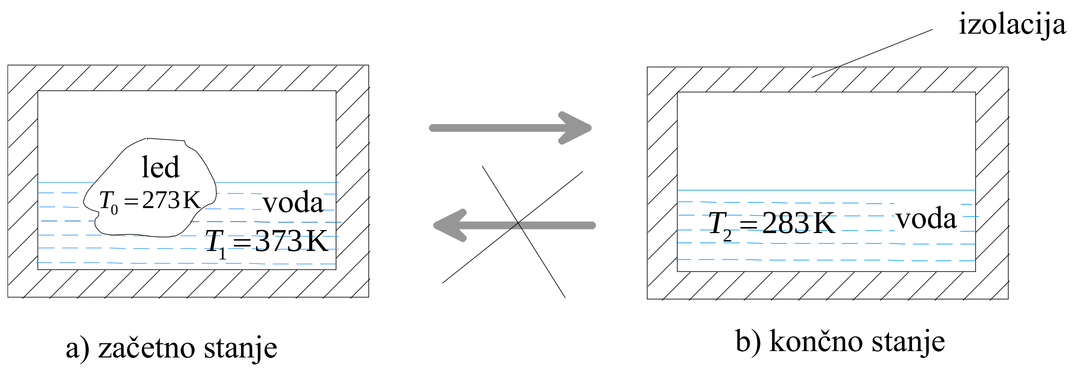
Entropija

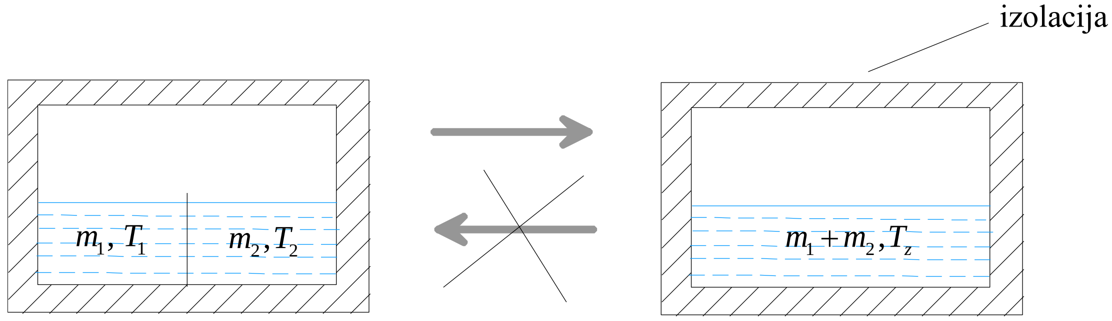
- **REVERZIBILNA sprememba**: možna je obrnjena sprememba preko enakih vmesnih stanj kot prvotna sprememba. Po obeh spremembah ne sme biti nobenih trajnih sprememb v bližnji in daljni okolici.

- **IREVERZIBILNA** sprememba: **ni** možna obrnjena sprememba (preko enakih vmesnih stanj).



a) začetno stanje

b) končno stanje



Entropijski zakon (2. zakon termodinamike)

- ni možna krožna sprememba, pri kateri bi sistem prejel toploto iz toplotnega rezervoarja in oddal enako veliko delo.

- ni možna krožna sprememba, pri kateri bi se prenesla toplota s hladnejšega telesa na toplejše telo brez vloženega dela

- matematična formulacija 2. zakona termodinamike: $\Delta S \geq \int \frac{dQ}{T}$ [J/K]

  $>$ ireverzibilna sprememba

  $=$ reverzibilna sprememba

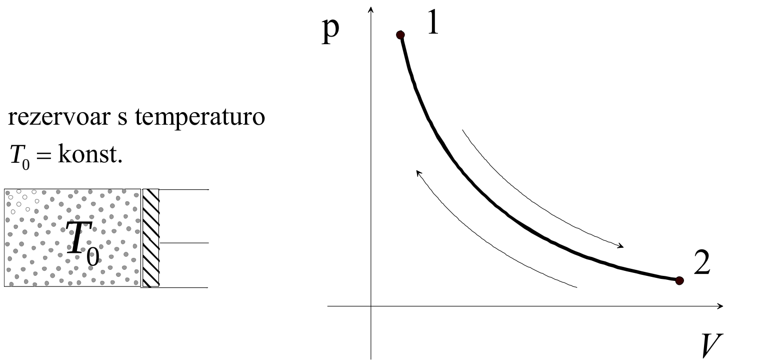
Primer: izotermno reverzibilno razpenjanje idealnega plina

$$T=\text{konst.}\Rightarrow \Delta T=0\Rightarrow \mathrm{d}W_n=\mathrm{d}Q-p\mathrm{d}V=c_v m\Delta T=0\Rightarrow$$

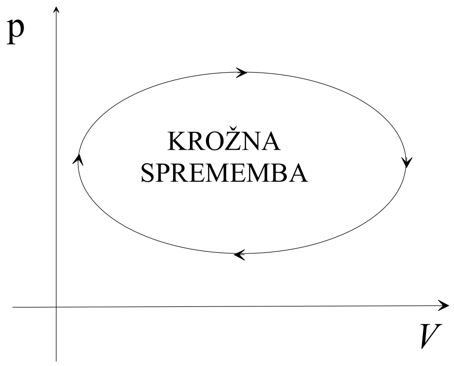
$$\Rightarrow \mathrm{d}Q=p\mathrm{d}V=\frac{m}{M}RT\frac{\mathrm{d}V}{V}\Rightarrow \frac{\mathrm{d}V}{V}\propto\frac{\mathrm{d}Q}{T}$$

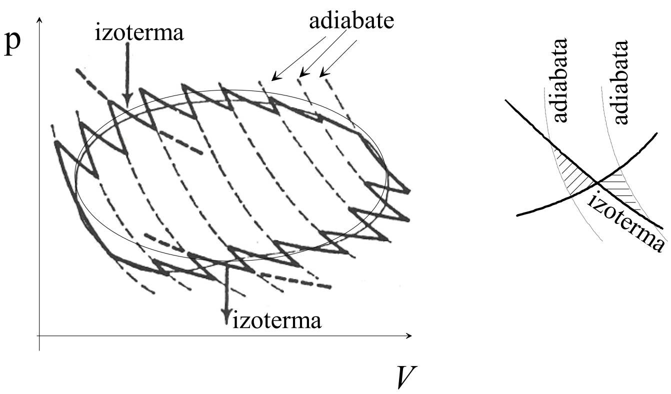
definiramo mero za »nered«: $\dfrac{\mathrm{d}V}{V}\propto\dfrac{\mathrm{d}Q}{T}$

definiramo infinitezimalno spremembo entropije: $\mathrm{d}S=\dfrac{\mathrm{d}Q}{T}\ [\mathrm{J/K}]$



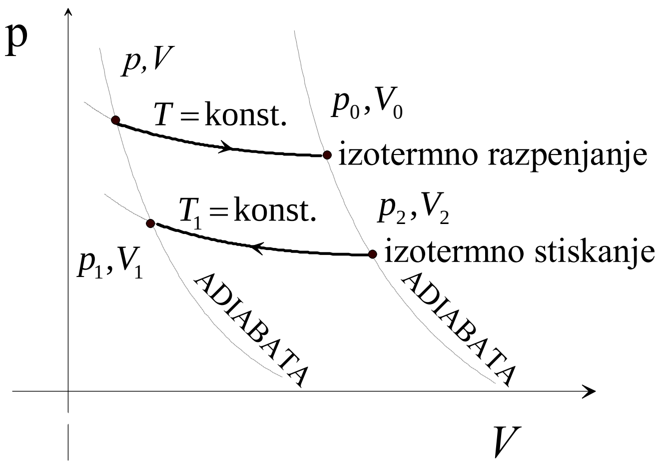
Poljubna univerzalna krožna sprememba z idealnim plinom :





Entropija je enolična funkcija stanja, zato pri krožni spremembi: $\oint dS = \oint \frac{dQ}{T} = 0$

Dokaz:



- če je T = konst. in sprememba reverzibilna:

T= konst. $\Rightarrow \mathrm{d}W_n = \mathrm{d}Q - p\mathrm{d}V = 0 \Rightarrow \mathrm{d}Q = p\mathrm{d}V$

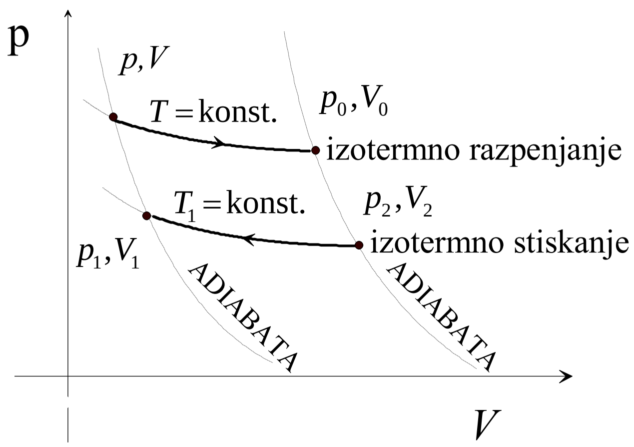
plinska enačba: $p = \frac{m}{M} RT \frac{1}{V}$

$$\Delta S = \int \frac{\mathrm{d}Q}{T} = \frac{1}{T}\int \mathrm{d}Q = \frac{1}{T}\int_{V'}^{V''} p\ \mathrm{d}V = \frac{1}{T}\frac{m}{M} RT \int_{V'}^{V''} \frac{\mathrm{d}V}{V} = \frac{m}{M} R \ln \frac{V''}{V'}$$

izoterme : $\Delta S = \frac{m}{M} R \ln \frac{V_0}{V}$

- na adiabatah :

$$\left.\begin{array}{l} T V^{\kappa-1} = T_1 V_1^{\kappa-1} \\ T V_0^{\kappa-1} = T_1 V_2^{\kappa-1} \end{array}\right\} \Rightarrow \frac{V_0}{V} = \frac{V_2}{V_1}$$



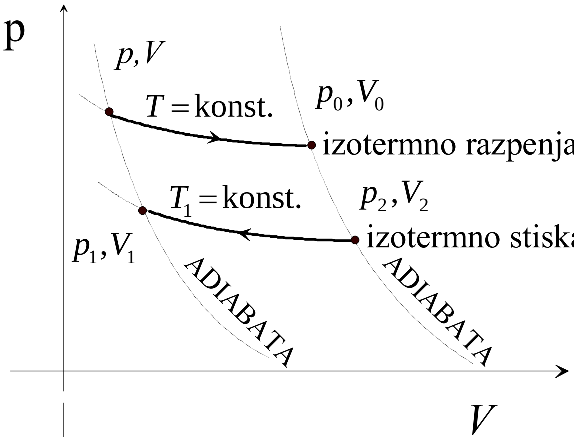
Sprememba entropije med izotermnim **razpenjanjem**: $\Delta S = \frac{m}{M} R \ln \frac{V_0}{V}$

Sprememba entropije med izotermnim **stiskanjem**:

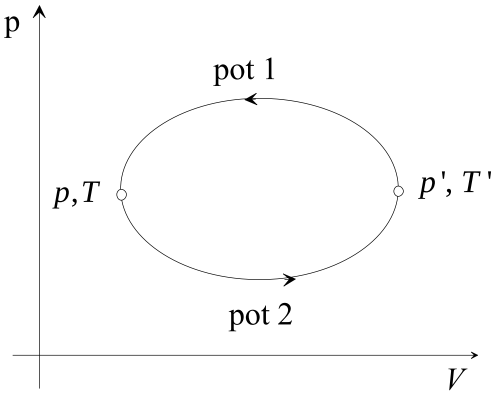
$$\frac{V}{V_0} = \frac{V_1}{V_2} \qquad \Delta S_1 = \frac{m}{M} R \ln \frac{V_1}{V_2} = \frac{m}{M} R \ln \frac{V}{V_0} = -\frac{m}{M} R \ln \frac{V_0}{V} = -\Delta S$$

skupna sprememba entropije : $\Delta S + \Delta S_1 = 0$

skupna sprememba entropije na obeh adiabatah je tudi nič



Zaključek: celotna sprememba entropije pri krožni spremembi je torej vedno enaka nič



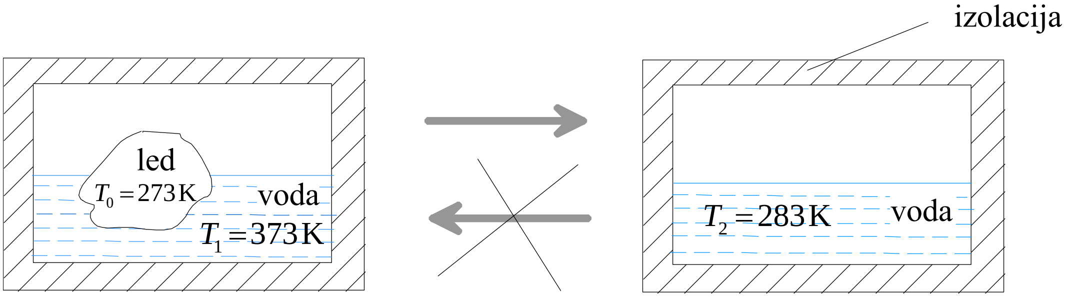
Posledica: Sprememba entropije ni odvisna od poti, pač pa samo od začetnega in končnega stanja:

$$\oint \frac{dQ}{T} = \underbrace{\int_{p',T'}^{p,T} \frac{dQ}{T}}_{\text{pot}\,1} + \underbrace{\int_{p,T}^{p',T'} \frac{dQ}{T}}_{\text{pot}\,2} = 0 \Rightarrow \underbrace{\int_{p',T'}^{p,T} \frac{dQ}{T}}_{\text{pot}\,1} = \underbrace{\int_{p',T'}^{p,T} \frac{dQ}{T}}_{\text{pot 2 v drugo smer}}$$

POSPLOŠITEV/SKLEP: če želimo izračunati spremembo entropije pri termodinamski spremembi (tudi ireverzibilni), lahko poiščemo poljubno reverzibilno (nadomestno) pot iz istega začetnega v isto končno stanje in po tej poti izračunati integral $\int \frac{dQ}{T}$.

Primeri računanja spremembe entropije ΔS pri ireverzibilnih spremembah

Primer: ireverzibilno taljenje ledu

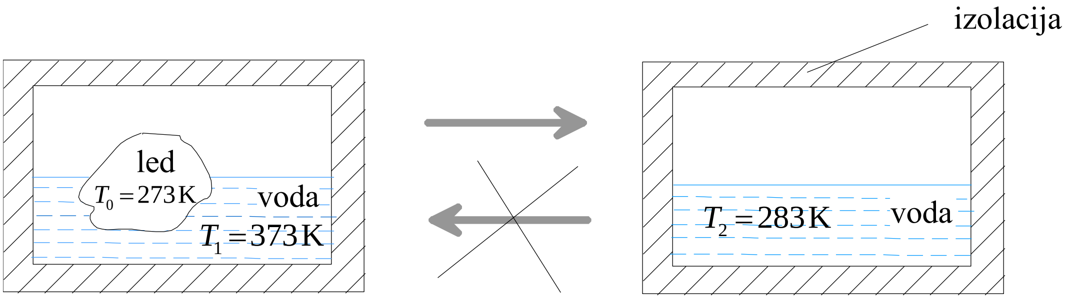


a) začetno stanje

b) končno stanje

1. zakon termodinamike (energijski zakon) dovoljuje obrnjeno spremembo!

Ker je sistem **izoliran** je $\int \frac{dQ}{T} = 0$



a) začetno stanje

b) končno stanje

Nadomestne reverzibilne spremembe I., II. in III.:

I. reverzibilno taljenje ledu: $\Delta S_0 = \dfrac{m_\ell q_{tal}}{T_0}$

II. reverzibilno segrevanje vode: $\Delta S_1 = \displaystyle\int_{T_0}^{T_2} \frac{m_\ell c_p \, dT}{T} = m_e c_p \ln \frac{T_2}{T_0}$

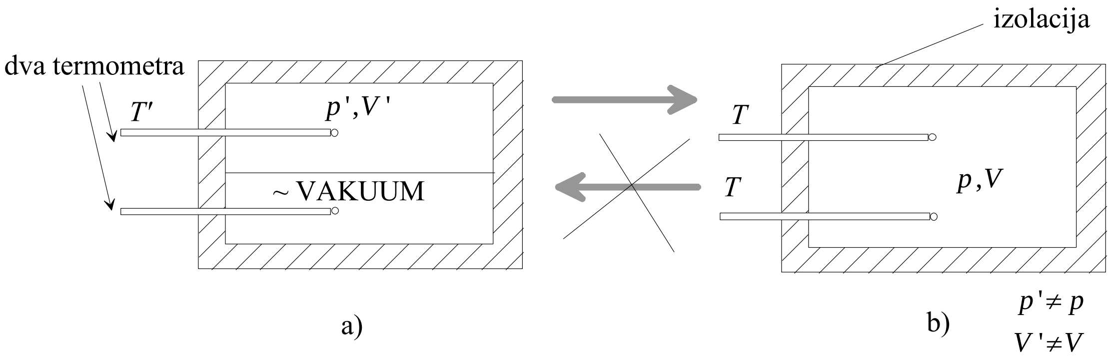
III. reverzibilno ohlajanje vode: $\Delta S_2 = \displaystyle\int_{T_1}^{T_2} \frac{m_v c_p \, dT}{T} = m_v c_p \ln \frac{T_2}{T_1}$

$\Rightarrow \Delta S = \Delta S_0 + \Delta S_1 + \Delta S_2 > 0$

torej:

$\Delta S > \int \frac{dQ}{T} = 0 \Rightarrow$ **spremememba je ireverzibilna**

Primer: **Hirnov poskus** z idealnim (razredčenim) plinom



Rezultat meritve: končna temperatura *T'* je enaka začetni temperaturi *T*

OPIS Hirnovega POSKUSA:

plin se razširi v vakuum : $\boxed{A=0}$

Sprememba je adiabatna : $\boxed{Q=0}$

$$\left.\begin{array}{l} A=0 \\ Q=0 \end{array}\right\} \Rightarrow \Delta W_n = A + Q = 0$$

$$\Delta W_n = 0 = c_v\, m \Delta T \Rightarrow \Delta T = 0 \Rightarrow T' = T$$

Računanje sprememb entropije za **nadomestno** izotermno **reverzibilno** razpenjanje idealnega plina :

Računanje sprememb entropije za **nadomestno** izotermno **reverzibilno** razpenjanje idealnega plina :

$$\mathrm{d}W_n = \mathrm{d}Q - p\,\mathrm{d}V \quad \leftarrow \quad \mathrm{d}S = \frac{\mathrm{d}Q}{T} \; oz. \;\; \mathrm{d}Q = T\mathrm{d}S$$

$$\mathrm{d}W_n = T\mathrm{d}S - p\,\mathrm{d}V$$

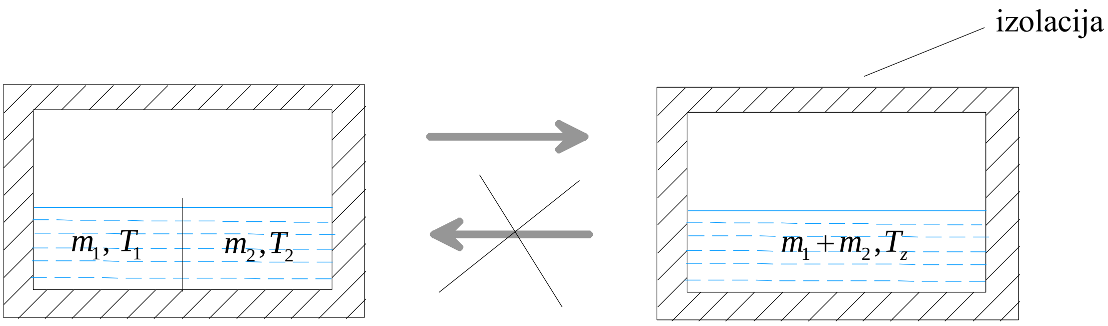
$$\underbrace{c_v m\,\mathrm{d}T}_{=0} = T\,\mathrm{d}S - p\,\mathrm{d}V = 0$$

$$\mathrm{d}S = \frac{p}{T}\mathrm{d}V \quad \leftarrow \quad \text{plinska enačba :} \; \frac{p}{T} = \frac{m}{M}R\frac{1}{V}$$

$$\Delta S = \int_{V'}^{V} \frac{p}{T}\mathrm{d}V = \int_{V'}^{V} \frac{m}{M}R\,\frac{\mathrm{d}V}{V}$$

$$\left.\begin{array}{l} \Delta S = \dfrac{m}{M}R\cdot\ln\dfrac{V}{V'} \; > \; 0 \\ \text{sistem je izoliran:} \quad \displaystyle\int\frac{\mathrm{d}Q}{T} = 0 \end{array}\right\} \Rightarrow \quad \Delta S > \int\frac{\mathrm{d}Q}{T} = 0 \quad \Rightarrow \; \text{sprememba je ireverzibilna}$$

Primer: ireverzibilno mešanje dveh vzorcev vode z različnima temperaturama



$$T_1 = 273\,\mathrm{K}, \;\; T_2 = 373\,\mathrm{K}, \; m_1 = 1\,\mathrm{kg}, \quad m_2 = 1\,\mathrm{kg},$$

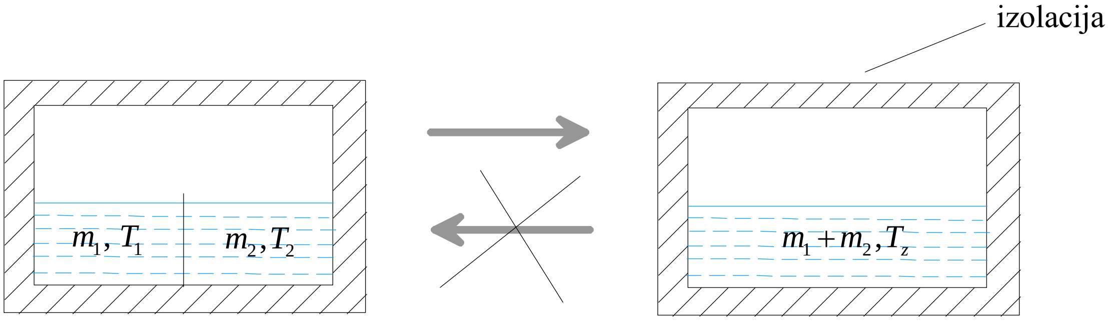
Računanje zmesne temperature T_z:

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

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

Računanje spremembe entropije **za nadomestno reverzibilno spremembo**:

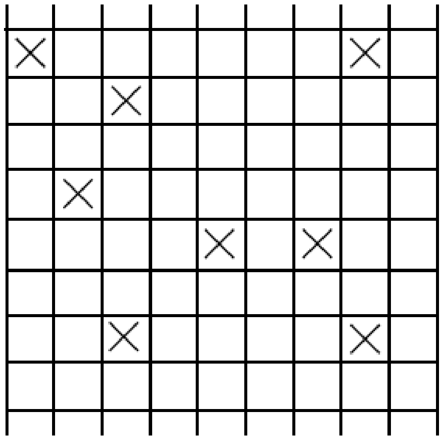
$$\left.\begin{aligned} &\Delta S = m_1 c_p \ln\frac{T_z}{T_1} + m_2 c_p \ln\frac{T_z}{T_2} > 0 \\ &\text{sistem je izoliran: } \int\frac{\mathrm{d}Q}{T} = 0 \end{aligned}\right\} \Rightarrow \Delta S > \int\frac{\mathrm{d}Q}{\mathrm{d}t} = 0 \Rightarrow \text{sprememba je ireverzibilna}$$



Statistična termodinamika: Izračun entropije in enačbe stanja idealnega plina v okviru mrežnega modela

Mrežni model

posamezna molekula plina (X) zaseda le eno mrežno mesto



$$V = M_0\, v_0$$

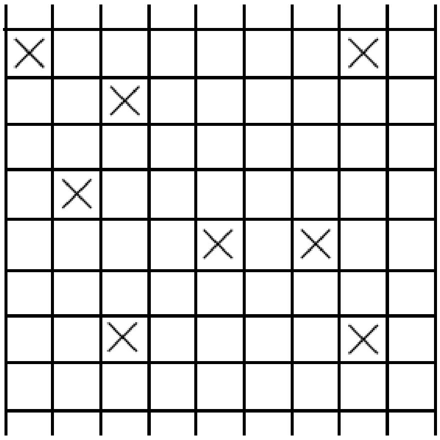
M_0 = število mrežnih mest

konfiguracijska entropija (Boltzmann) : $S = k \ln W$

W = število vseh možnih razporeditev N molekul plina na M_0 mrežnih mest

Enačba predstavlja zgodovinski temelj statistične termodinamike

A. Iglič, V. Kralj-Iglič, D. Drobne: Nanostructures in Biological Systems: Theory and ApplicationsPan Stanford Publishing Pte. Ltd. in CRC Press, 2015



$$W = \frac{M_0\left(M_0-1\right)\left(M_0-2\right)\cdots\left(M_0-\left(N-1\right)\right)}{N!} \qquad N < M_0$$

Opomba: a faktorjem $N!$ v imenovalcu upoštevamo, da so molekule **nerazločljive**

$$W = \frac{M!}{N!\left(M_0-N\right)!}$$

Stirling-ova aproksimacija za velike N: $\ln N! \simeq N\ln N - N$

$$\ln W = M_0\ln M_0 - M_0 - N\ln N + N - \left(M_0-N\right)\ln\left(M_0-N\right) + \left(M_0-N\right)$$

$$\ln W = M_0\ln M_0 - N\ln N - \left(M_0-N\right)\ln\left(M_0\left(1-\frac{N}{M_0}\right)\right) =$$

$$= M_0\ln M_0 - N\ln N - \left(M_0-N\right)\ln M_0 - \left(M_0-N\right)\ln\left(1-\frac{N}{M_0}\right) =$$

$$= -N\ln N + N\ln M_0 - \left(M_0-N\right)\ln\left(1-\frac{N}{M_0}\right).$$

$$\ln W = -N\ln\left(\frac{N}{M_0}\right) - \left(M_0-N\right)\ln\left(1-\frac{N}{M_0}\right)$$

$$S = k\ln W \qquad \ln W = -N\ln\left(\frac{N}{M_0}\right) - \left(M_0-N\right)\ln\left(1-\frac{N}{M_0}\right)$$

$$S = -k\left(N\ln\frac{N}{M_0} + (M_0 - N)\ln\left(1 - \frac{N}{M_0}\right)\right)$$

razredčen (idealni) plin : $\frac{N}{M_0} << 1$ zato $\ln\left(1 - \frac{N}{M_0}\right) \cong -\frac{N}{M_0}$

$$(M_0 - N)\ln\left(1 - \frac{N}{M_0}\right) \cong (M_0 - N)\left(-\frac{N}{M_0}\right) = -N + \frac{N^2}{M_0} = -N\left(1 - \frac{N}{M_0}\right) \cong -N$$

$$S = -k\left(N\ln\frac{N}{M_0} - N\right)$$

Primer: izotermna sprememba volumna idealnega plina

$$\Delta S = S_2 - S_1 = \left[-k\left(N\ln\frac{N}{M_2} - N\right)\right] - \left[-k\left(N\ln\frac{N}{M_1} - N\right)\right] =$$

$$= kN\left[\ln\frac{N}{M_1} - \ln\frac{N}{M_2}\right] = k\,N\ln\frac{M_2}{M_1} = k\,N\ln\frac{V_2}{V_1}$$

začetni volumen plina $V_1 = M_1 v_0$

končni volumen plina $V_2 = M_2 v_0$

$$\Delta S = \frac{k\,N_A\,N\,m_1}{N_A\,m_1}\ln\frac{V_2}{V_1} = R\frac{m}{M}\ln\frac{V_2}{V_1}$$

$R = k\,N_A$

$m = N\,m_1$

$M = N_A m_1$

$\Delta S = R\frac{m}{M}\ln\frac{V_2}{V_1}$ že izpaljali s pomočjo $\Delta S = \int\frac{dQ}{T}$

Uporaba : zaprt sistem (N = konst.)

$$\mathrm{d}W_n = dQ - p\,\mathrm{d}V \quad \text{in} \quad dQ_n = T\,\mathrm{d}S \quad \text{sledi} \quad \mathrm{d}W_n = T\,\mathrm{d}S - p\,\mathrm{d}V$$

$$\mathrm{d}S = \left(\frac{1}{T}\right)\mathrm{d}W_n + \left(\frac{p}{T}\right)\mathrm{d}V$$

druga izražava : $\mathrm{d}S = \left(\frac{\partial S}{\partial W_n}\right)_{V,N} \mathrm{d}W_n + \left(\frac{\partial S}{\partial V}\right)_{W,N} \mathrm{d}V$.

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{W_n,N} \qquad S = -k\left(N \ln \frac{N}{M_0} - N\right)$$

$$V = M_0\, v_0 \qquad \frac{p}{T} = \left(\frac{\partial S}{\partial (v_0 M_0)}\right)_{W_n,N} = \frac{1}{v_0}\left(\frac{\partial S}{\partial M_0}\right)_{W_n,N}$$

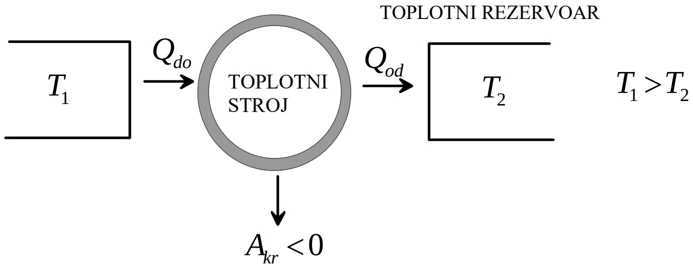
$$\frac{p}{T} = \frac{1}{v_0} k \frac{N}{M_0} = \frac{k\,N}{V}$$

$$p = \frac{N}{V} k\,T$$

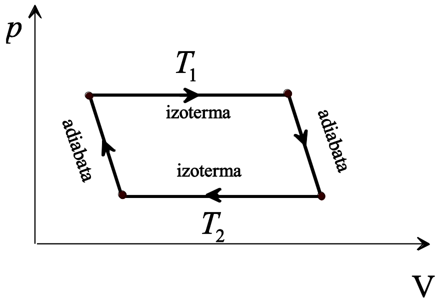
Toplotni in hladilni stroji

Idealni toplotni stroj

- krožna sprememba je reverzibilna
- stroj ponavlja Carnotovo krožno spremembo



$A_{kr} \equiv$ delo pri krožni spremembi



Stroj prejema in oddaja delo in pri tem ponavlja krožno spremembo:

$$\Delta W_n = A_{kr} + Q_{do} - |Q_{od}| = 0 \qquad \Rightarrow \quad |A_{kr}| = -A_{kr} = Q_{do} - |Q_{od}|$$

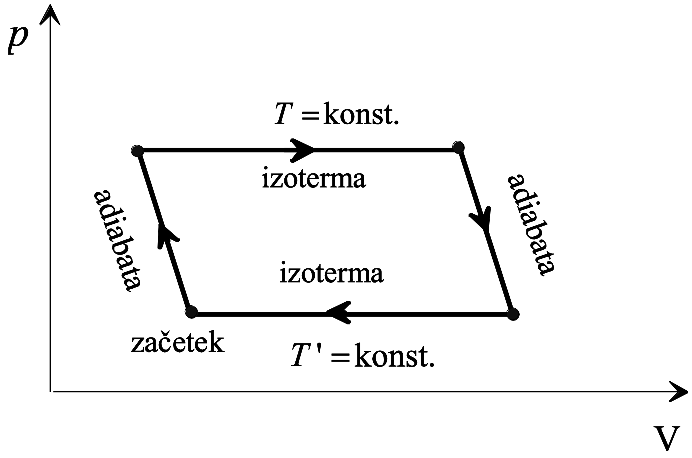
$$\Delta S = \frac{Q_{do}}{T_1} - \frac{|Q_{od}|}{T_2} = 0 \qquad \Rightarrow \frac{|Q_{od}|}{Q_{do}} = \frac{T_2}{T_1}$$

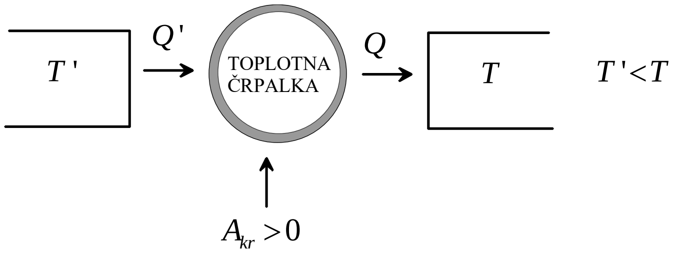
izkoristek $\equiv \eta = \dfrac{|A_{kr}|}{Q_{do}} = \dfrac{Q_{do} - |Q_{od}|}{Q_{do}} = 1 - \dfrac{|Q_{od}|}{Q_{do}} = 1 - \dfrac{T_2}{T_1}$,

oziroma: $|A_{kr}| = Q_{do}\left(1 - \dfrac{T_2}{T_1}\right)$.

če $T_2 = T_1 \Rightarrow |A_{kr}| = 0 \quad \Rightarrow$ **izotermnega toplotnega stroja ni**

Idealni hladilni stroj





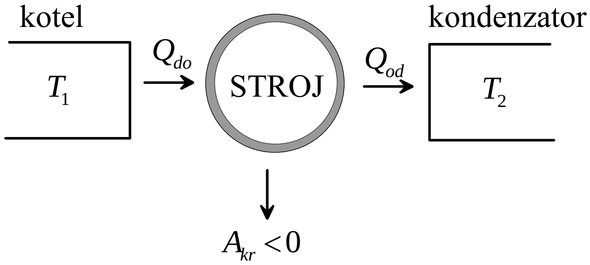
$$\Delta W_n = A_{kr} + Q' - |Q| = 0 \quad \Rightarrow A_{kr} = |Q| - Q'$$

$$\Delta S = \frac{Q'}{T'} - \frac{|Q|}{T} = 0 \quad \Rightarrow \frac{|Q|}{Q'} = \frac{T}{T'}$$

$$\frac{A_{kr}}{Q'} = \frac{|Q| - Q'}{Q'} = \frac{|Q|}{Q'} - 1 = \left(\frac{T}{T'} - 1\right)$$

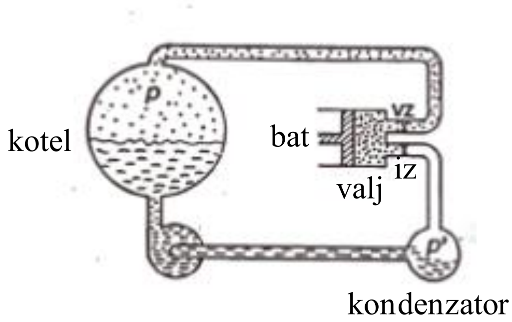
$$Q' = \frac{A_{kr}}{\left(\frac{T}{T'} - 1\right)}$$

Primer: parni stroj



- Idealni parni stroj:

- Realni parni stroj:



slika: J. Strnad, Fizika I. del