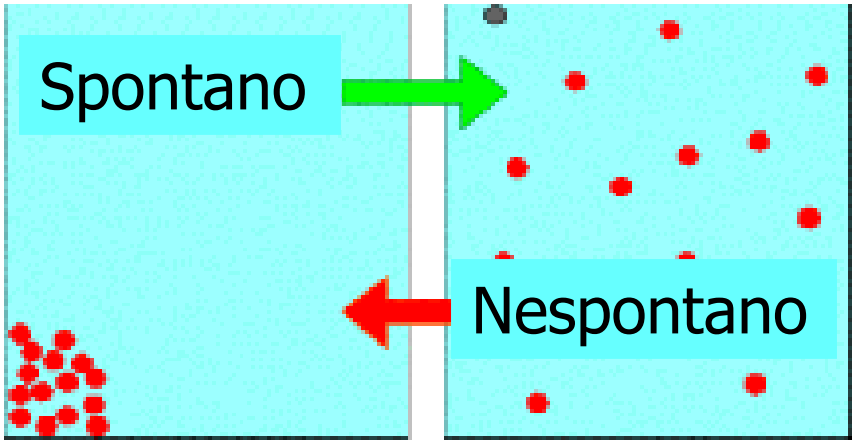
Spontani i nespontani procesi

Prvi zakon termodinamike ne govori o smjeru procesa niti o stanju ravnoteže.

Ne govori koji je proces spontan.

Spontani i nespontani procesi

-Širenje plina difuzijom



-Prijelaz topline s toplijeg tijela na hladnije

-Korozija željeza

$$2Fe(s)+\frac{3}{2}O_2(g)\rightarrow Fe_2O_3$$



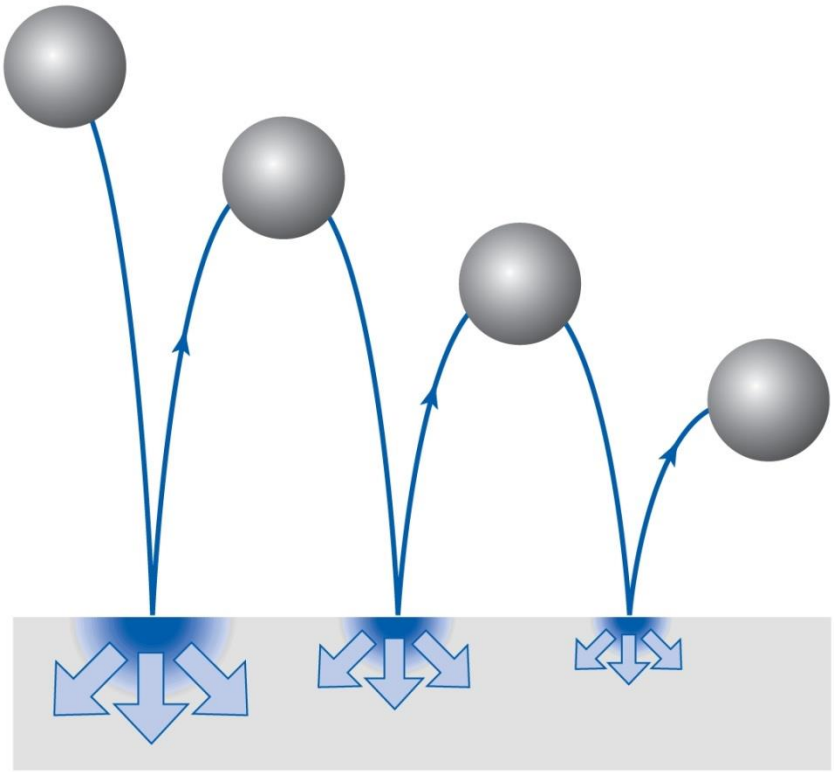




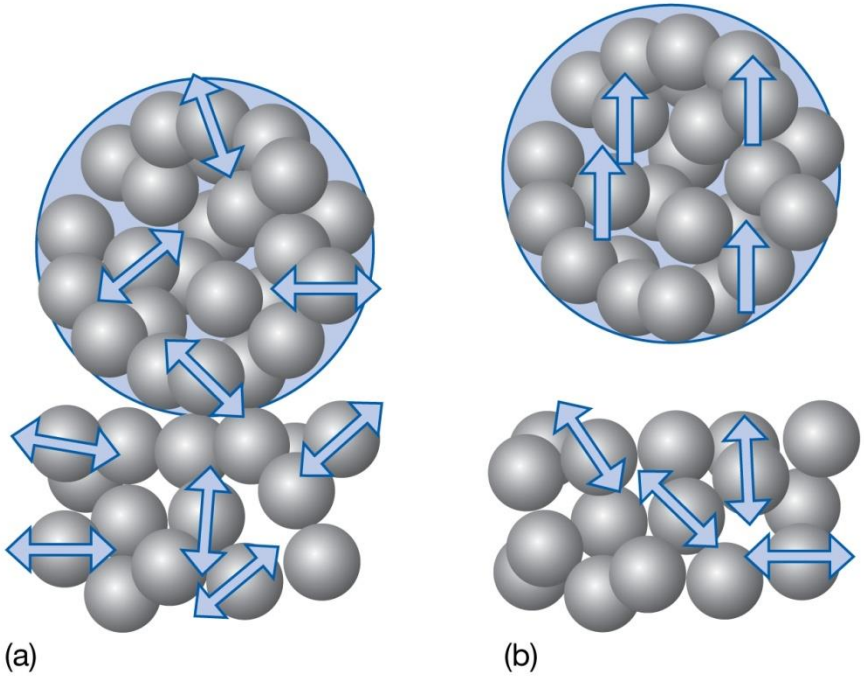
$p_{int} >> p_{ext}$ → spontano pomicanje klipa
→ ireverzibilna (nepovratna) promjena

(mala promjena p_{ext} neće promijeniti smjer procesa)

Što određuje smjer spontanog procesa?



Pri svakom udaru lopte dio energije se "degradira" u termičko gibanje atoma tla



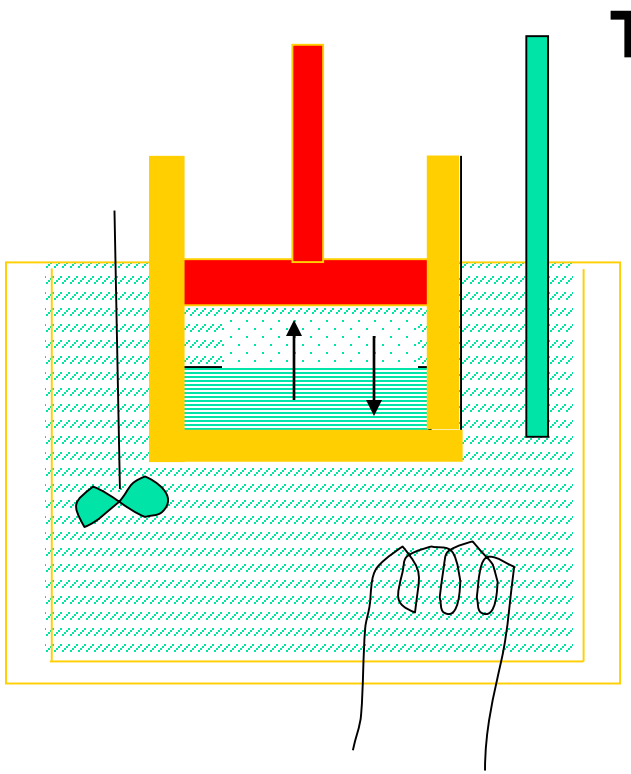
Lopta na toploj površini (toplinsko, neusmjereno gibanje atoma)

Da bi se lopta digla uvis nasumično gibanje atoma trebalo bi se promijeniti u koordinirano usmjereno gibanje

Vrlo mala vjerojatnost!

Spontani procesi praćeni su disperzijom energije u njezin neusmjereni -kaotični oblik- toplinsku energiju

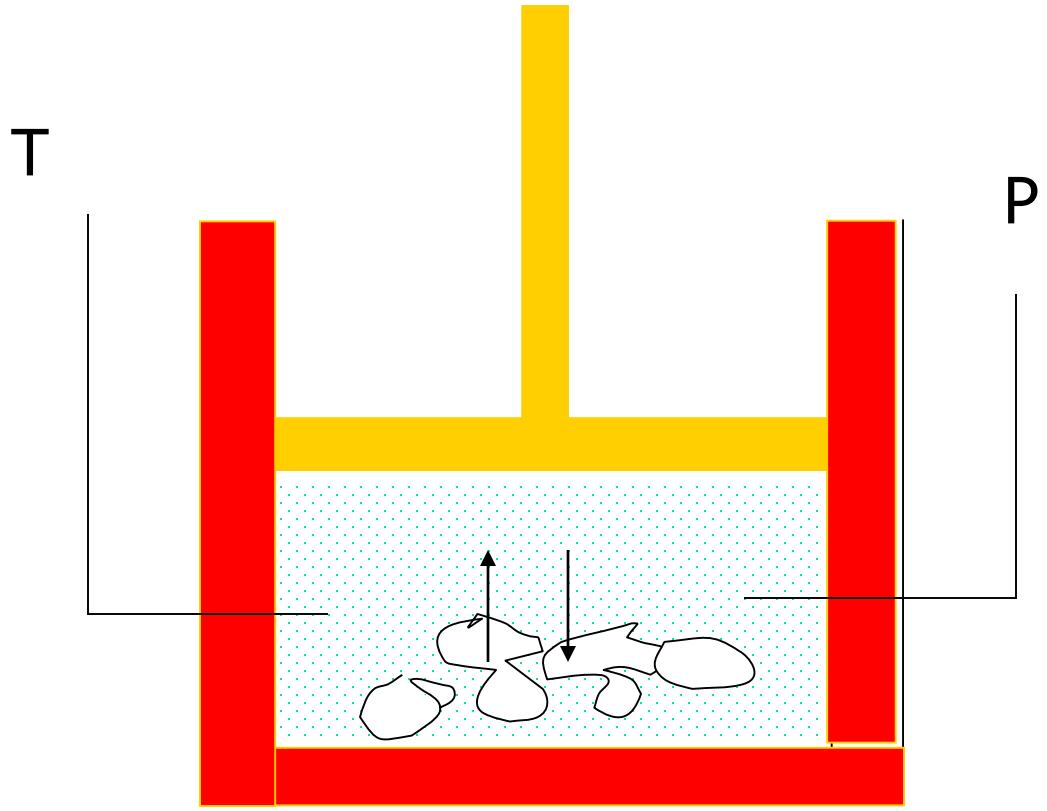
Stanje ravnoteže



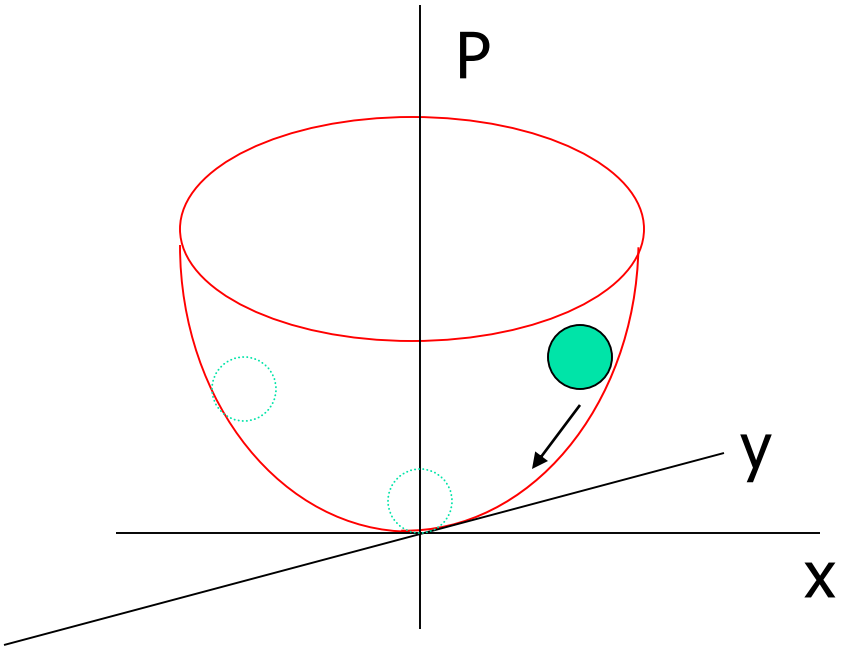
Dinamička ravnoteža

Isparavanje -kondenzacija

Promjenom **temperature/tlaka** -narušavamo ravnotežu ali se ona nakon nekog vremena ponovno uspostavlja



$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$



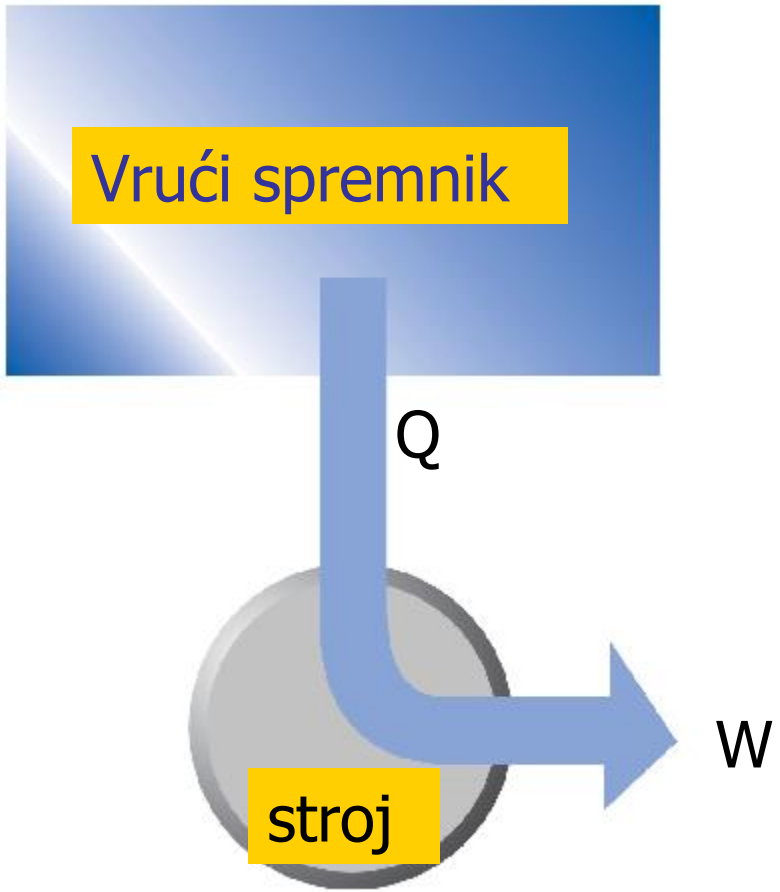
P=f(x,y)

$$dP = \left(\frac{\partial P}{\partial x}\right)_y dx + \left(\frac{\partial P}{\partial y}\right)_x dy$$

U ravnoteži: **dP=0**

Treba naći veličinu stanja koja će govoriti o smjeru procesa i o stanju ravnoteže (ΔH i ΔU o tome ne govore).

?Veličina stanja=f(T, p)

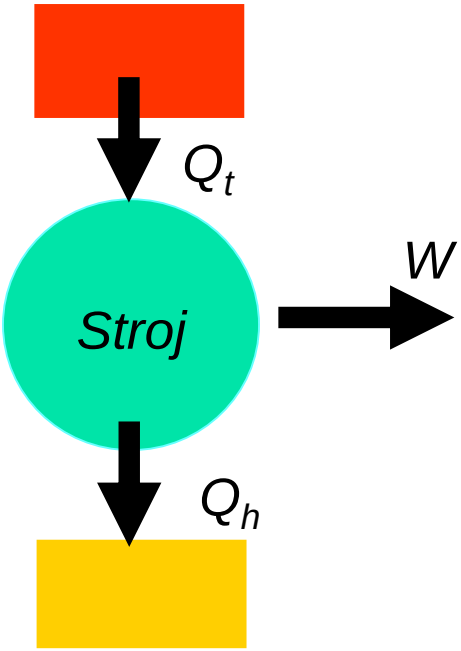


SVU TOPLINU NE MOŽEMO PRETVORITI U RAD

Proces se ne kosi s I. zakonom termodinamike

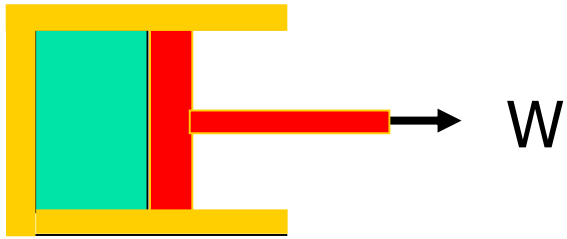
Toplinski strojevi

-2 spremnika: topliji i hladniji



Dio topline može se pretvoriti u rad a ostatak se predaje hladnijem spremniku

Dobiveni rad dostiže maksimalnu vrijednost ako su svi procesi koji posreduju pri pretvorbi topline u rad reverzibilni.



$p_{int} \approx$ili samo malo veći od p_{ext}

$\rightarrow$beskonačno sporo pomicanje klipa $\rightarrow$

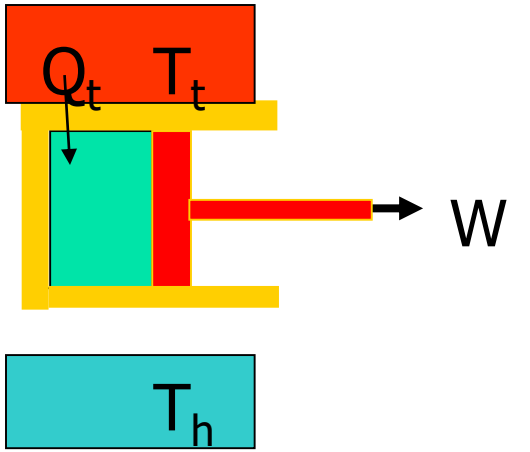
reverzibilna (povrativa) promjena

(malo povećanje $p_{ext} \rightarrow$malo smanjenje volumena

(pomicanje klipa u suprotnom smjeru)

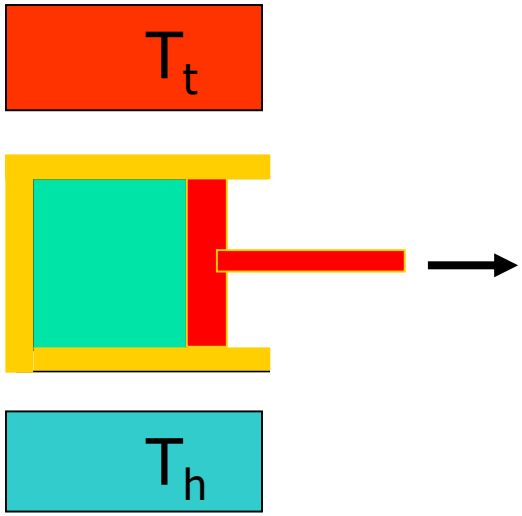
Relaciju između topline odvedene s toplijeg spremnika i dobivenog rada izvodimo preko Carnot-ovog kružnog procesa.



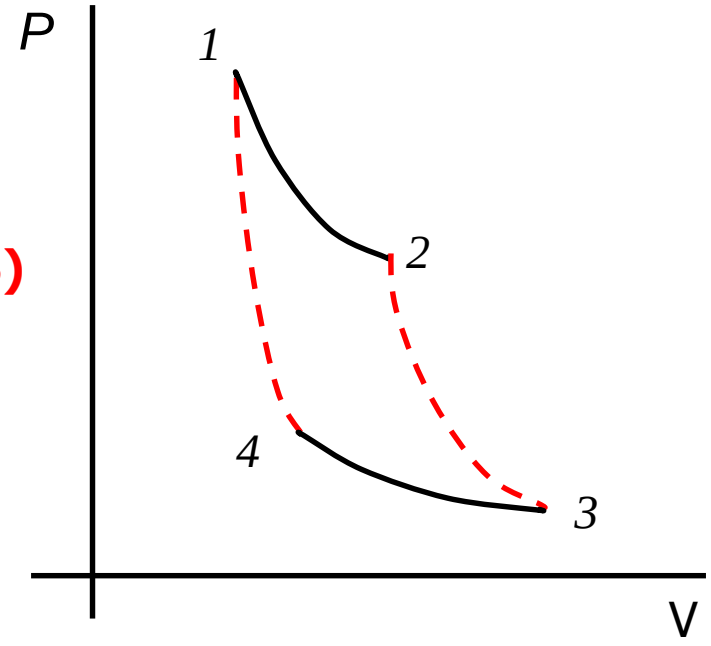


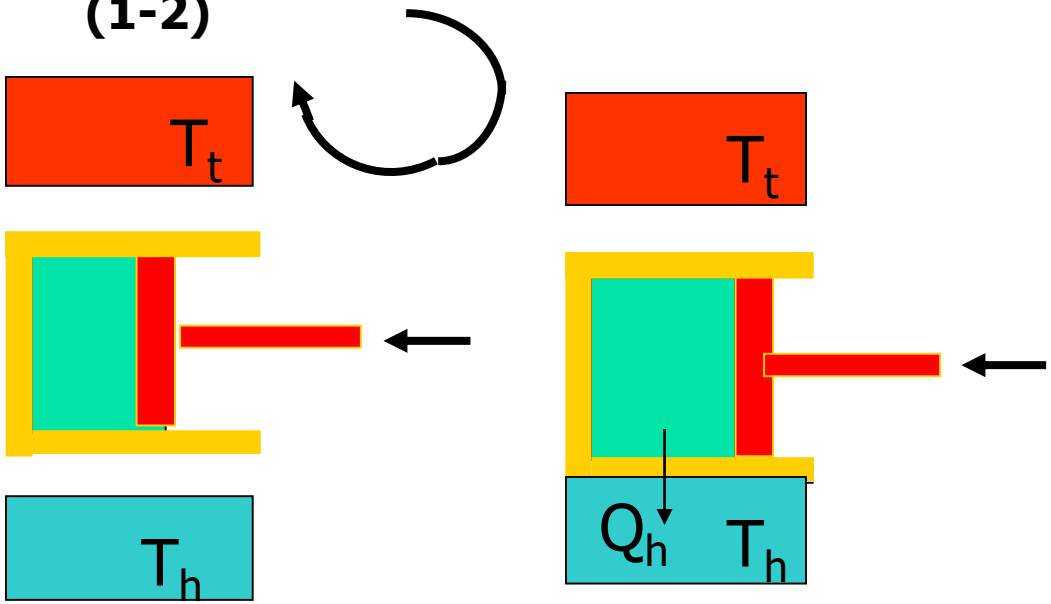
Izotermna ekspanzija

(1-2)



Adijabatska ekspanzija (2-3)





Adijabatska kompresija

(4-1)

Izotermna kompresija

(3-4)

Reverzibilna izotermna ekspanzija (1-2)

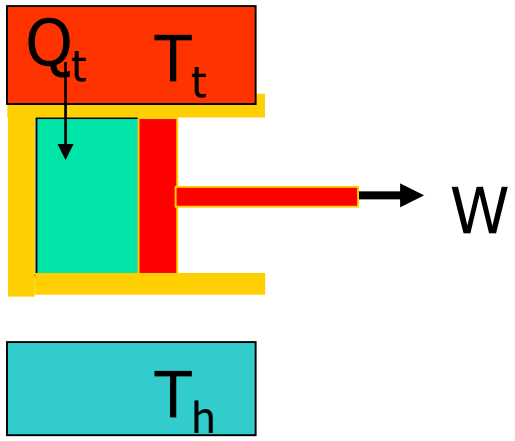
$$\delta W = -pdV$$

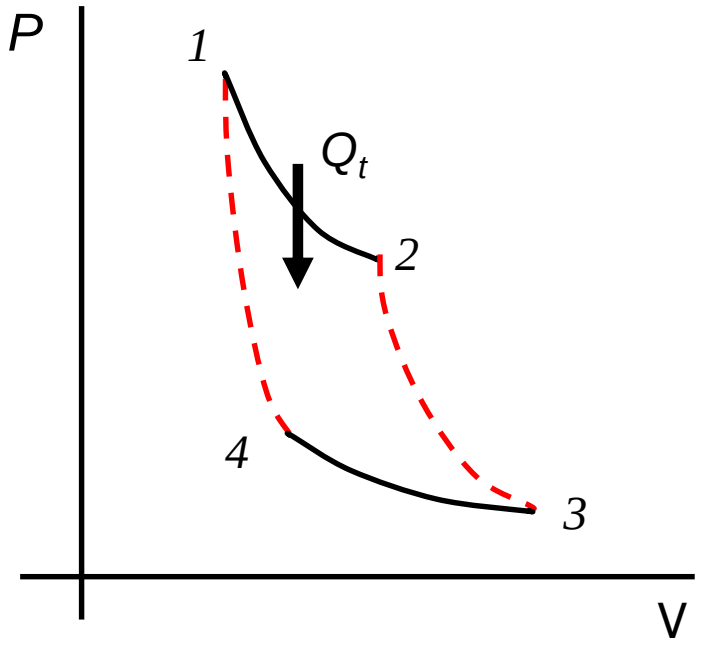
$$p = \frac{nRT}{V}$$

$$W = -nRT \int_{V_1}^{V_2} d \ln V$$

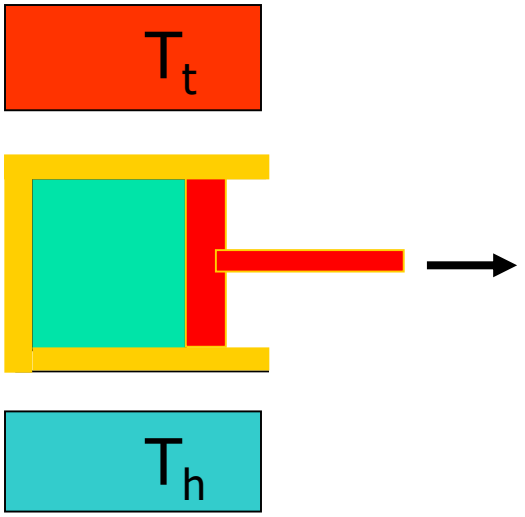
$$W_1 = -nRT_t \ln \frac{V_2}{V_1} < 0$$

$$Q_t = nRT_t \ln \frac{V_2}{V_1} > 0$$



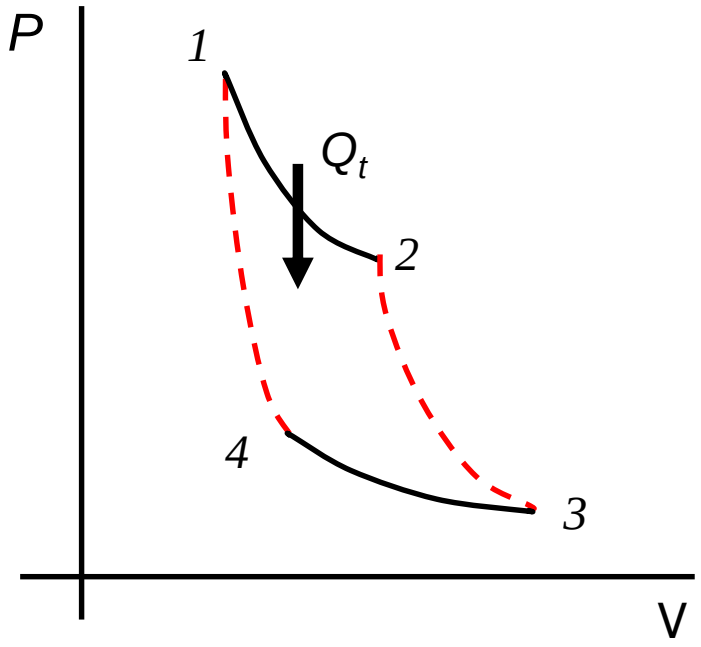


Reverzibilna adijabatska ekspanzija (2-3)

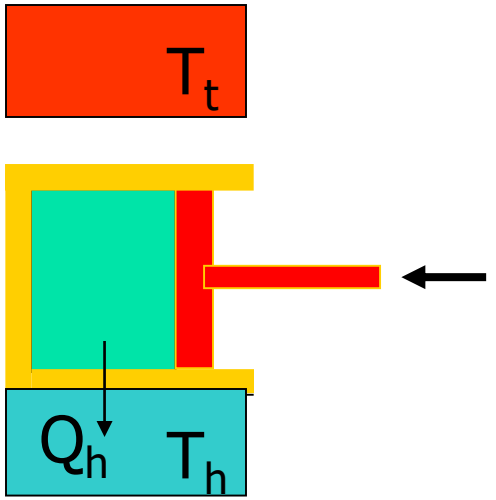


$$W_2 = \frac{nR}{\gamma - 1}(T_h - T_t) < 0$$

$$Q = 0$$



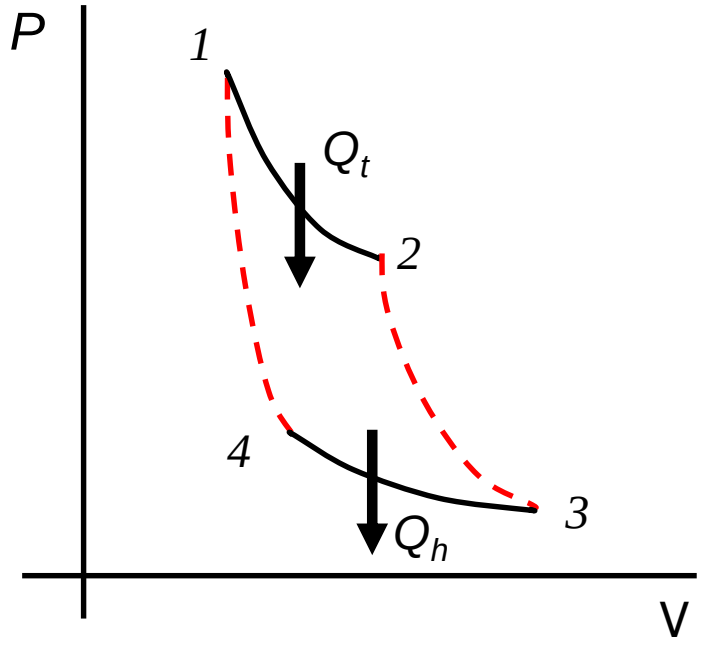
Reverzibilna izotermna kompresija (3-4)



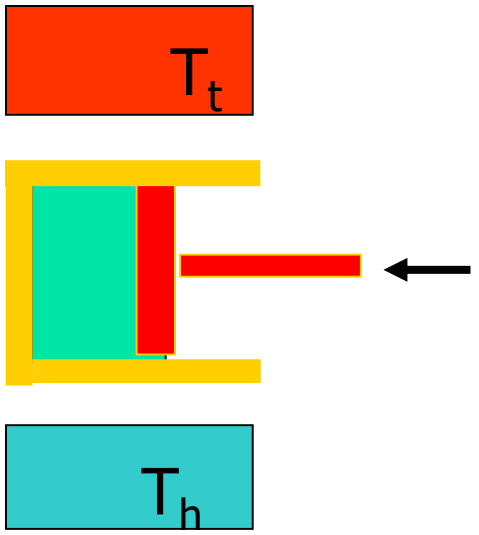
$$W_3 = nRT_h \ln \frac{V_3}{V_4} > 0$$

$$Q_h = -nRT_h \ln \frac{V_3}{V_4} < 0$$

$$Q_h = nRT_h \ln \frac{V_4}{V_3} < 0$$

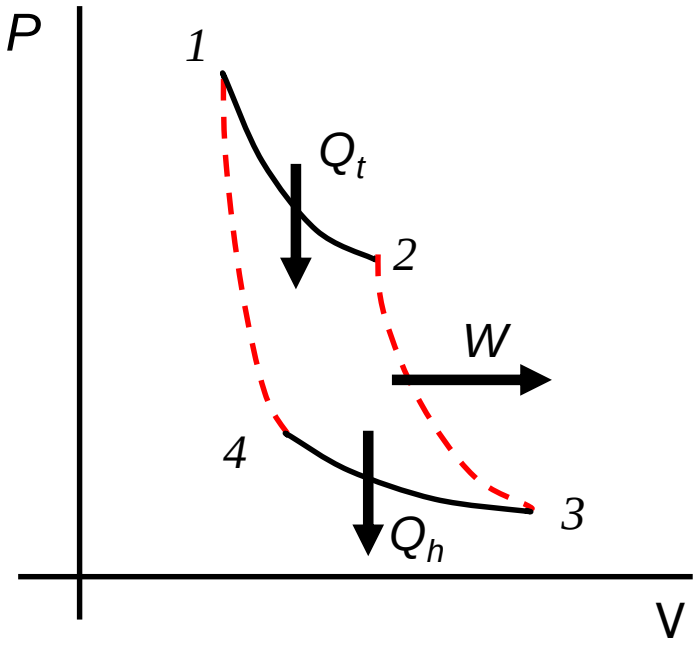


Reverzibilna adijabatska kompresija (4-1)



$$W_4 = \frac{nR}{\gamma - 1}(T_t - T_h) > 0$$

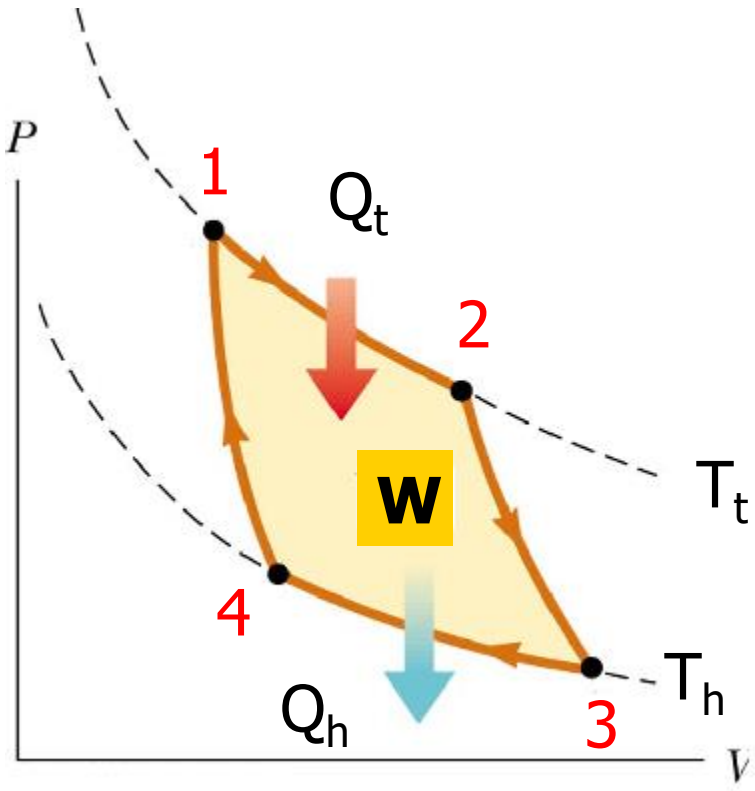
$$Q = 0$$

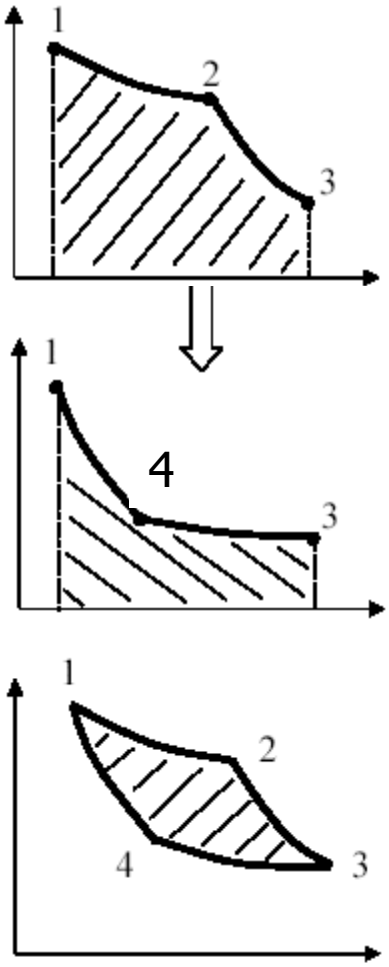


$$W_{uk} = W_1 + W_2 + W_3 + W_4 = -nRT_t \ln \frac{V_2}{V_1} + \frac{nR}{\gamma - 1}(T_h - T_t)$$

$$+ nRT_h \ln \frac{V_3}{V_4} + \frac{nR}{\gamma - 1}(T_t - T_h) =$$

$$= -nR(T_t \ln \frac{V_2}{V_1} + T_h \ln \frac{V_4}{V_3})$$


P
1
Q_t
2
w
T_t
4
T_h
Q_h
3
V

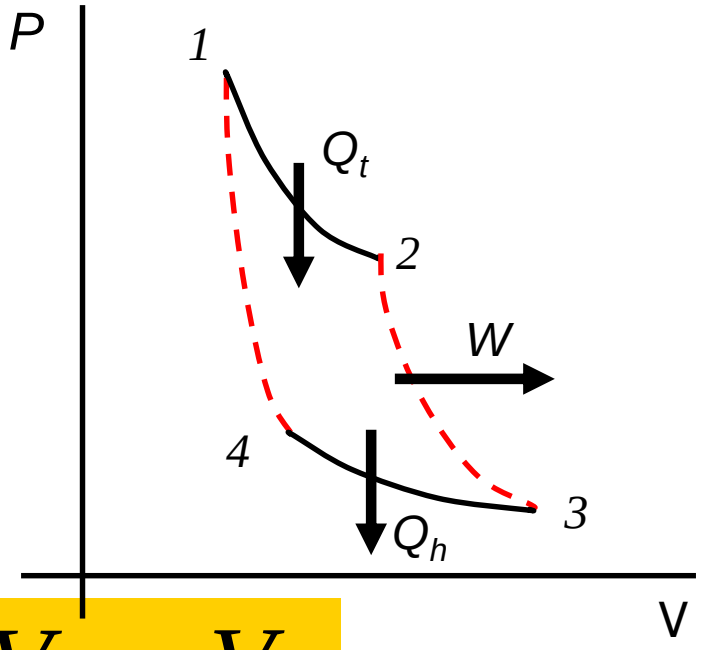

1-2-3
1
2
3
1
4
3
1
2
4
3

$$Q_{uk} = Q_t + Q_h = nRT_t \ln \frac{V_2}{V_1} + nRT_h \ln \frac{V_4}{V_3} =$$

$$= nR(T_t \ln \frac{V_2}{V_1} + T_h \ln \frac{V_4}{V_3})$$

Korisni efekt Carnot-ovog stroja

$$\eta = \frac{|W_{uk}|}{Q_t} = \frac{nR(T_t \ln \frac{V_2}{V_1} + T_h \ln \frac{V_4}{V_3})}{nRT_t \ln \frac{V_2}{V_1}}$$



Adijabatske promjene:

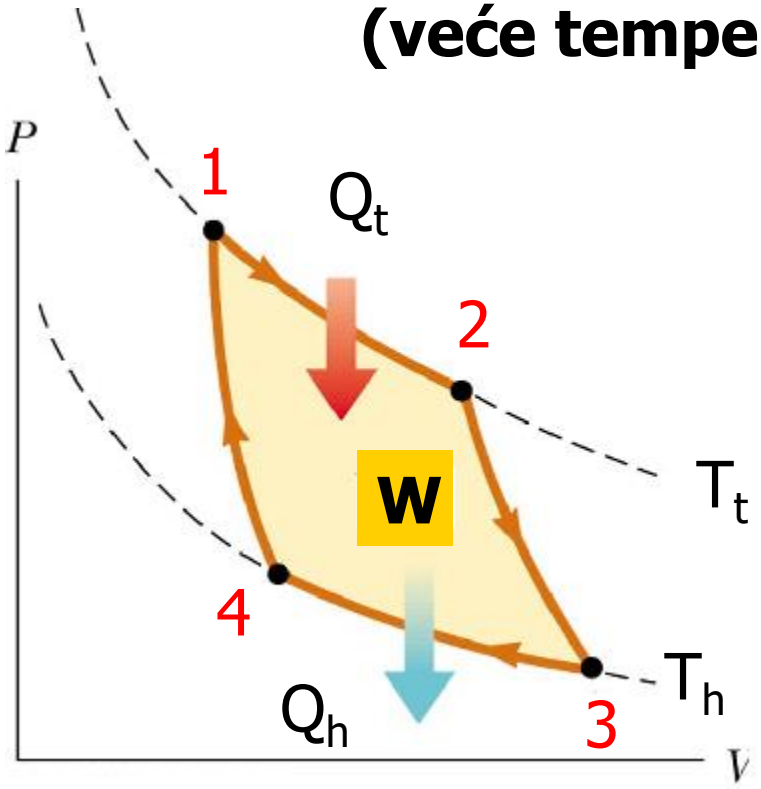
Faza 2 CKP: $T_t V_2^{\gamma-1} = T_h V_3^{\gamma-1}$

Faza 4 CKP $T_t V_1^{\gamma-1} = T_h V_4^{\gamma-1}$

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\eta = \frac{|W_{uk}|}{Q_t} = \frac{T_t \ln \frac{V_2}{V_1} - T_h \ln \frac{V_2}{V_1}}{T_t \ln \frac{V_2}{V_1}} = \frac{T_t - T_h}{T_t}$$

I **Bilanca pretvorbe topline u rad biti će pozitivna ako su temperature između kojih radi toplinski stroj različite.**
(veće temperaturne razlike→veći rad)



II **Toplinski stroj može stalno davati radnju ako se ciklus stalno ponavlja**

III **Maksimalni korisni efekt ($\eta = 1$) je kad je temperatura $T_h = 0K$ (temperatura apsolutne nule)**

IV **Pri svakoj pretvorbi topline u rad ne može se sva toplina pretvoriti u rad već jedan dio topline prelazi na nižu temperaturu (degradira se).**
(Neka određena količina topline na višoj temperaturi je sa stanovišta iskorištenja u obliku rada vrednija nego ista količina topline na nižoj temperaturi).

$$W_{uk} = Q_t - Q_h$$

II ZAKON TERMODINAMIKE

W. Thomson (Lord KELVIN)

Kružnim procesom nemoguće je svu toplinu preuzetu iz toplinskog spremnika konstantne temperature pretvoriti u mehanički rad a da pritom ne dolazi do drugih promjena.

Clausius

Toplina ne može spontano prelaziti s hladnijeg na topliji spremnik.

Boltzmann:

Svaki proces u prirodi spontano teži iz stanja manje u stanje veće vjerojatnosti