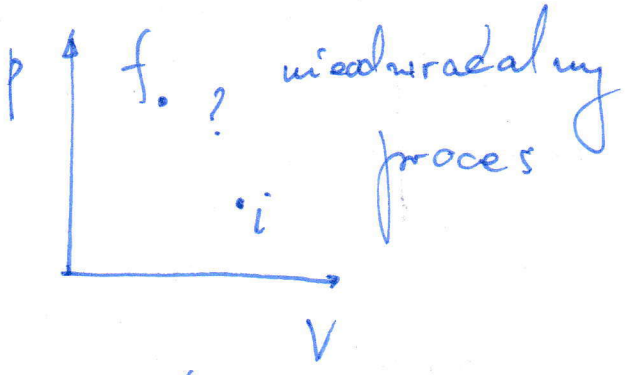
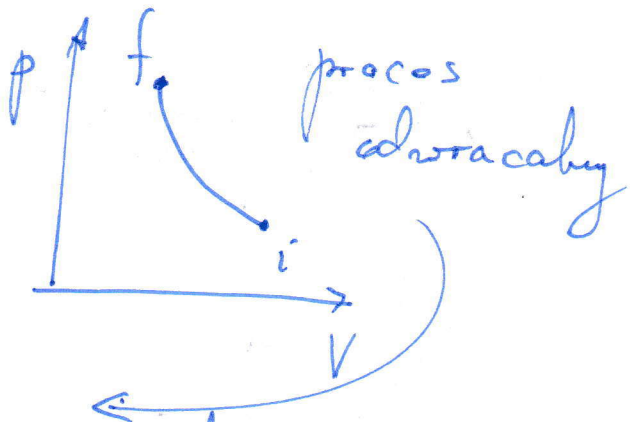
Entropia i II zasada TD

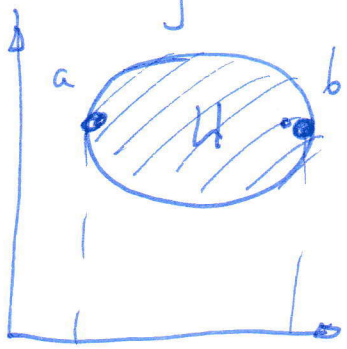


niedwracalny proces



proces odwracalny

$\oint dW = 0$



Za pomocą różniczkowej zmiany otoczenia można wywołać p. odwrotny

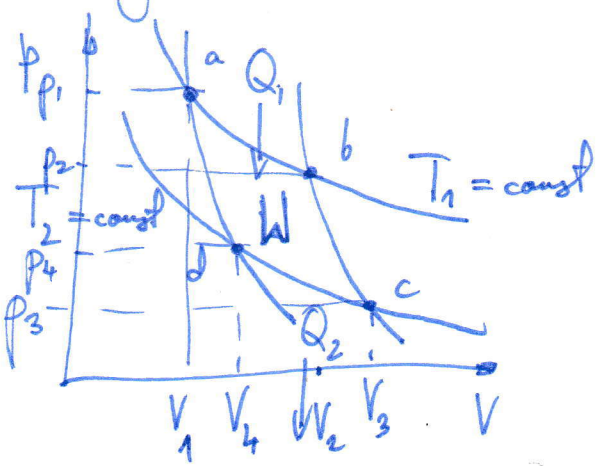
Silnik cieplny

$W = Q_1 - Q_2$

Sprawność

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

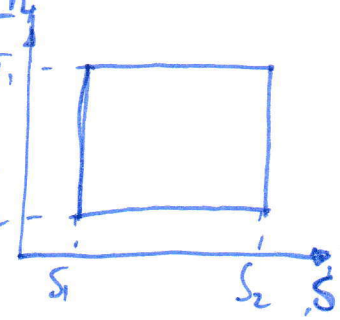
Cykl Carnota



$$Q_1 = W_1 = R T_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$Q_2 = W_2 = R T_2 \ln\left(\frac{V_3}{V_4}\right)$$

$$\frac{Q_1}{Q_2} = \frac{T_1 \ln \frac{V_2}{V_1}}{T_2 \ln \frac{V_3}{V_4}}$$



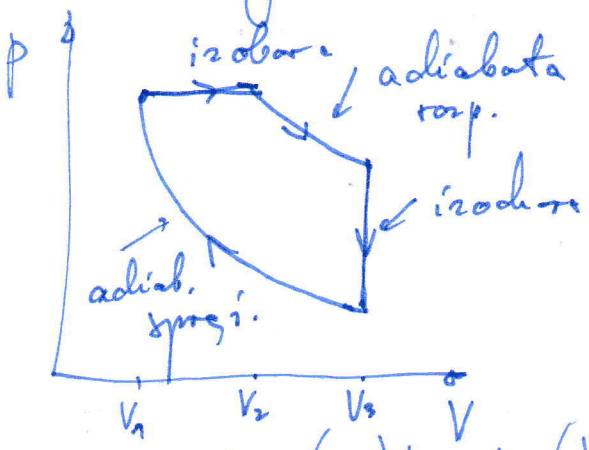
ale

$$\left.\begin{aligned} p_1 V_1 &= p_2 V_2 \\ p_3 V_3 &= p_4 V_4 \\ p_2 V_2^{\kappa} &= p_3 V_3^{\kappa} \\ p_4 V_4^{\kappa} &= p_1 V_1^{\kappa} \end{aligned}\right\} \Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

czyli

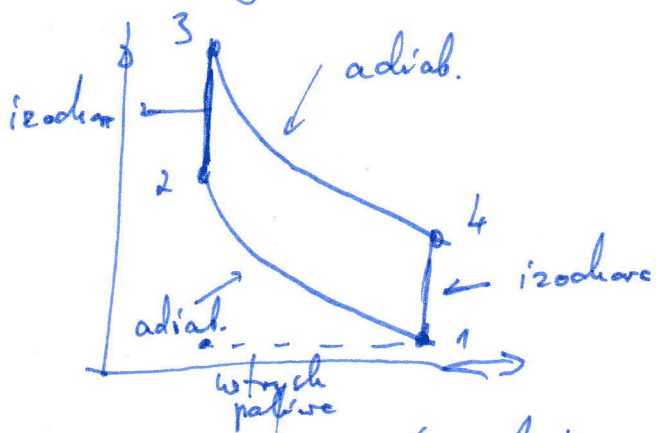
$$\eta = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}$$

Cykl Diesla



$$\eta = 1 - \frac{C_v}{C_p}\left(\frac{V_2}{V_3}\right)^{\kappa-1}\frac{1-\left(\frac{V_1}{V_2}\right)^{\kappa}}{1-\frac{V_1}{V_2}}$$

Cykl Otto

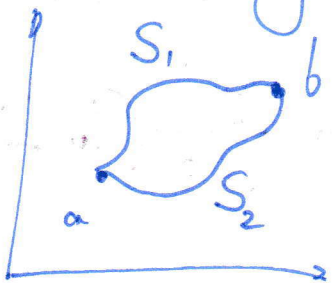


$$\eta = 1 - \left(\frac{V_1}{V_2}\right)^{1-\kappa}$$

Entropia #1

$dS = \frac{dQ}{T}$ w procesach odwracalnych

$$\oint dS = 0 \Rightarrow \int_a^b dS_1 + \int_b^a dS_2 = 0$$



Rozróżnienie procesów odwracalnych i nieodwracalnych za pomocą entropii

II zasada TD

Procesy termodyn. przebiegają samorzutnie w takim kierunku aby entropia nie zmalała

$$\boxed{dS \geq 0}$$

p. odwracalny $S_f = S_i$

p. nieodwracalny $S_f > S_i$

- Rozprężanie gazu $T = const$

$dQ = pdV$

$dS = \frac{dQ}{T} = \frac{pdV}{T}$ ale $pV = RT$

$\int_i^f dS = R \int_{V_i}^{V_f} \frac{dV}{V} \Rightarrow S_f - S_i = R \ln \frac{V_f}{V_i}$ (entropia rośnie!)

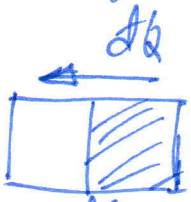
- Topnienie lodu

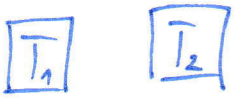
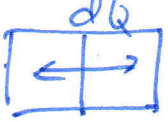
$S_{wody} - S_{lodu} = \int \frac{dQ}{T} = \frac{Q}{T} = \frac{7.96 \cdot 10^4 \, cal}{273 \, K} = 1220 \frac{cal}{K}$

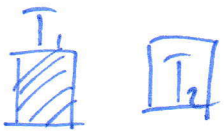
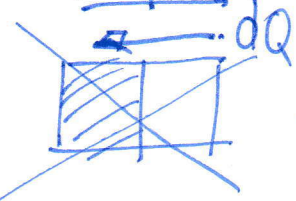
Entropia # 2 (miara nieporządku)

Def. statystyczna (Boltzmanna) $S = -k_B \sum_i p_i \ln p_i$

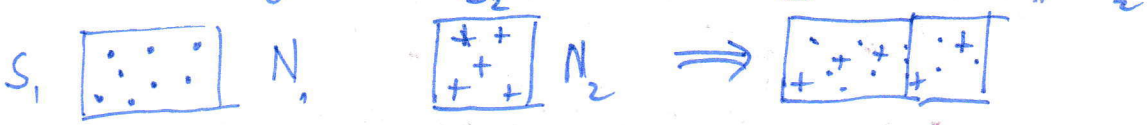
$\boxed{S = k_B \ln P}$ P – prawdopodobieństwo całk.

$T_1 < T_2$  spontaniczne →  $dS = dQ\left(\frac{1}{T_1} - \frac{1}{T_2}\right) > 0$

$T_1 = T_2$  możliwa →  $dS = dQ\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = 0$

$T_1 > T_2$  niemożliwe ⇒  $dS = dQ\left(\frac{1}{T_1} - \frac{1}{T_2}\right) < 0$

Entropia mieszania



$$\Delta S_m = S - (S_1 + S_2) = k_B N_1 \ln \frac{N}{N_1} + k_B N_2 \ln \frac{N}{N_2}$$

Rozprężanie gazu

N cząstek 

$P_1 = \left(\frac{1}{2}\right)^N$ $P_2 = 1 - \left(\frac{1}{2}\right)^N$

$$\frac{P_1}{P_2} = \frac{\left(\frac{1}{2}\right)^N}{1 - \left(\frac{1}{2}\right)^N} \approx \left(\frac{1}{2}\right)^N$$

$$S_2 - S_1 = \Delta S = k_B \ln P_2 - k_B \ln P_1 = k_B \ln \frac{P_2}{P_1} = + k_B \ln 2^N = k_B N \ln 2$$

Mały rozkład kanoniczny

$$Z = \sum_i e^{-\beta E_i}$$

$$\beta = (k_B T)^{-1}$$

funkcja rozdziału pozwala wyznaczyć f. TD

$$U = \frac{\partial}{\partial \beta}(\ln Z)$$

energia wewn.

Duży rozkład kanoniczny "ensemble"

$$\Xi^* = \sum_{i,n} e^{[-\beta E_i + \mu\beta n)} = \sum_{i,n} e^{+\beta(-E_i + n\mu)}$$

μ – potencjał chemiczny

$$F = -k_B T \ln Z$$

energia swobodna

zmienne termiczne: T, S

zmienne mechan: p, V

Równowaga TD

jeśli $dT = 0$, $dV = 0$ $\Rightarrow F = F_{min}$

jeśli $dp = 0$, $dQ = 0$ $\Rightarrow H = H_{min}$

jeśli $dT = 0$, $dp = 0$ $\Rightarrow G = G_{min}$

Helmholtza $F = U - TS$

entalpia $H = U + pV$

Gibbs $G = U + pV - TS = F + pV =$

entalpia swobodna $H - TS$