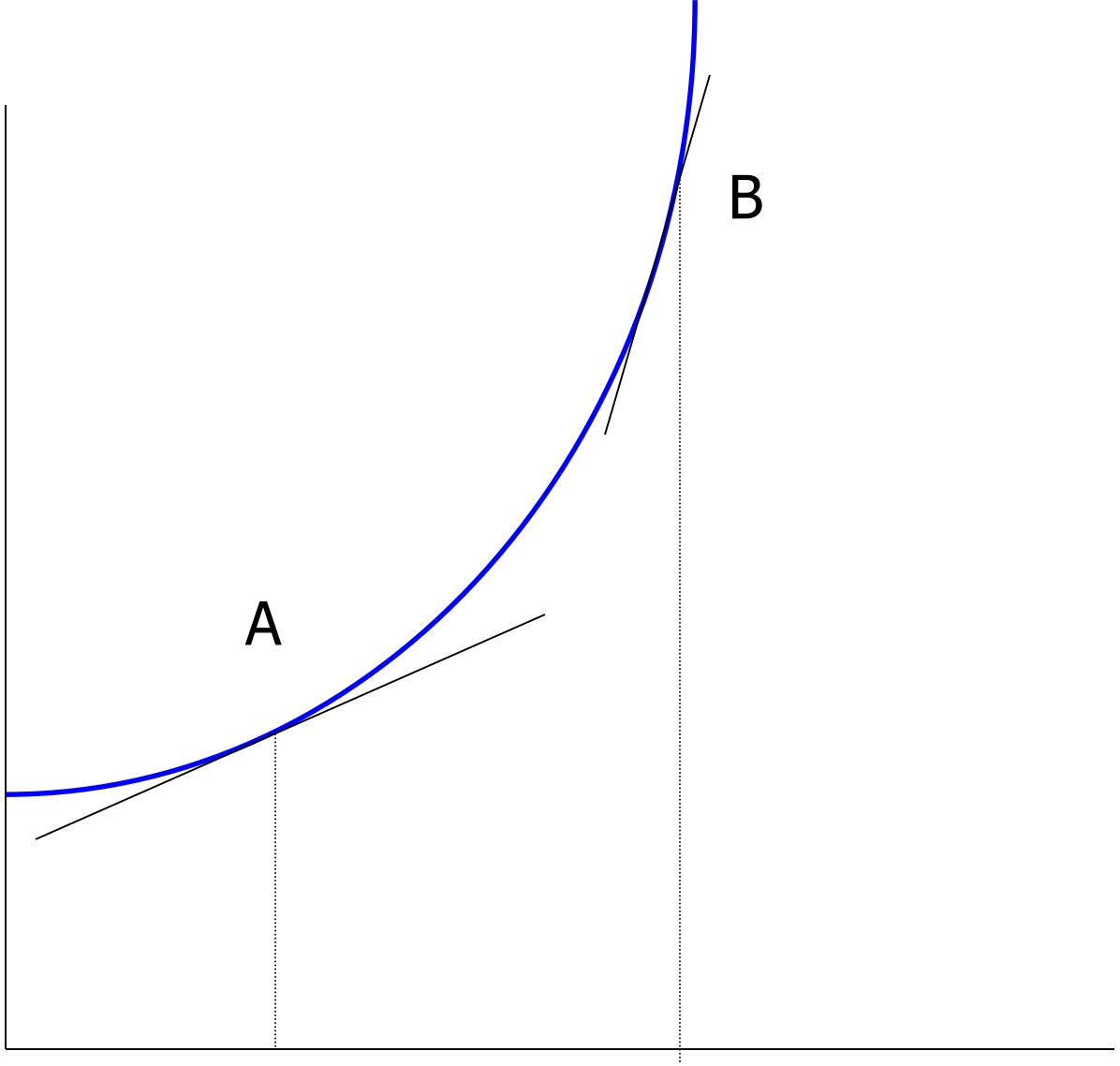
$$dH = \delta Q - pdV + pdV + Vdp$$

$$p = konst. \rightarrow dp = 0$$

$$dH = (\delta Q)_p$$

$$\left(\frac{dH}{dT}\right)_p \equiv \left(\frac{\delta Q}{dT}\right)_p = C_p$$

Toplinski kapacitet pri konstantnom tlaku



p=konst.

Nagib tangente na krivulji je toplinski kapacitet sustava, c_p, na danoj temperaturi.

$$dH = C_p dT$$

/ $\int$

$$H_2 - H_1 = \Delta H = \int_{T_1}^{T_2} C_p dT$$

$$\Delta H_m = \int_{T_1}^{T_2} C_{p,m} dT$$

? Veza između C_p i C_v

$$dU = \delta Q - pdV$$

$$\delta Q = dU + pdV$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$\delta Q = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + pdV$$

$$C_V$$

$$\delta Q = C_V dT + \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] dV$$

$/ \div dT$

$$p = konst.$$

$$\left(\frac{\delta Q}{dT} \right)_p = C_V + \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \frac{dV}{dT}$$

$$C_p = C_V + \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \frac{dV}{dT}$$

$$C_p > C_V$$

Idealni plinovi

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$pV = nRT \qquad V = \frac{nR}{p}T$$

$$dV = \frac{nR}{p}dT$$

$$C_p = C_V + \cancel{p}\frac{nR}{\cancel{p}} \qquad /\div n$$

$$C_{p,m} = C_{V,m} + R$$

Realni plinovi

$$\left(\frac{\partial U}{\partial V}\right)_T <> 0$$

$$C_{p,m} - C_{V,m} \cong 8$$

Za čvrste tvari i kapljevine:

$$C_{p,m} \approx C_{V,m}$$

$$(C_{p,m} - C_{V,m} < 0{,}02\, J mol^{-1} K^{-1})$$

KINETIČKO-MOLEKULARNO TUMAČENJE TOPLINSKIH KAPACITETA

Tablica. Toplinski kapaciteti plinova

Plin	$C_{v,m}$ /JK^{-1}mol^{-1}		$C_{p,m}$ /JK^{-1}mol^{-1}	
	300 K	1500 K	300 K	1500 K
He	12,47	12,47	20,78	20,78
Ar	12,47	12,47	20,78	20,78
H_2	20,54	23,96	28,85	32,19
N_2	20,79	26,54	29,10	34,20
O_2	21,05	28,25	29,36	36,16
HCl	21,00	25,65	29,58	34,39
Cl_2	25,44	29,71	34,07	37,91

Tablica. Toplinski kapaciteti plinova, kont.

Plin	$C_{v,m}$ /JK^{-1}mol^{-1}		$C_{p,m}$ /JK^{-1}mol^{-1}	
	300 K	1500 K	300 K	1500
CO_2	28,87	40,05	37,28	57,02
H_2O(g)	25,15	38,67	33,63	45,98
NH_3	27,2		35,56	67,33
CH_4	27,24		35,87	95,34
SO_2	31,46		39,87	
C_2H_2	35,98		43,93	

Uz pretpostavku da je unutarnja energija približno jednaka E_k translacijskog gibanja:

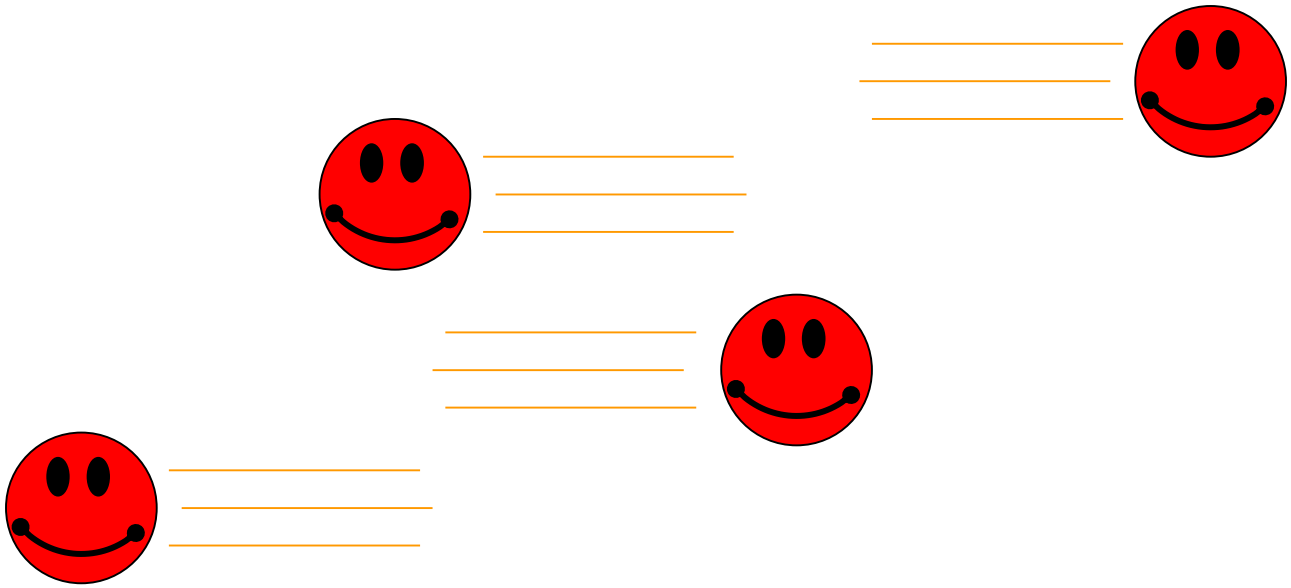
$$U \cong E_k$$

$$E_k = \frac{1}{2} M u^2 \qquad \bar{u} = \sqrt{\frac{3RT}{M}}$$

$$M \bar{u}^2 = 3RT$$

$$\overline{E_k} = \frac{1}{2} M \bar{u}^2 = \frac{3}{2} RT$$

- Monoatomni plinovi
  - Energija je rezultat translacijskog gibanja



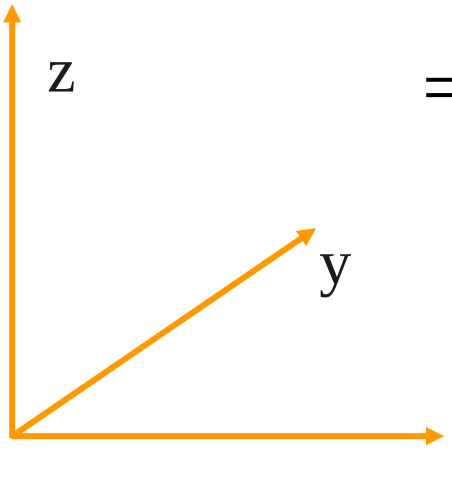
Translacijsko gibanje molekula može se rastaviti na tri komponente s istim srednjim sadržajem energije-tri stupnja slobode

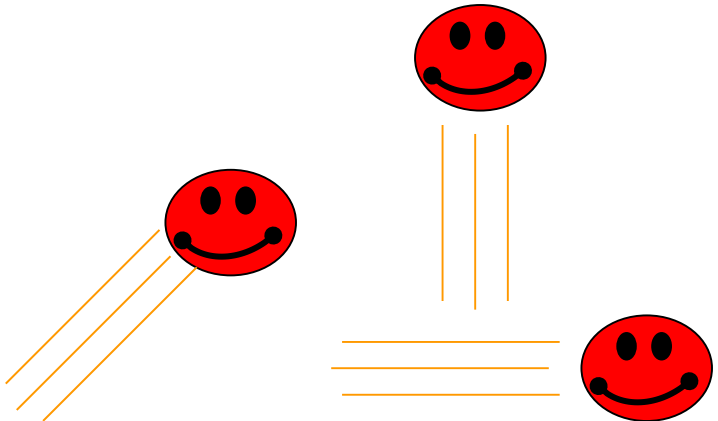
$$U_m \cong \frac{3}{2} RT$$

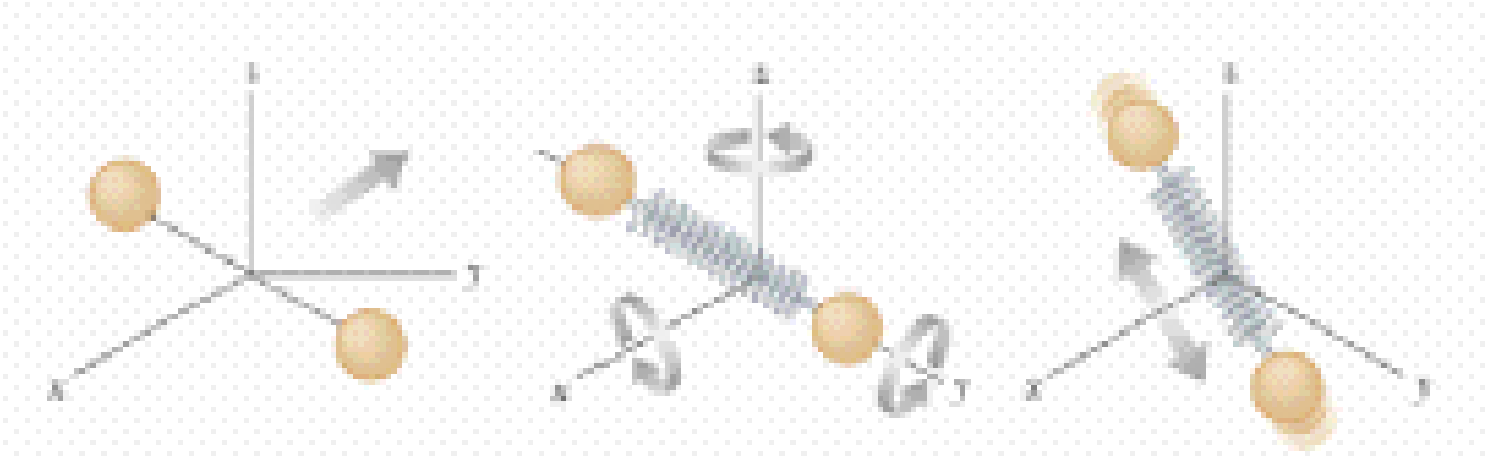
$$\left(\frac{dU_m}{dT} \right)_V = C_{V,m} = \frac{3}{2} R = 12,47\, Jmol^{-1}K^{-1}$$

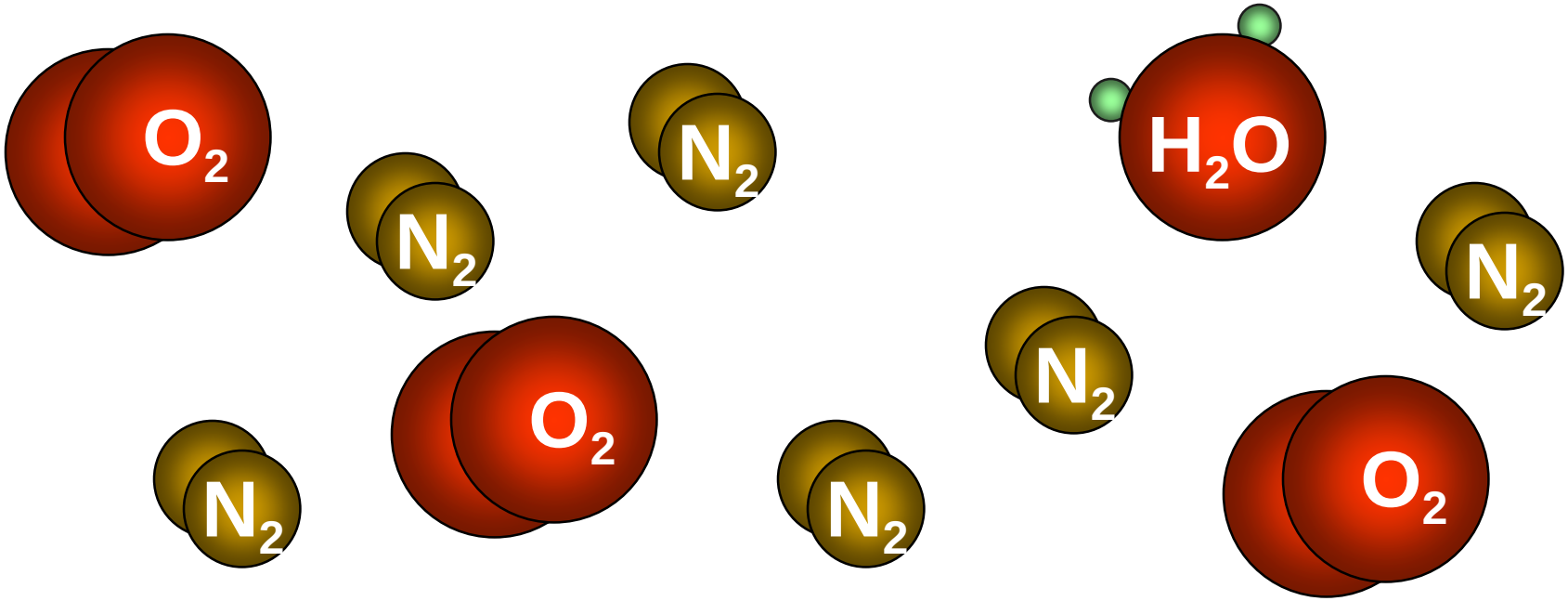
$$C_{p,m} = C_{V,m} + R = \frac{3}{2} R + R = \frac{5}{2} R =$$

$$= \frac{5}{2} \cdot 8,314 = 20,78\, Jmol^{-1}K^{-1}$$

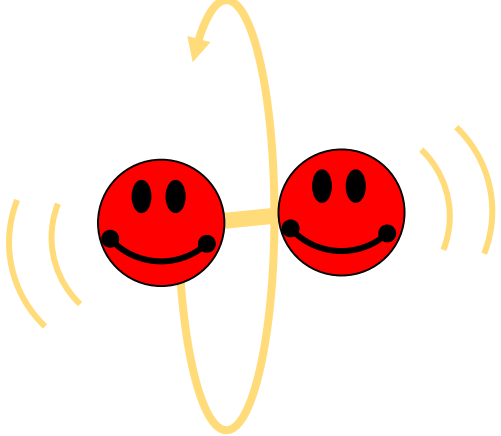




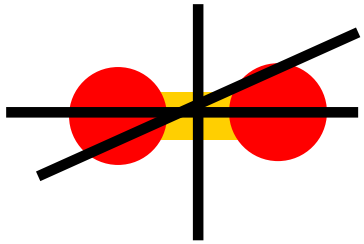



O_2
N_2
N_2
H_2O
N_2
N_2
O_2
N_2
N_2
O_2

- Dvoatomne molekule, npr.



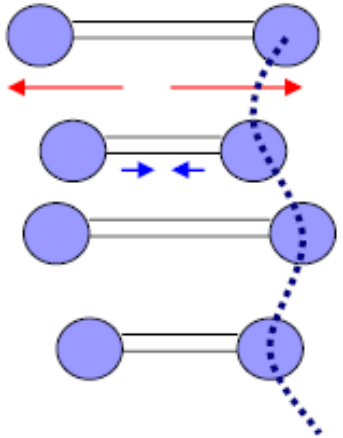
Ukupna energija molekula	**=**	**Kinetička energija uslijed translacijskog gibanja**	**+**	**Kinetička energija uslijed rotacijskog i oscilacijskog gibanja**



- Rotacijsko gibanje
- -oko 3 osi rotacije-3 stupnja slobode

$$E_{rot,\max} = \frac{3}{2} RT$$

- Oscilacijsko gibanje uzduž jedne osi:
- Harmonični oscilator
- Potencijalna energija: u prosjeku jednaka kinetičkoj energiji



-2 stupnja slobode

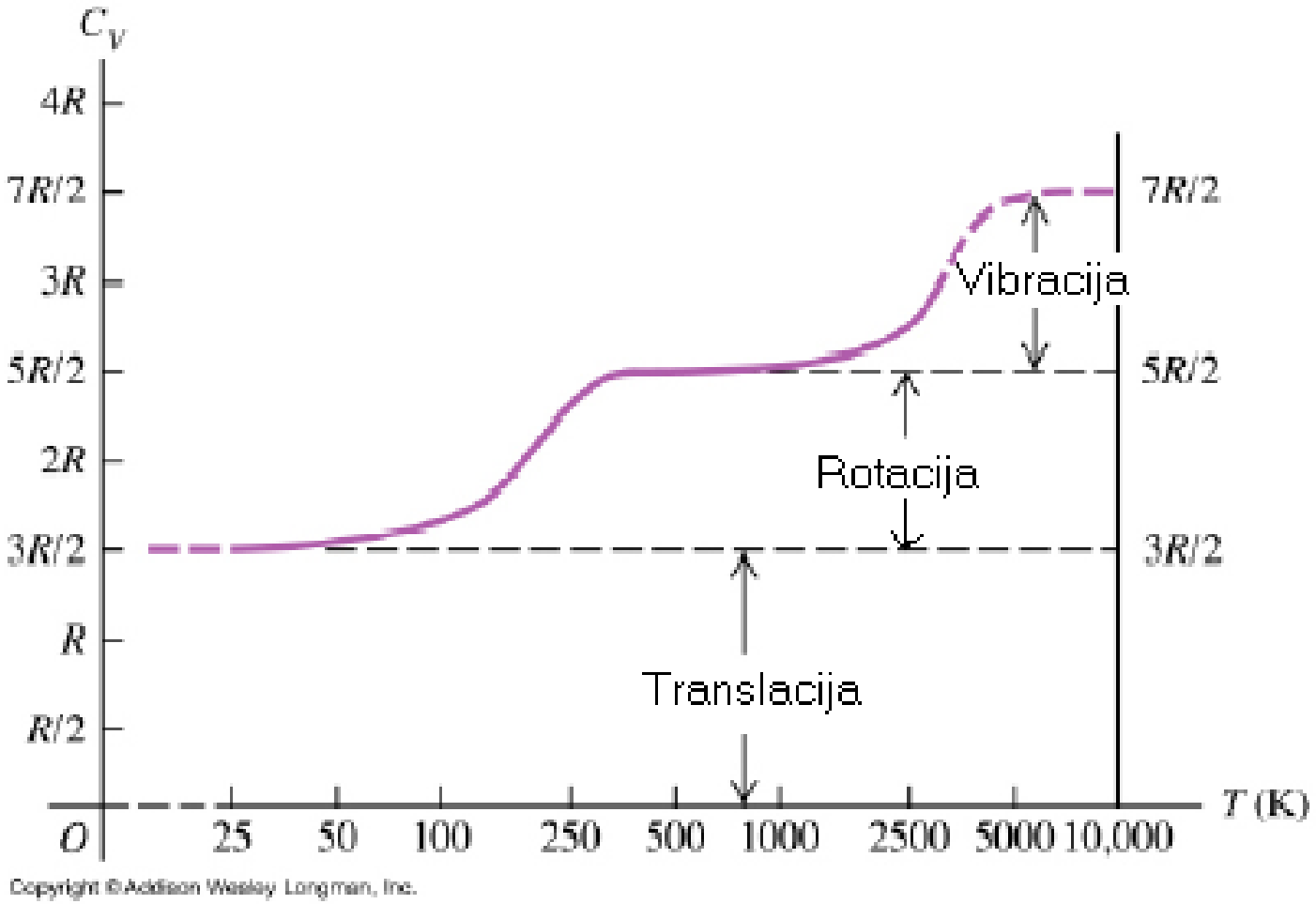
E_k i E_p=1/2RT

- Oscilacijsko gibanje uzduž tri osi:

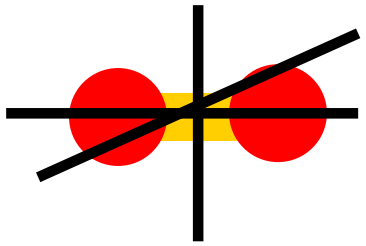
$$E_{osc,\max} = \frac{3}{2}RT + \frac{3}{2}RT = 3RT$$

- Prema klasičnoj fizici dvoatomne molekule trebale bi imati 8 stupnjeva slobode
- 3(translacije)+3(rotacije)+2(oscilacije)

- *Mjerenja* C_p i C_V za $H_{2\ npr.}$:
  - T< 70 K: $f = 3$
  - Sobna temp.: $f = 5$
  - iznad 5000 K: $f = 7$

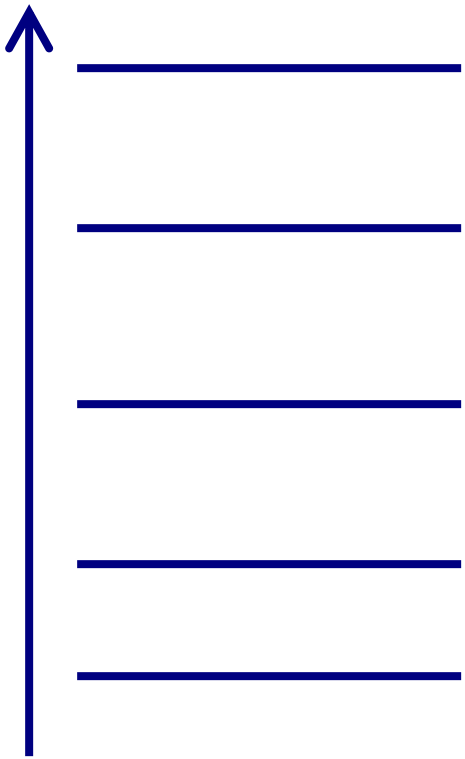


Toplinski kapacitet H_2

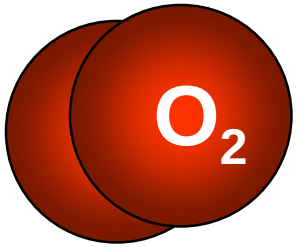


- Kvantna mehanika: rotacijska i vibracijska (oscilacijska) energija nisu kontinuirane već kvantizirane

- Rotacijska stanja
  - Oko dvije osi-mali razmaci, gotovo kontinuirana
  - Veliki razmaci oko 3. osi (kroz atome)
  - Čak pri $T=10^4$ K nema rotacije oko 3.osi



Za kisik npr. kod sobne temp.



$$U_m = \frac{3}{2}RT + \frac{2}{2}RT + 0 = \frac{5}{2}RT$$

Translacijsko gibanje

Rotacijsko gibanje

(3. radijus rotacije vrlo mali)

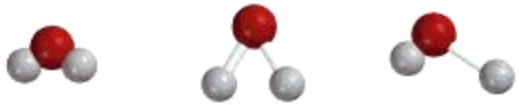
Oscilacijsko gibanje

(zanemariv doprinos oscilacijske energije)

$$\left(\frac{dU_m}{dT}\right)_V = C_{V,m} = \frac{5}{2}R = 20,8\,Jmol^{-1}K^{-1}$$

Tablica!!

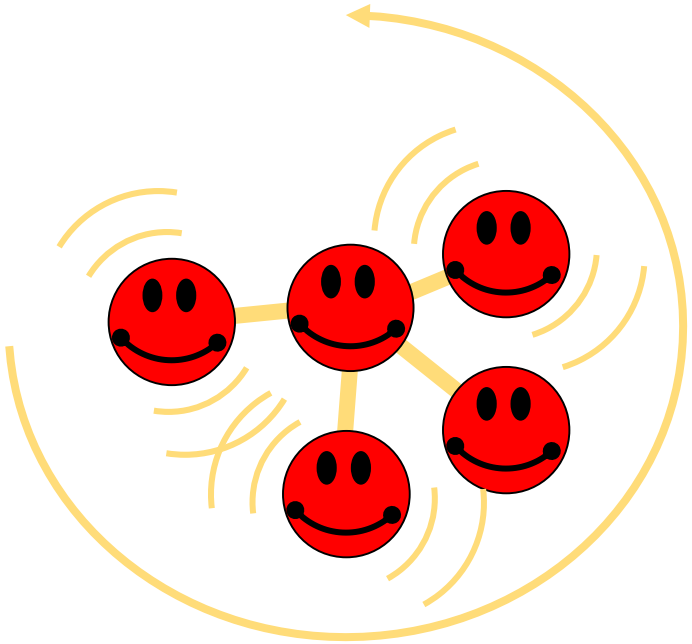
Kod visokih temperatura moramo dodati i oscilacijsku (vibracijsku) energiju



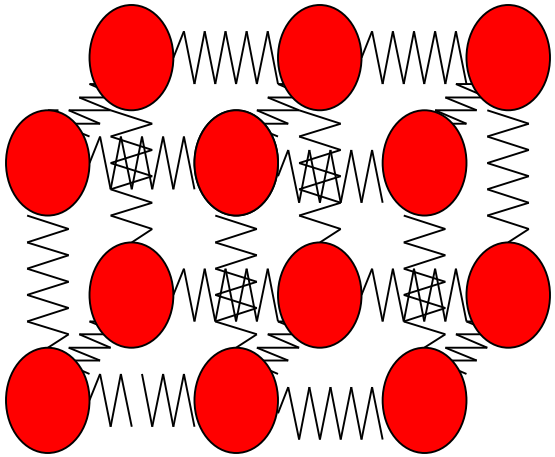
- Višeatomne molekule

$$U_m = \frac{3}{2}RT + \frac{3}{2}RT + osc.energ.$$

$$C_V > 25 \rightarrow oscilacije!!$$



- U kristalnoj rešetki
- -nema translacijskog ni rotacijskog gibanja



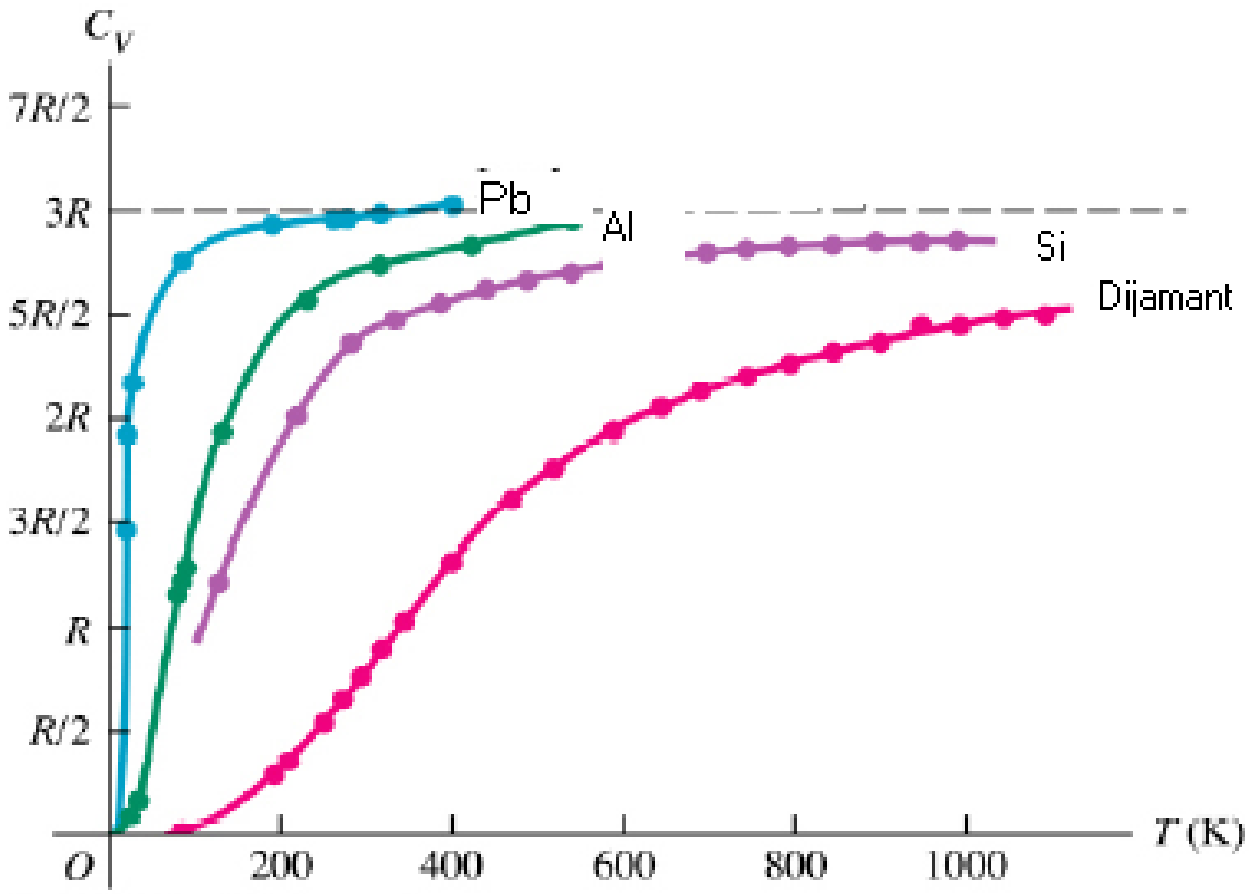
- Oscilacijski doprinos

$$U_m = E_{osc,\max} = 3\left(\frac{2}{2}RT\right) = 3RT$$

$$\left(\frac{\partial U_m}{\partial T}\right)_V = C_{V,m} = 3R \cong 25\,Jmol^{-1}K^{-1}$$

- Dulong-Petit-ovo empirijsko pravilo:

- Toplinski kapaciteti elemenata s porastom temperature asimptotski se približavaju vrijednosti od 25 J $mol^{-1}K^{-1}$


C_V
7R/2
3R
5R/2
2R
3R/2
R
R/2
O
200
400
600
800
1000
T (K)
Pb
Al
Si
Dijamant

Tablica. Toplinski kapaciteti čvrstih tvari

Tvar	C_p/JK^{-1}mol^{-1} 300 K
C (dijamant)	5,90
B	13,97
Si	20,71
Al	23,85
Cu	23,43
Bi	25,94
NaCl	49,92
SiO_2	44,43

Tablica. Toplinski kapaciteti kapljevina

Tvar	C_p/JK^{-1}mol^{-1} 300 K
H_2O (l)	75,31
CH_3OH	77,82
Hg	27,61