Carnotov kružni proces

$$\eta = \frac{T_t - T_h}{T_t}$$

? Neiskorišteni dio topline pri pretvorbi u rad

$$1-\eta = 1-\frac{T_t - T_h}{T_t} \equiv 1-\frac{Q_{uk}}{Q_t} = 1-\frac{Q_t + Q_h}{Q_t}$$

$$\frac{\cancel{T_t} - \cancel{T_t} + T_h}{T_t} = \frac{\cancel{Q_t} - \cancel{Q_t} - Q_h}{Q_t}$$

$$\frac{T_h}{T_t} = -\frac{Q_h}{Q_t}$$

$$\frac{Q_t}{T_t} = -\frac{Q_h}{T_h}$$

$$\frac{Q_t}{T_t} + \frac{Q_h}{T_h} = 0$$

$$\Sigma \frac{Q_{rev}}{T} = 0$$

Suma reduciranih toplina jednaka je nuli kad su procesi reverzibilni

Za kružni proces s beskonačno mnogo faza:

$$\oint \frac{\delta Q_{rev}}{T} = 0$$

Entropija

grč. mijenjati se, smjerati

$$S = \frac{Q_{rev}}{T} \qquad \textbf{(JK}^{\textbf{-1}}\textbf{)}$$

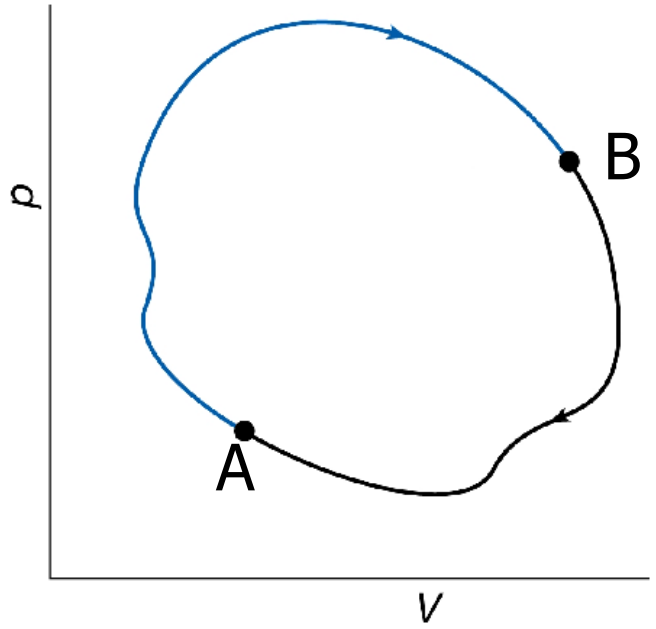
$$dS = \frac{\delta Q_{rev}}{T}$$

$$\Delta S = \int_1^2 \frac{\delta Q_{rev}}{T}$$

$$\oint dS = 0$$ **Za reverzibilne kružne procese**

Entropija je funkcija stanja

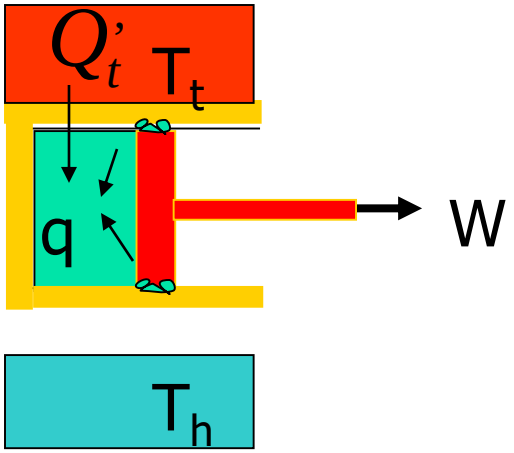
Reverzibilni kružni proces



$$\oint dS = \int_A^B \frac{\delta Q_{rev}}{T} + \int_B^A \frac{\delta Q_{rev}}{T} =$$

$$= \int_A^B dS + \int_B^A dS = S_B - S_A + S_A - S_B = 0$$

Ireverzibilni kružni proces



$$Q_t' + q = Q_t$$

$$Q_t' < Q_t$$

$$\frac{Q_t'}{T_t} < \frac{Q_t}{T_t}$$

$$\frac{Q_t}{T_t} = -\frac{Q_h}{T_h}$$

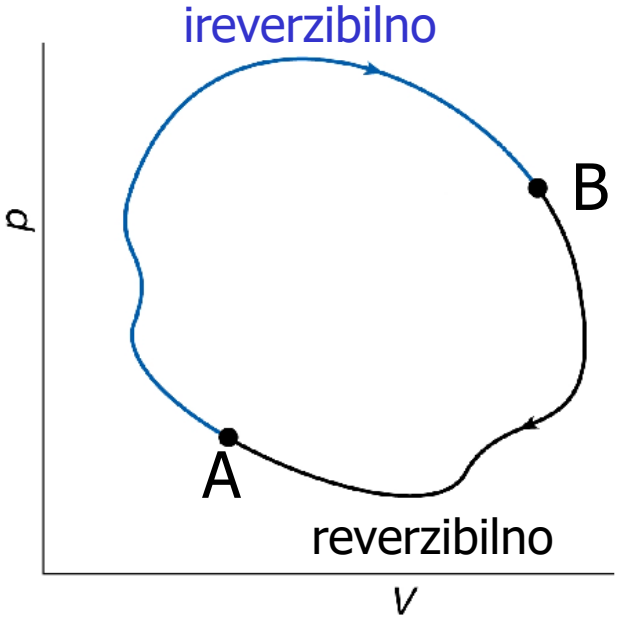
$$\frac{Q_t'}{T_t} < -\frac{Q_h}{T_h}$$

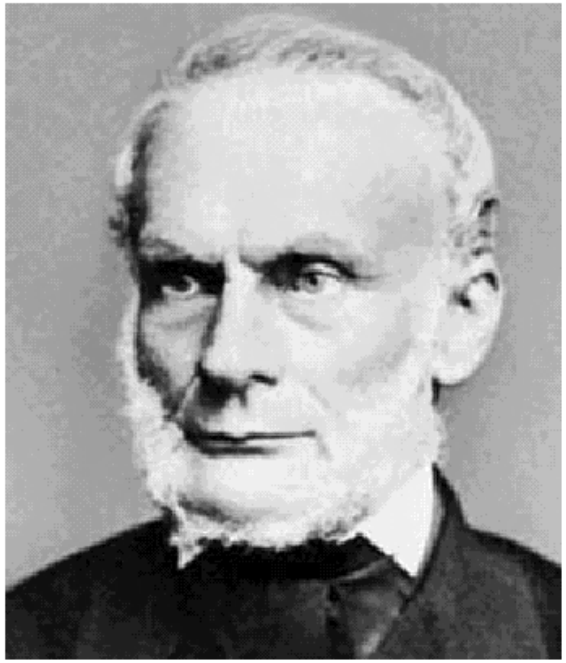
Brzi pomak klipa ⟶ trenje

(nekontrolirana pretvorba mehaničke energije u toplinsku)

$$\frac{Q_t'}{T_t} + \frac{Q_h}{T_h} < 0$$

Clausius-ov teorem: Ako je bilo koji dio cikličkog procesa ireverzibilan tada je kružni integral negativan.



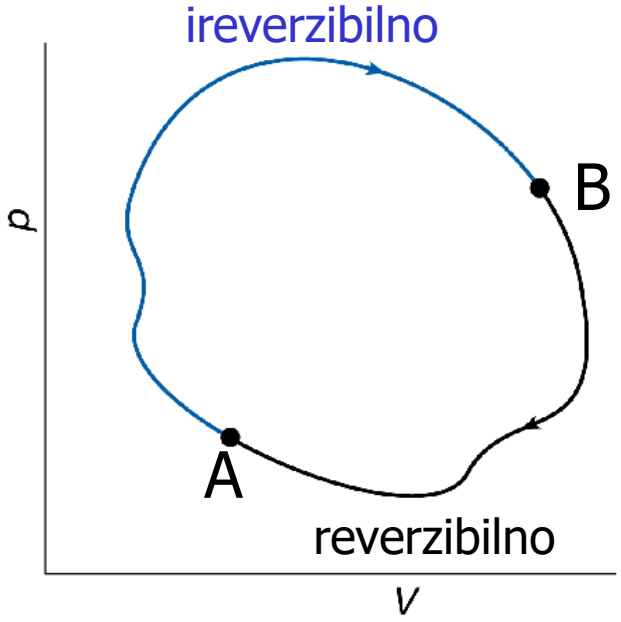


Rudolf Clausius (1822 - 1888)

German physicist who explicitly stated the first and second laws of thermodynamics.

Introduced the entities internal energy and entropy in 1868.

Clausius-ov teorem: Ako je bilo koji dio cikličkog procesa ireverzibilan tada je kružni integral negativan.



$$\oint \frac{\delta Q}{T} = \int_A^B \frac{\delta Q_{irev}}{T} + \int_B^A \frac{\delta Q_{rev}}{T} < 0$$

$$\int_A^B \frac{\delta Q_{irev}}{T} + \int_B^A dS < 0$$

$$\int_A^B \frac{\delta Q_{irev}}{T} + S_A - S_B < 0$$

$$S_B - S_A > \int_A^B \frac{\delta Q_{irev}}{T}$$

Pretpostavka:ireverzibilni kružni proces se događa u izoliranom sustavu

$$\delta Q = 0$$

$$S_B - S_A > 0$$

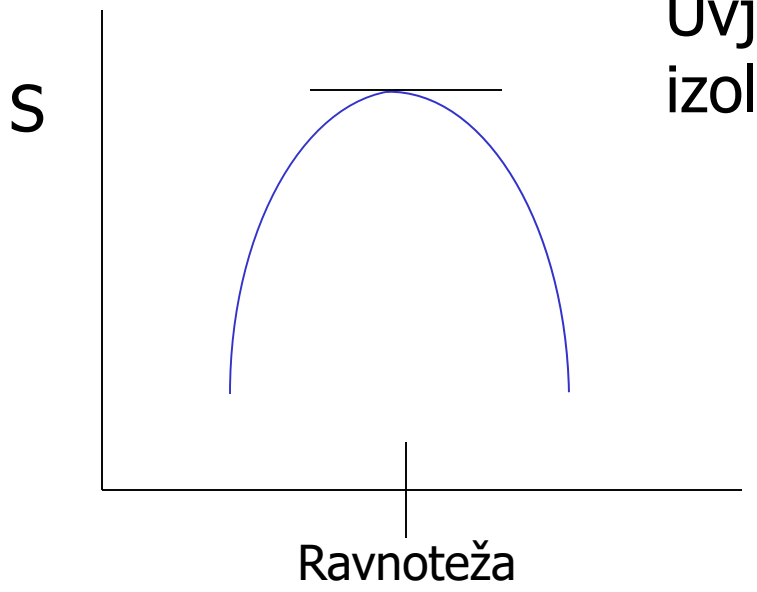
$$S_B > S_A$$

Pri ireverzibilnim procesima u izoliranom sustavu entropija raste

Entropija je veličina koja govori o smjeru ireverzibilnog (spontanog) procesa.

Entropija raste dok ne nastupi stanje ravnoteže

Entropija ima maksimum u stanju ravnoteže



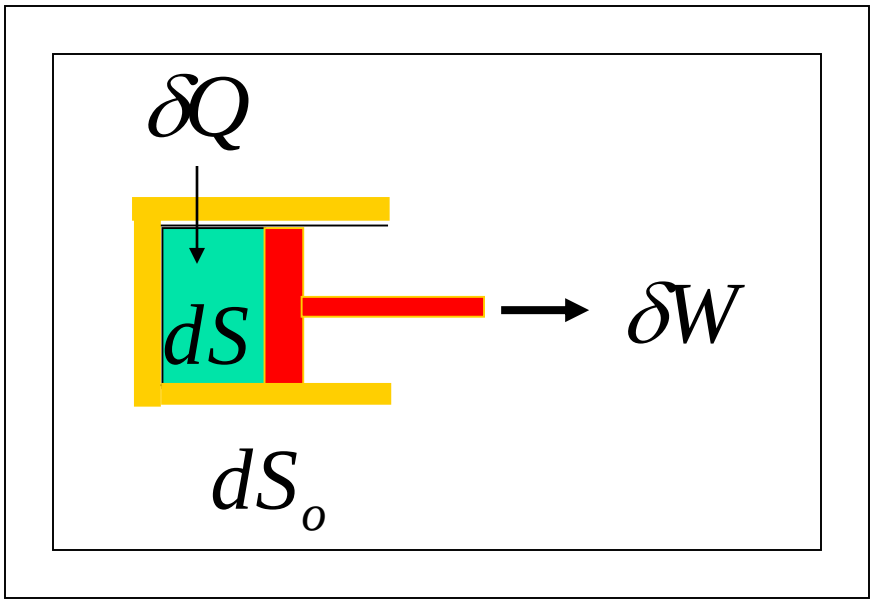
Uvjet ravnoteže u izoliranom sustavu: $dS=0$

Zatvoreni sustav koji se spontano približava stanju ravnoteže-dvije istovremene težnje:

-stanje minimalne energije

-stanje maksimalne entropije

J.Wilard Gibbs



Zatvoren sustav (cilindar s klipom) smješten u jedan veći izolirani sustav

Uvjet ravnoteže za izolirani sustav:

$$dS + dS_o = 0$$

Ukupna energija izoliranog sustava je konstantna pa je ukupna entropijska promjena jednaka nuli.

Za zatvoreni sustav vrijedi

$$dU = \delta Q + \delta W = \delta Q - pdV$$

$$dQ = dU + pdV$$

$$H = U + pV$$

$$dH = dU + pdV + Vdp$$

$$dU = dH - pdV - Vdp$$

$$dQ = dH - pdV - Vdp + pdV$$

$$dQ = dH - Vdp$$

$$dS = \frac{\delta Q}{T} = \frac{dH - Vdp}{T}$$

Promjena entropije u zatvorenom sustavu

$$dS_o = -\frac{dH - Vdp}{T}$$

Promjena entropije u izoliranom sustavu

$$dS - \frac{dH - Vdp}{T} = 0 \qquad /\cdot T$$

$$TdS - dH + Vdp = 0$$

p=konst., T=konst.

$$TdS - dH = 0$$

$$TdS - dH = 0$$

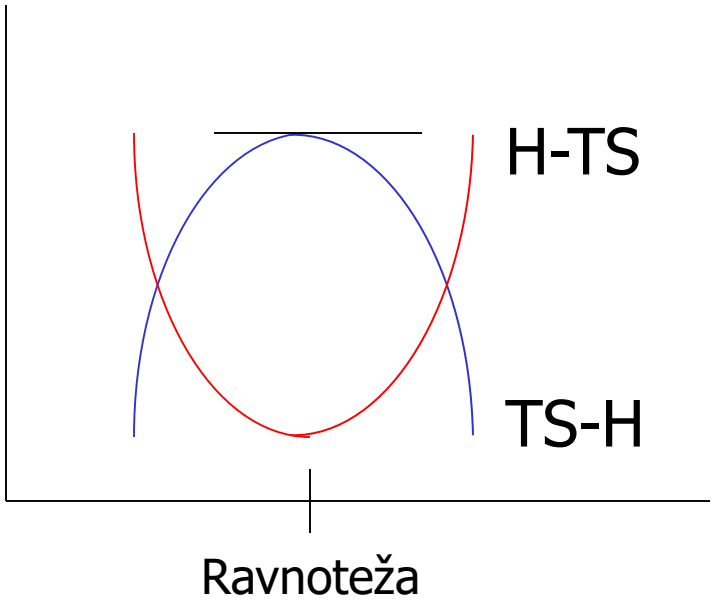
$$d(TS) - dH = 0$$

Razlika diferencijala jednaka je diferencijalu razlike

$$d(TS - H) = 0$$

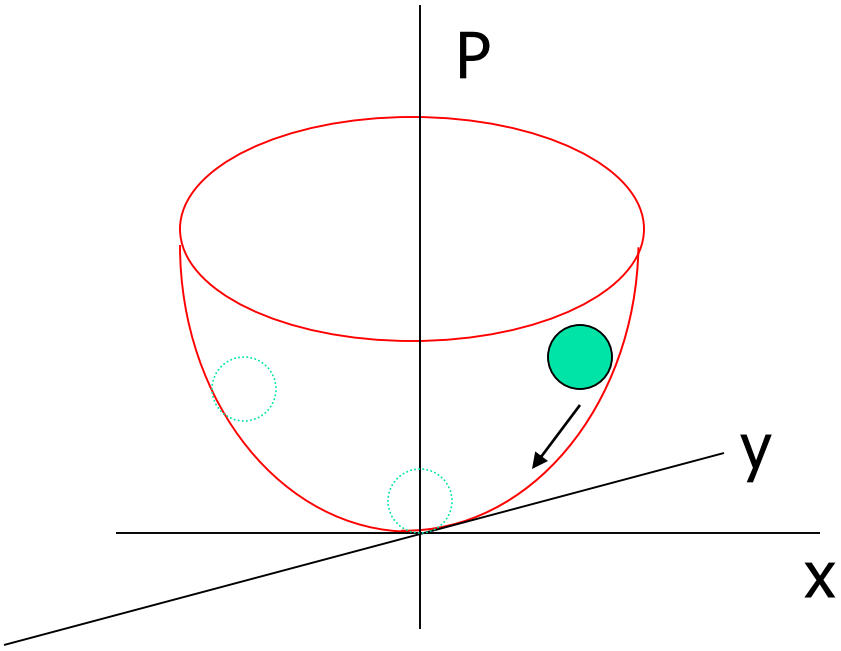
Uvjet ravnoteže u zatvorenom sustavu

Maksimum u stanju ravnoteže



$$d(H - TS) = 0$$

Minimum u stanju ravnoteže



P=f(x,y)

$$G = H - TS$$

Gibbsova energija

$$dG = dH - TdS - SdT$$

p=konst., T=konst.

$$dG = dH - TdS$$

"termodinamički potencijal pri izotermno-izobarnim uvjetima"

$$\Delta G = \Delta H - T\Delta S$$

"slobodna entalpija"

"maksimalni rad"

$$\Delta H = \Delta G + T\Delta S$$

$$Q_t = W + Q_h$$

(Carnotov proces)

Iskoristivi dio energije

Maksimalni neekspanzijski rad

Za one koji žele znati više!

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$H = U + pV$$

$$dH = dU + pdV + Vdp =$$

$$= \delta Q + \delta W + pdV + Vdp$$

$$dG = \delta Q + \delta W + pdV + Vdp - TdS - SdT$$

p,T=konst

$$dG = \delta Q + \delta W + pdV - TdS$$

$$dG = \delta Q + \delta W + pdV - TdS$$

Reverzibilna promjena

$$\delta Q_{rev} = TdS$$

$$dG = TdS + \delta W_{rev} + pdV - TdS$$

$$\delta W_{rev} = -pdV + \delta W_{dodatni,rev}$$

ekspanzijski

neekspanzijski

$$dG = -pdV + \delta W_{dodatni,rev} + pdV$$

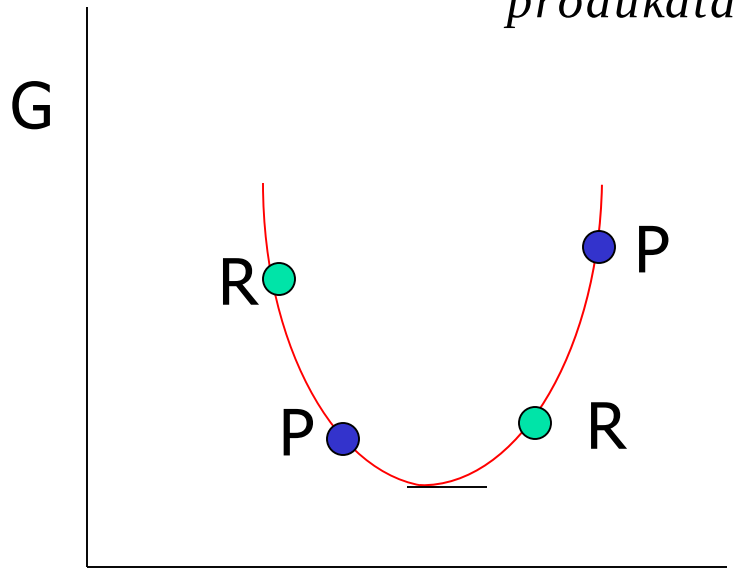
$$dG = \delta W_{dodatni,rev} = \delta W_{dodatni,\max}$$

$$\Delta G = \Delta W_{dodatni,\max}$$

Npr.električni rad koji mogu proizvesti gorivne ili elektrokemijske ćelije

$$CaCO_3 \leftrightarrow CaO + CO_2$$

$$\Delta G = \Sigma G_{produkata} - \Sigma G_{reaktanata}$$



$\Delta G < 0$ Reakcija spontano ide s lijeva na desno

$\Delta G > 0$ Reakcija spontano ide s desna na lijevo

$\Delta G = 0$

Stanje ravnoteže

$$\Delta G = \Delta H - T\Delta S$$

$3O_2(g) \rightarrow 2O_3(g)$

ΔH	ΔS	Niske T	Visoke T
+	+	$\Delta G > 0$	$\Delta G < 0$
+	-	$\Delta G > 0$	$\Delta G > 0$
-	+	$\Delta G < 0$	$\Delta G < 0$
-	-	$\Delta G < 0$	$\Delta G > 0$

Taljenje,

isparavanje

Kristalizacija

kondenzacija

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$