

Dakle: $\boxed{ds = \frac{\delta Q}{T}} \rightarrow \int ds = 0$

Clausius: količina toplina reverzibilno izmjenjena na T izolirani sustav $\rightarrow \delta Q = 0 \rightarrow \underline{ds = 0} \rightarrow$ ekstrem!

Izolirani sustav u ravnoteži $\boxed{S = S_{max}}$ iskusno eksperiment

II zakon termodinamike

$\boxed{ds = 0}$ $\boxed{S = S_{max}}$ \rightarrow za izolirani sustav

U ireverzibilnom procesu med sustav ide prema ravnoteži entropija raste.

Pr: $\boxed{\dots}$ plin, pregrada \rightarrow ekstenzivna veličine

I. zakon

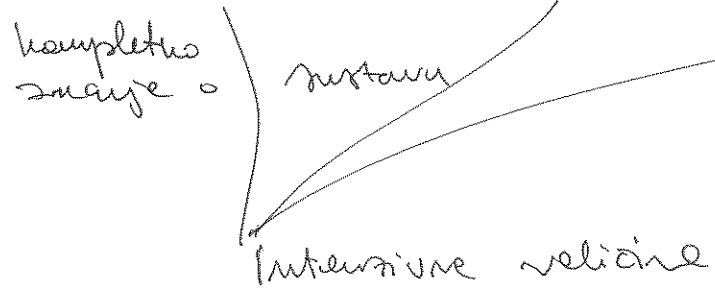
$du = \delta Q_{rev} + \delta W_{rev} = Tds - pdv + \pi dN \rightarrow du(s, v)$

dodamo li $\pi dN \rightarrow U \rightarrow U(s, v, N)$

$U(s, v, N)$ --- funkcija prirodnih varijabli:

iz I:

$T = \left. \frac{\partial U}{\partial S} \right|_{v, N}$; $-P = \left. \frac{\partial U}{\partial V} \right|_{s, v}$; $\pi = \left. \frac{\partial U}{\partial N} \right|_{s, v}$



I zadatak

$$dU = TdS - pdV + \mu dN \quad H dM, E dP$$

↳ ext funkcija ext. varijabla

$$U(\alpha S, \alpha V, \alpha N) = \alpha U(S, V, N) \rightarrow \text{homogeno 1. reda}$$

$$\text{pr. } f(x) = x$$

$$f(\alpha x) = \alpha x = \alpha f(x)$$

Intenzivne varijabla su
homogene 0. reda

$f(x^2)$ nije homogene

$$T(\alpha S, \alpha V, \alpha N) = T(S, V, N) \quad f(x) = C$$

$$f(\alpha x) = C$$

$$\alpha = 1 + \varepsilon, \quad \varepsilon \rightarrow 0$$

$$U[(1+\varepsilon)S, (1+\varepsilon)V, (1+\varepsilon)N] = (1+\varepsilon)U$$

$$\approx U(S, V, N) + \frac{\partial U}{\partial S} \Big|_{S, V, N} \varepsilon S + \frac{\partial U}{\partial V} \Big|_{S, V, N} \varepsilon V + \frac{\partial U}{\partial N} \Big|_{S, V, N} \varepsilon N$$

↓
T

↓
-P

↓
μ

$$\rightarrow U + \varepsilon U = U + \varepsilon TS - \varepsilon PV + \varepsilon \mu N$$

$$\rightarrow \boxed{U = TS - PV + \mu N} \quad \text{Eulerova relacija}$$

$$dU = SdT + TdS - pdV - Vdp + \mu dN + Nd\mu$$

$$dU = SdT - pdV + \mu dN$$

$$\boxed{SdT - Vdp + Nd\mu = 0} \quad \text{Gibbs-Duhemova relacija}$$

Intenzivne varijabla nisu
nezavisne!

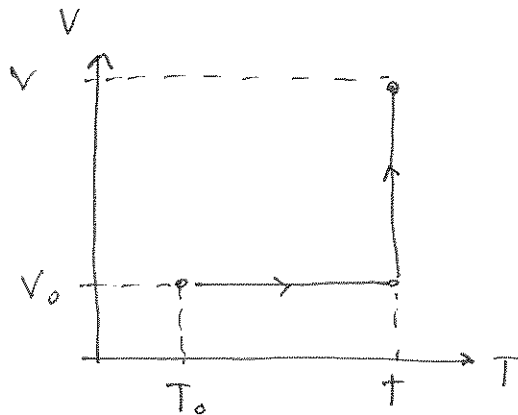
$$S = S(T, V)$$

$$\text{I. Zakon} \quad dU = TdS - PdV \rightarrow \boxed{dS = \frac{1}{T} dU + \frac{P}{T} dV}$$

$$\text{iz} \quad \boxed{U = \frac{3}{2} NkT} \quad \boxed{PV = NkT}$$

$$dU = \frac{3}{2} Nk dT \quad P = \frac{NkT}{V}$$

$$dS = \frac{3}{2} Nk \frac{dT}{T} + Nk \frac{dV}{V}$$



$$V_0, T_0 \rightarrow V, T$$

$$S = \int_{T_0}^T dS \Big|_{V=V_0=\text{const}} + \int_{V_0}^V dS \Big|_{T=T=\text{const}}$$

$$S = \frac{3}{2} Nk \int_{T_0}^T \frac{dT}{T} \Big|_{V=V_0=\text{const}} + Nk \int_{V_0}^V \frac{dV}{V} \Big|_{T=T=\text{const}}$$

$$+ \frac{3Nk}{2} \int_{V_0}^V \frac{dT}{T} \Big|_{T=T=\text{const}} + Nk \int_{V_0}^V \frac{dV}{V} \Big|_{T=T=\text{const}}$$

$$= \frac{3}{2} Nk \ln \frac{T}{T_0} + Nk \ln \frac{V}{V_0} + S_0(T_0, V_0)$$

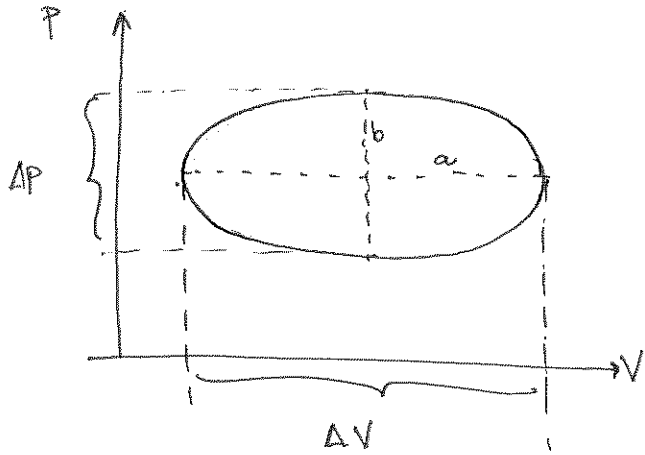
$$S(T, V) - S_0(T_0, V_0) = \frac{3}{2} Nk \ln \frac{T}{T_0} + Nk \ln \frac{V}{V_0} = Nk \ln \left[\left(\frac{T}{T_0} \right)^{3/2} \frac{V}{V_0} \right]$$

$$S(T, P) - S_0(T_0, P_0) = Nk \ln \left[\left(\frac{T}{T_0} \right)^{5/2} \frac{P_0}{P} \right]$$

$$\left. \begin{array}{l} \backslash \\ \quad \end{array} \right\} V \sim \frac{T}{P}$$

ZAD PV dijagram kružnog procesa, u kojemu sustav prima toplinu od okolice, ima oblik elipse.

Koliko puta moramo ponoviti ciklus da bi ukupna primljena toplina bila $\Delta Q = 2,82 \text{ MJ}$ ako je razlika između maksimalnog i minimalnog tlaka $\Delta P = 48 \text{ kPa}$, a max i min volumena $\Delta V = 1,5 \text{ m}^3$?



• nakon svakog ciklusa $\Delta U = 0$
 → po ciklusu onda imamo da je primljena toplina = radu rad 1. ciklusa?

$$W = A_0 \text{ (površina elipse)}$$

$$a = \Delta V / 2$$

$$b = \Delta P / 2$$

$$A = ab\pi$$

$$A_0 = \frac{\Delta P \Delta V}{4} \pi$$

$$A_0 = Q_{1 \text{ ciklus}}$$

u n ciklusa primi n puta A_0 toplinu

$$\Delta Q = n A_0$$

$$n = \frac{\Delta Q}{A_0} = \frac{4 \Delta Q}{\pi \Delta P \Delta V} = 50$$

ZAD (Sa ispitnog radom).

$$S(U, V, N) = \frac{a}{b} (UVN)^{1/3}$$

a, b pozitivne konst

a) $T = ?$ b) $p = ?$

c) Mogu li, i ako da, koje vrijednosti moraju imati konstante a i b da bismo dobili jednačine stanja za idealni plin?

a) $T = ?$

$$dU = TdS - pdV$$

$$\frac{1}{T} = \frac{\partial S}{\partial U}$$

$$\frac{\partial S}{\partial U} = \frac{a}{b} (VN)^{1/3} \frac{1}{3} U^{-2/3} = \frac{1}{T}$$

$$\rightarrow T = \frac{b}{a} \frac{3U^{2/3}}{(VN)^{1/3}}$$

b) $p = ?$

$$\frac{p}{T} = \frac{\partial S}{\partial V}$$

$$\frac{\partial S}{\partial V} = \frac{a}{b} (UN)^{1/3} \frac{1}{3} V^{-2/3} = \frac{p}{T}$$

$$p = T \frac{a}{b} (UN)^{1/3} \frac{1}{3} V^{-2/3}$$

$$p = \frac{b}{a} \frac{3U^{2/3}}{(VN)^{1/3}} \cdot \frac{a}{b} (UN)^{1/3} \frac{1}{3} V^{-2/3}$$

$$\rightarrow p = \frac{U}{V}$$

c) $pV = U \rightarrow$ Nihilno ne možemo namjestiti a i b

(da bi bila jedn. idealnog plina moru biti $3/2 U$)