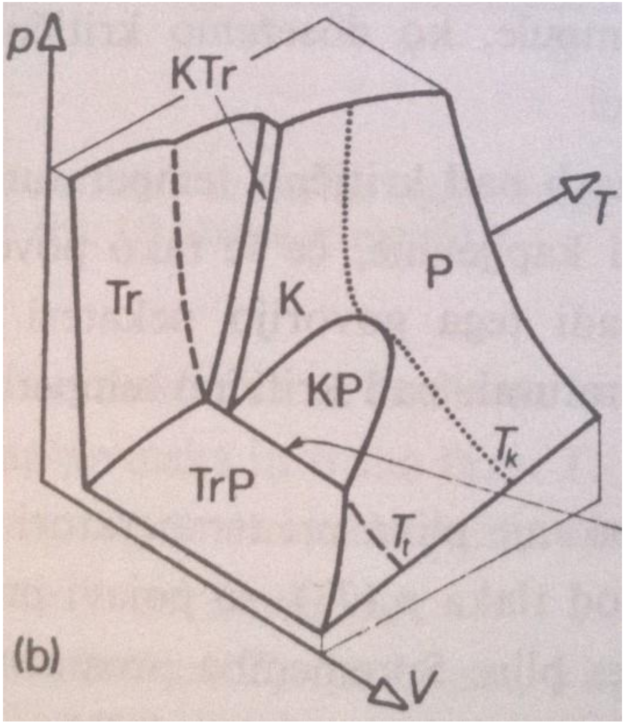
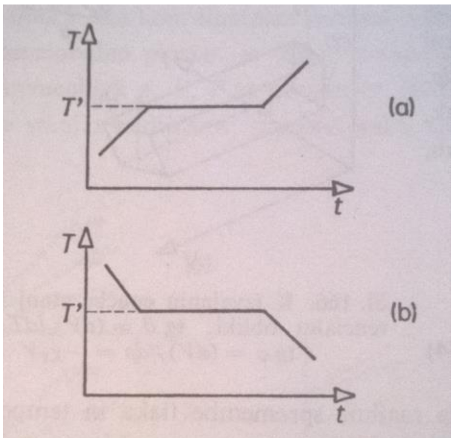
Specifična toplota, talilna toplota, izparilna toplota, ……





Sl. 167. Časovni potek temperature med dovajanjem toplote pri konstantnem tlaku (a). V sistemu pride do fazne spremembe: taljenja, izparevanja ali sublimacije. Časovni potek temperature med odvajanjem toplote pri konstantnem tlaku (b). V sistemu pride do fazne spremembe: strjevanja, utekočinjanja ali izločanja kristalov iz plina

$$\mathrm{d}W_n = \mathrm{d}Q + \mathrm{d}A \qquad V = \text{konst.} \qquad \mathrm{d}A = -p\,\mathrm{d}V = 0$$

$$(\mathrm{d}Q)_V = \mathrm{d}W_n = m\,c_V\,\mathrm{d}T$$

entalpija $\quad H = W_n + pV$

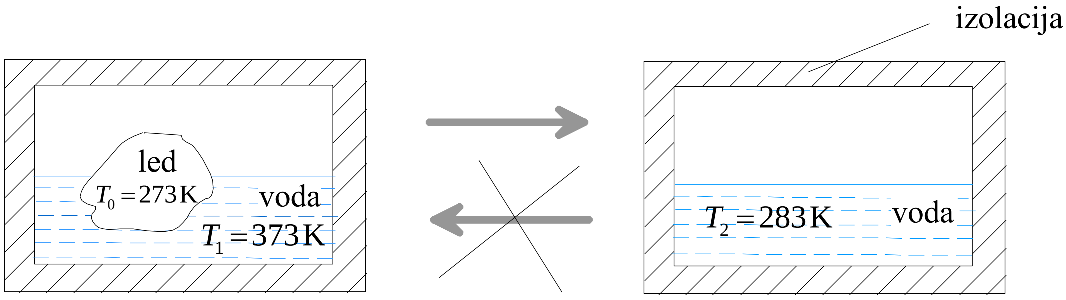
$$\mathrm{d}H = \mathrm{d}W_n + p\,\mathrm{d}V + V\mathrm{d}p = \mathrm{d}Q - p\,\mathrm{d}V + p\,\mathrm{d}V + V\mathrm{d}p = \mathrm{d}Q + V\mathrm{d}p$$

$p = \text{konst.}: \qquad (\mathrm{d}Q)_p = \mathrm{d}H$

linearni približek : $(\mathrm{d}Q)_p = \mathrm{d}H = c_p\,m\,\mathrm{d}T$

snov	izmerjena c_v pri T=273K
svinec	130 J/kg K
srebro	230 J/kg K
baker	380 J/kg K
železo	450 J/kg K
aluminij	880 J/kg K

Primer : $q_{tal} = 0.336$ MJ/kg $\quad c_p = 4186$ J/kgK



a) začetno stanje

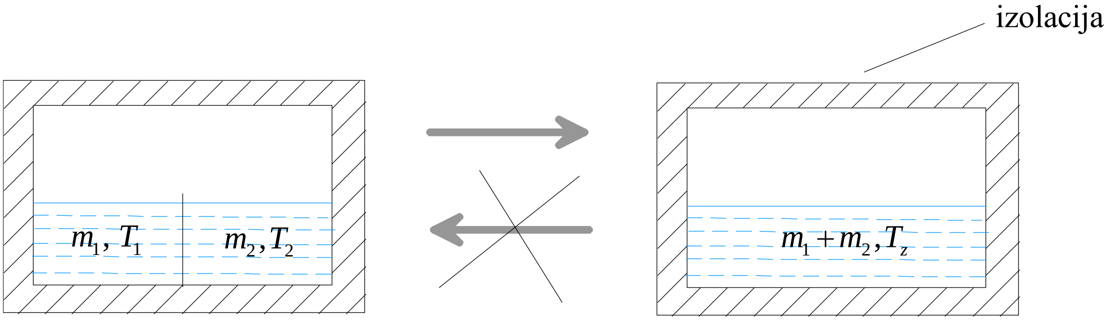
b) končno stanje

LED VODA LED

$$m_L q_{tal} + m_v c_p (T_2 - T_1) + m_L (T_2 - T_0) = 0$$

>0 $\quad <0$ $\quad >0$

Primer: ireverzibilno mešanje dveh vzorcev vode z različnima temperaturama



$T_1 = 273\,\mathrm{K}$, $\mathrm{T}_2 = 373\,\mathrm{K}$, $\mathrm{m}_1 = 1\,\mathrm{kg}$, $\mathrm{m}_2 = 1\,\mathrm{kg}$,

Računanje zmesne temperature T_z:

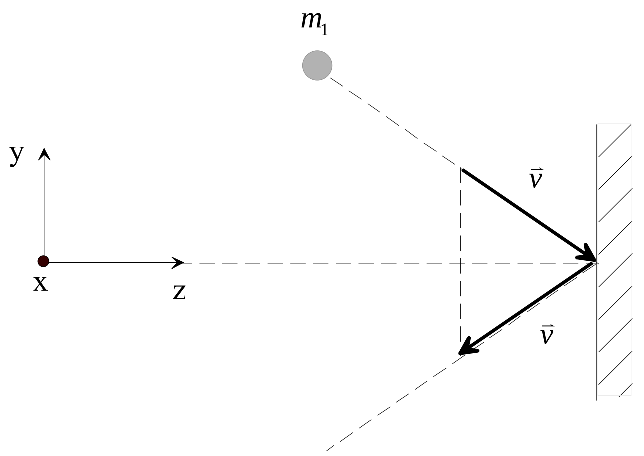
$$Q = m_1\, c_p \left(T_z - T_1\right) + m_2\, c_p \left(T_z - T_2\right) = 0$$

$$T_z = \frac{m_1\, T_1 + m_2\, T_2}{\left(m_1 + m_2\right)} = 323\,\mathrm{K}$$

Kinetična teorija plinov

Predpostavka :
tlak na stene posode s plinom je posledica trkov molekul plina ob stene

$$\vec{v} = (v_x, v_y, v_z)$$

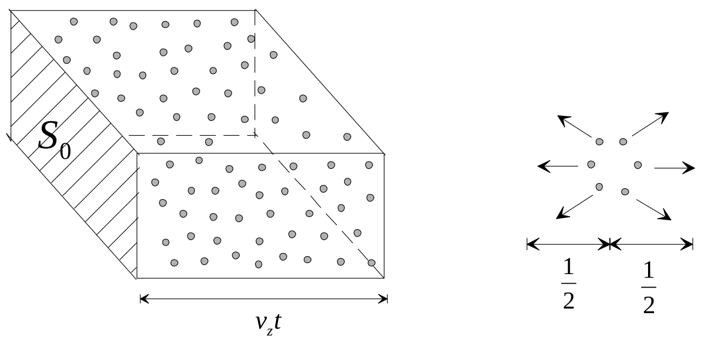


sunek sile stene na molekulo :

$$\int F_S \, dt = -m_1 v_z - m_1 v_z = -2 m_1 v_z$$

$$\int F_1 dt = -\int F_S dt = 2 m_1 v_z$$

$$N_0 = \frac{1}{2} n S_0 v_z t \qquad n = \frac{N}{V}$$



skupni sunek sile N_0 molekul na del stene s površine S_0 v času t :

$$N_0 \int_0^t F_1 \, dt = N_0 \, 2 m_1 v_z \qquad N_0 = \frac{1}{2} n S_0 v_z t \qquad p = \frac{N_0 \int_o^t F_1 \, dt}{S_0 t} = \frac{N_0 \, 2 m_1 v_z}{S_0 t}$$

$$p = \frac{N_0 \int_o^t F_1 \, \mathrm{d}t}{S_0 \, t} = \frac{N_0 \, 2 m_1 v_z}{S_0 \, t} \qquad N_0 = \frac{1}{2} n S_0 v_z t$$

$$p = n m_1 v_z^2$$

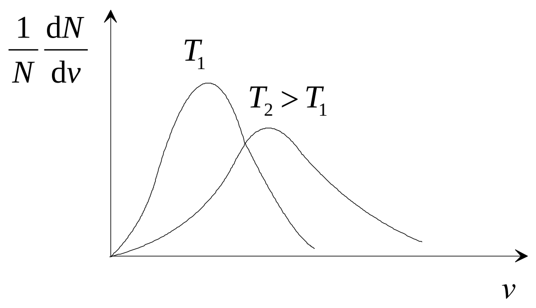
$$p = n m_1 \langle v_z^2 \rangle$$

Porazdelitev molekul po velikosti hitrosti

$$v = \left(v_x^2 + v_y^2 + v_z^2\right)^{\frac{1}{2}}$$

1931 eksperimentalno določil I. F. Zartman

teorija : **Maxwell-Boltzmanova** porazdelitvena funkcija



Normalizirana porazdelitev (verjetnostna gostota):

$$\rho(v) = \frac{1}{N}\frac{\mathrm{d}N}{\mathrm{d}v} = A v^2 \exp\left(-\frac{W_t}{kT}\right)$$

$k = 1.38 \cdot 10^{-23}$ J/K Boltzmanova konstanta $\qquad$ A = normalizacijska konstanta

translacijska kinetična energija ene molekule plina :

$$W_t = \frac{1}{2} m_1 v^2 = \frac{1}{2} m_1 \left(v_x^2 + v_y^2 + v_z^2\right)$$

Ludwig Boltzmann
(1844 - 1906)

$$\rho(v) = \frac{1}{N}\frac{\mathrm{d}N}{\mathrm{d}v} = A v^2 \exp\left(-\frac{W_t}{kT}\right)$$

$$\int_0^\infty \rho(v)\,\mathrm{d}v = \int_0^\infty A v^2 \exp\left(-\frac{m_1 v^2}{2kT}\right)\mathrm{d}v = 1$$

Opomba: faktor v^2 v Maxwell–Boltzmanovi porazdelitvi izhaja iz integracije verjetnostne gostote $\rho(v) \propto \exp\left(-\frac{m_1 v^2}{2kT}\right)$ po celem prostoru velikosti hitrosti $\mathrm{d}V_v = 4\pi v^2 \mathrm{d}v$.

nova spremenljivka : $x^2 = \frac{m_1 v^2}{2kT}$

$$\int_0^\infty A\left(\frac{2kT}{m_1}\right)^{\frac{3}{2}} x^2 e^{-x^2}\mathrm{d}x = 1$$

$$\int_0^\infty x^2 e^{-x^2}\mathrm{d}x = \frac{\pi^{\frac{1}{2}}}{4}$$

$$A = \left(\frac{m_1}{2kT}\right)^{\frac{3}{2}} \frac{4}{\pi^{\frac{1}{2}}}$$

$$\rho(v) = \left(\frac{m_1}{2kT}\right)^{\frac{3}{2}} \frac{4}{\pi^{\frac{1}{2}}} v^2 \exp\left(-\frac{m_1 v^2}{2kT}\right)$$

$$\langle v^2 \rangle = \int_0^\infty v^2 \rho(v)\,\mathrm{d}v = \frac{3kT}{m_1}$$

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = \frac{3kT}{m_1}$$

Če predpostavimo velja $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$

$$\langle v_x^2 \rangle = \frac{kT}{m_1} \qquad \langle v_y^2 \rangle = \frac{kT}{m_1} \qquad \langle v_z^2 \rangle = \frac{kT}{m_1}$$

$$p = n m_1 \langle v_z^2 \rangle \qquad p = nkT$$

$$pV = \frac{m}{M} RT$$

$n = N/V \qquad M = N_A m_1 \qquad R = N_A k = 8314\ \mathrm{J/kmol\,K}$

$N_A = 6 \cdot 10^{26}/\mathrm{kmol}$ = Avogadrovo število

Porazdelitev po velikosti hitrosti (kroglice)

Notranja energija idealnega plina enoatomnih molekul

$$W_n = N\langle W_t\rangle = N\left\langle \frac{1}{2} m_1 v^2 \right\rangle = N\left(\frac{1}{2} m_1 \langle v_x^2\rangle + \frac{1}{2} m_1 \langle v_y^2\rangle + \frac{1}{2} m_1 \langle v_z^2\rangle \right)$$

$$\langle v_x^2\rangle = \frac{kT}{m_1} \qquad \langle v_y^2\rangle = \frac{kT}{m_1} \qquad \langle v_z^2\rangle = \frac{kT}{m_1}$$

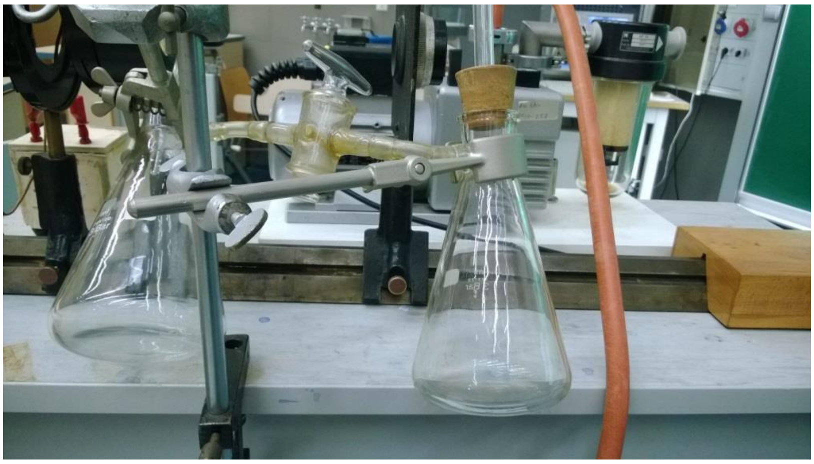
$$\frac{1}{2} m_1 \langle v_x^2\rangle = \frac{1}{2} kT \qquad \frac{1}{2} m_1 \langle v_y^2\rangle = \frac{1}{2} kT \qquad \frac{1}{2} m_1 \langle v_z^2\rangle = \frac{1}{2} kT$$

$$W_n = N\,\frac{3}{2} kT$$

$$W_n = m\left(\frac{3}{2}\frac{R}{M}\right)T \qquad m = N\,m_1$$

idealni plin : $\mathrm{d}W_n = m c_V\,\mathrm{d}T$ $\qquad c_v = \frac{3}{2}\frac{R}{M}$ $\qquad$ vedno !

HIRNOV POSKUS (za idealni plin)



splošno : $\mathrm{d}W_n = \mathrm{d}Q + \mathrm{d}A \qquad (\mathrm{d}Q)_V = \mathrm{d}W_n = m c_V\,\mathrm{d}T$ samo za V = konst.

splošno : p = konstanten

$$H = W_n + pV$$

$$\mathrm{d}H = \mathrm{d}W_n + p\,\mathrm{d}V + V\mathrm{d}p = \mathrm{d}Q - p\,\mathrm{d}V + p\,\mathrm{d}V + V\mathrm{d}p = \mathrm{d}Q + V\mathrm{d}p$$

$$(\mathrm{d}Q)_p = \mathrm{d}H = c_p\, m\,\mathrm{d}T$$

idealni plin

izobarna sprememba idealnega plina iz stanja p, V, T v stanje p_1, V_1, T_1

$$\Delta W_n = c_v\, m(T_1 - T) \qquad (Q)_p = c_p m(T_1 - T) \qquad (A)_p = -p(V_1 - V)$$

$$\Delta W_n = (Q)_p + (A)_p$$

$$c_v\, m(T_1 - T) = c_p\, m(T_1 - T) - p(V_1 - V)$$

$$pV_1 = \frac{m}{M}RT_1 \quad pV = \frac{m}{M}RT$$

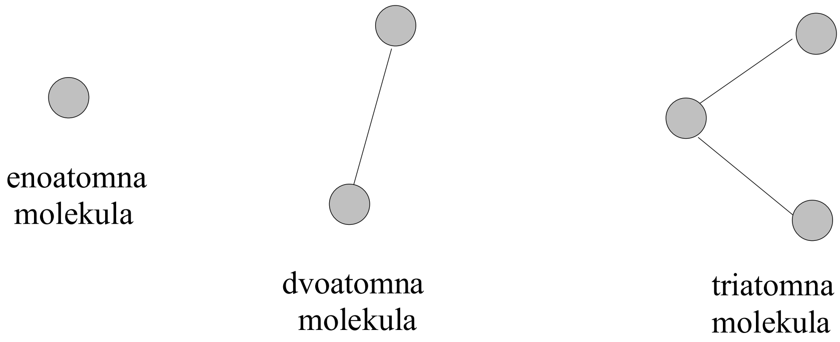
$$c_v\, m(T_1 - T) = c_p\, m(T_1 - T) - m\frac{R}{M}(T_1 - T)$$

$$c_v = c_p - \frac{R}{M} \qquad c_p = c_v + \frac{R}{M}$$

idealni plin : $c_v = \frac{3}{2}\frac{R}{M}$ $\qquad c_p = c_v + \frac{R}{M} = \frac{3}{2}\frac{R}{M} + \frac{R}{M} = \frac{5}{2}\frac{R}{M}$

$$c_p = \frac{5}{2}\frac{R}{M}$$

idealni plin : **dvoatomne** ali **triatomne** molekule



OPOZORILO: pri kinetični energiji 1-atomne molekule upoštevali le $W_{trans} = \frac{1}{2} m v^2$

W_{rot} smo zanemarili, ker so vztrajnostni momenti okoli vseh glavnih osi $J_i = \int r_i^2 \mathrm{d}m \approx 0$

rotacijska kinetična energija

2-atomna molekula : $^2W_r = \frac{1}{2} J_1 \omega_1^2 + \frac{1}{2} J_2 \omega_2^2$

3-atomna molekula : $^3W_r = \frac{1}{2} J_1 \omega_1^2 + \frac{1}{2} J_2 \omega_2^2 + \frac{1}{2} J_3 \omega_3^2$

J_1, J_2 in J_3 = vztrajnostni momenti okrog treh glavnih osi in $\vec{\omega} = (\omega_1, \omega_2, \omega_3)$

Celotna kinetična energija :

2-atomne molekule : $^2W_k = W_t + {}^2W_r = \frac{1}{2} m_1 v_x^2 + \frac{1}{2} m_1 v_y^2 + \frac{1}{2} m_1 v_z^2 + \frac{1}{2} J_1 \omega_1^2 + \frac{1}{2} J_2 \omega_2^2$

3-atomne molekule : $^3W_k = W_t + {}^3W_r = \frac{1}{2} m_1 v_x^2 + \frac{1}{2} m_1 v_y^2 + \frac{1}{2} m_1 v_z^2 + \frac{1}{2} J_1 \omega_1^2 + \frac{1}{2} J_2 \omega_2^2 + \frac{1}{2} J_3 \omega_3^2$

2-atomne molekule

$$\langle {}^2W_k \rangle = \left\langle \frac{1}{2} m_1 v_x^2 \right\rangle + \left\langle \frac{1}{2} m_1 v_y^2 \right\rangle + \left\langle \frac{1}{2} m_1 v_z^2 \right\rangle + \left\langle \frac{1}{2} J_1 \omega_1^2 \right\rangle + \left\langle \frac{1}{2} J_2 \omega_2^2 \right\rangle$$

3-atomne molekule

$$\langle {}^3W_k \rangle = \left\langle \frac{1}{2} m_1 v_x^2 \right\rangle + \left\langle \frac{1}{2} m_1 v_y^2 \right\rangle + \left\langle \frac{1}{2} m_1 v_z^2 \right\rangle + \left\langle \frac{1}{2} J_1 \omega_1^2 \right\rangle + \left\langle \frac{1}{2} J_2 \omega_2^2 \right\rangle + \left\langle \frac{1}{2} J_3 \omega_3^2 \right\rangle$$

Velja : $\left\langle \frac{1}{2} m_1 v_x^2 \right\rangle = \left\langle \frac{1}{2} m_1 v_y^2 \right\rangle = \left\langle \frac{1}{2} m_1 v_z^2 \right\rangle = \frac{1}{2} kT$

Predpostavimo : 2-atomne molekule : $\left\langle \frac{1}{2} J_1 \omega_1^2 \right\rangle = \left\langle \frac{1}{2} J_2 \omega_2^2 \right\rangle = \frac{1}{2} kT$

3-atomne mokeluke $\left\langle \frac{1}{2} J_1 \omega_1^2 \right\rangle = \left\langle \frac{1}{2} J_2 \omega_2^2 \right\rangle = \left\langle \frac{1}{2} J_3 \omega_3^2 \right\rangle = \frac{1}{2} kT$

2-atomne molekule : $W_n = N \langle {}^2W_k \rangle = N \frac{5}{2} kT$

3-atomne molekule : $W_n = N \langle {}^3W_k \rangle = N \frac{6}{2} kT$

2-atomne molekule : $W_n = m \left(\frac{5}{2} \frac{R}{M} \right) T$ $c_v = \frac{5}{2} \frac{R}{M}$

3-atomne molekule : $W_n = m \left(\frac{6}{2} \frac{R}{M} \right) T$ $c_v = \frac{6}{2} \frac{R}{M}$

$$c_p = c_v + \frac{R}{M}$$

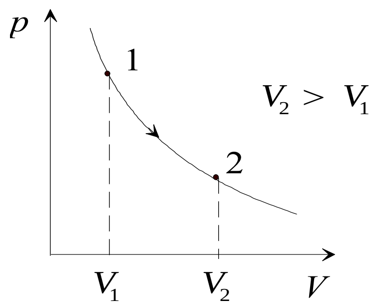
vrsta plina	c_v	c_p	$\kappa = c_p / c_v$
enoatomni	$\frac{3}{2}\frac{R}{M}$	$\frac{5}{2}\frac{R}{M}$	$\frac{5}{3} \simeq 1.66$
dvoatomni	$\frac{5}{2}\frac{R}{M}$	$\frac{7}{2}\frac{R}{M}$	$\frac{7}{5} = 1.4$
triatomni	$\frac{6}{2}\frac{R}{M}$	$\frac{8}{2}\frac{R}{M}$	$\frac{4}{3} \simeq 1.33$

izmerjene vrednosti za nekatere razredčene pline pri T = 291 K

plin	$\kappa = c_p / c_v$
helij (He)	1.66
neon (Ne)	1.64
vodik (H_2)	1.41
dušik (N_2)	1.40
kisik (O_2)	1.40
ogljikov dioksid (CO_2)	1.30
vodna para (H_2O)	1.30
žveplov dioksid (SO_2)	1.29

T = konst. $\Delta W_n = A_T + Q_T = 0$ $Q_T = -A_T$

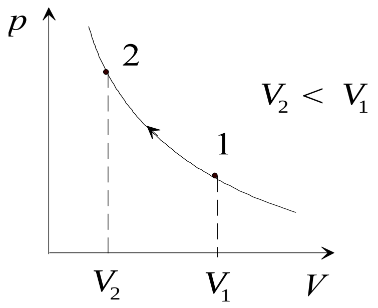
Izotermno razpenjanje plina:



$$A_T = -\int_{V_1}^{V_2} p\,\mathrm{d}V = -\int_{V_1}^{V_2} \frac{p_1 V_1}{V}\,\mathrm{d}V = -p_1 V_1 \ln V \Big|_{V_1}^{V_2} = p_1 V_1 \ln\frac{V_1}{V_2} < 0\,, \quad \text{ker } V_2 > V_1$$

izotermno **razpenjanje** idealnega plina $A_T < 0, \quad Q_T > 0$

Izotermno stiskanje plina:



$$A_T = -\int_{V_1}^{V_2} p\,\mathrm{d}V = p_1 V_1 \ln\frac{V_1}{V_2} > 0, \text{ ker } V_2 < V_1$$

izotermno **stiskanjanje** idealnega plina $A_T > 0, \quad Q_T < 0$

Adiabatne spremembe

dobro izoliran sistem in/ali če sprememba stanja idealnega plina zelo hitra : $Q \simeq 0$

$$\Delta W_n = A + Q \qquad A_Q = \Delta W_n = c_v\, m \Delta T$$

$$-p\mathrm{d}V = c_v\, m\, \mathrm{d}T$$

$$p = \frac{m}{M}\frac{RT}{V} \qquad -\frac{m}{M}RT\frac{\mathrm{d}V}{V} = c_v\, m\, \mathrm{d}T$$

$$\frac{\mathrm{d}T}{T} = -\frac{R}{M}\frac{1}{c_v}\frac{\mathrm{d}V}{V}$$

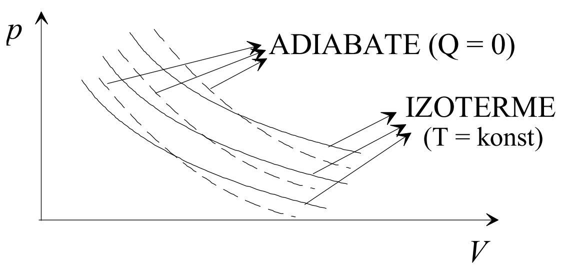
$$\frac{R}{M} = c_p - c_v \qquad \frac{\mathrm{d}T}{T} = -\left(\frac{c_p}{c_v} - 1\right)\frac{\mathrm{d}V}{V} \qquad \frac{\mathrm{d}T}{T} = -(\kappa - 1)\frac{\mathrm{d}V}{V}$$

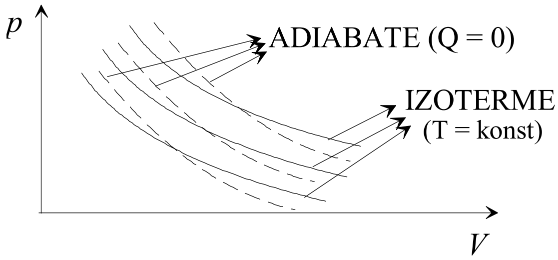
$$\int_T^{T_1}\frac{\mathrm{d}T}{T} = -(\kappa - 1)\int_V^{V_1}\frac{\mathrm{d}V}{V} \qquad \ln\frac{T_1}{T} = -(\kappa - 1)\ln\frac{V_1}{V}$$

$$\frac{T_1}{T} = \left(\frac{V}{V_1}\right)^{\kappa - 1} \qquad T_1 V_1^{\kappa - 1} = T V^{\kappa - 1}$$

Z uporabo $pV = \frac{m}{M}RT$

$$p_1 V_1^{\kappa} = p V^{\kappa} \qquad \frac{T_1^{\kappa}}{p_1^{\kappa - 1}} = \frac{T^{\kappa}}{p^{\kappa - 1}}$$





Izotermna stisljivost idealnega plina:

$$pV = \text{konst.} \;\Rightarrow p\,\mathrm{d}V + V\,\mathrm{d}p = 0 \;\Rightarrow$$

$$\Rightarrow \text{stisljivost} \quad \chi_T = -\frac{1}{V}\left(\frac{\mathrm{d}V}{\mathrm{d}p}\right)_T = \frac{1}{p}$$

Adiabatna stisljivost idealnega plina:

$$pV^{\kappa} = \text{konst.} \;\Rightarrow p\,\kappa V^{\kappa-1}\mathrm{d}V + V^{\kappa}\,\mathrm{d}p = 0 \;\Rightarrow$$

$$\Rightarrow \text{stisljivost} \quad \chi_Q = -\frac{1}{V}\left(\frac{\mathrm{d}V}{\mathrm{d}p}\right)_Q = \frac{1}{\kappa p}$$

$$\chi_Q < \chi_T$$