TERMODINAMIKAREN HIRUGARREN PRINTZIPIOA

* SARRERA

* HOZKETA-PROZESUAK
  - TENPERATURA HOZKETA-PARAMETRO MODURA
  - BOLUMENA HOZKETA-PARAMETRO MODURA
    - ESPANTSIO ADIABATIKO ITZULGARRIA
    - ESPANTSIO ASKEA
    - ADIBIDEA : GAS IDEALA
  - PRESIOA HOZKETA-PARAMETRO MODURA
    - ESPANTSIO ADIABATIKO ITZULGARRIA
    - ESTRANGULATZE-PROZESUA
    - ADIBIDEA : GAS IDEALA
      VAN DER WAALS-EN FLUIDOA
  - EREMU MAGNETIKOA HOZKETA-PARAMETRO MODURA *
    - ESPANTSIO ADIABATIKO ITZULGARRIA
    - KANPO-EREMU MAGNETIKOA KONSTANTEA

* HIRUGARREN PRINTZIPIOAREN ENUNTZIATUAK
  - PLANCK
  - NERNST
  - NERNST/SIMON
  - IV POSTULATUA
  - ENUNTZIATUEN ARTEKO BALIOKIDETASUNA

* HIRUGARREN PRINTZIPIOAREN APLIKAZIO FISIKOKIMIKOAK

* SISTEMA MAGNETIKOAK
  - SISTEMAREN DESKRIPZIOA
  - LAN MAGNETIKOA
  - H ETA G POTENTZIALEN ERAIKUNTZA

- HELBURUA : TENPERATURA JAISTEA

SISTEMA EZAUGARRITZEKO : T PARAMETRO INTENTSIBOA

Z PARAMETROA : INTENTSIBOA

ESTENTSIBOA

TENPERATURA JAISTEKO Z PARAMETROA ALDATUKO DUGU

$$\boxed{\left(\frac{\partial T}{\partial Z}\right)_{\boxed{X}}}$$

KALKULATU BEHARREKO KOEFIZIENTEA

$X \rightarrow$ BALDINTZEN ARABERAKOA

$$\boxed{Z = \{ V, P, \mathcal{H} \}}$$

(1) - BOLUMENA HOZKETA-PARAMETRO INDEPENDENTE MODURA :

(i) - ESPANTSIO ADIABATIKO ITZULGARRIA : $\boxed{S = Kte}$

$\delta Q = dU - \delta W$ $\quad\quad$ $\delta W = -pdV$ $\quad$ SISTEMA HIDROSTATIKOA , PROZESU KUASIESTATIKOA

$\delta Q = TdS$ $\quad$ PROZESU ITZULGARRIA , ADIABATIKOA $\delta Q = 0$

$$dU = pdV$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} = -\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\frac{T}{T}\left(\frac{\partial S}{\partial T}\right)_V} = -\frac{T}{C_V}\frac{\alpha}{\kappa_T}$$

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{V}\frac{\alpha}{\kappa_T}} \quad T > 0 \; ; \; C_V > 0 \; ; \; \alpha > 0 \; ; \; \kappa_T > 0 \implies \boxed{\left(\frac{\partial T}{\partial V}\right)_S < 0}$$

(ii) - ESPANTSIO ASKEA (BALIOKIDE ITZULGARRIA) : $\boxed{U = Kte}$

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V} \quad \implies \boxed{\left(\frac{\partial T}{\partial V}\right)_U = \frac{-1}{C_V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]}$$

$$\left.\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial S}{\partial V}\right)_T - p\left(\frac{\partial V}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p \\ \left(\frac{\partial U}{\partial T}\right)_V &= C_V\end{aligned}\right\}$$

IRUZKINAK : (1) - GAS IDEALAREN KASUA $[\quad] = 0$

(2) - $\left(\frac{\partial T}{\partial V}\right)_U$ FAKTOREA : $\left(\frac{\partial T}{\partial V}\right)_U = \left(\frac{\partial T}{\partial V}\right)_S + \left(\frac{\partial T}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_U$

(3) - ADIERAZPIDE GRAFIKOA $T = T(V)$

(2) – PRESIOA HOZKETA-PARAMETRO INDEPENDENTE MODURA:

(i) – ESPANTSIO ADIABATIKO ITZULGARRIA: $\boxed{S = kte}$

$\delta Q = dU - \delta W$ $\quad \delta W = -p dV$ SISTEMA HIDROSTATIKOA, PROZESU KUASIESTATIKOA

$\delta Q = T dS$ PROZESU ITZULGARRIA, ADIABATIKOA $\delta Q = 0$

$dU = p dV$

$$\left(\frac{\partial T}{\partial p}\right)_S = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p} = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\frac{T}{T}\left(\frac{\partial S}{\partial T}\right)_p} = \frac{T}{C_p} V\alpha$$

$$\boxed{\left(\frac{\partial T}{\partial p}\right)_S = \frac{T}{C_p} V\alpha} \qquad T > 0 \;;\; C_p > 0 \;;\; \alpha > 0 \quad \Rightarrow \quad \boxed{\left(\frac{\partial T}{\partial p}\right)_S > 0}$$

(ii) – ESTRANGULATZE-PROZESUA (BALIOKIDE "ITZULGARRIA"): $\boxed{H = kte}$

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} \quad \Rightarrow \quad \boxed{\left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]}$$

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T - V\left(\frac{\partial p}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T - V = T\left(\frac{\partial V}{\partial T}\right)_p - V$$

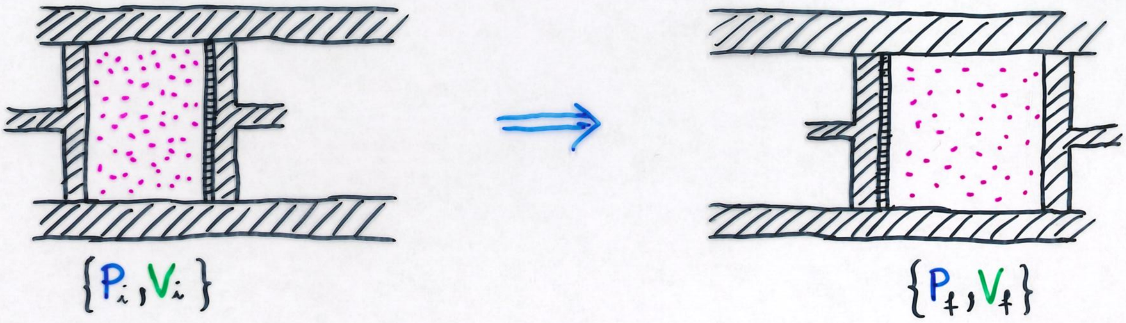
$$\left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p - V\cancel{\left(\frac{\partial p}{\partial T}\right)_p}^{\,0} = T\left(\frac{\partial S}{\partial T}\right)_p = C_p$$

IRUZKINAK: (1) – GAS IDEALAREN KASUA [ ] = 0

(2) – $\left(\frac{\partial T}{\partial p}\right)_H$ FAKTOREA $\left(\frac{\partial T}{\partial p}\right)_H = \left(\frac{\partial T}{\partial p}\right)_S + \left(\frac{\partial T}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_H$

(3) – ADIERAZPIDE GRAFIKOA $T = T(p)$

ESTRANGULATZE - PROZESUA : JOULE/KELVIN (J/K) EFEKTUA ; $\boxed{\mu_{J/K}}$



$$\delta W = -\,p\,dV$$

$$W = -\int_{V_i}^{0} P_i\,dV + \left[-\int_{0}^{V_f} P_f\,dV\right]$$

$$\boxed{W = P_i V_i - P_f V_f}$$

$$Q = \Delta U - W$$

$Q = 0$ ADIABATIKOA

$$\Delta U = W$$

$$U_f - U_i = P_i V_i - P_f V_f$$

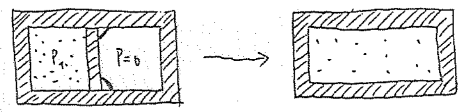
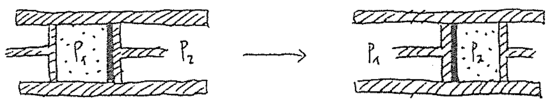
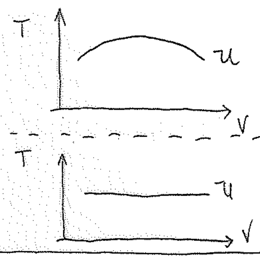
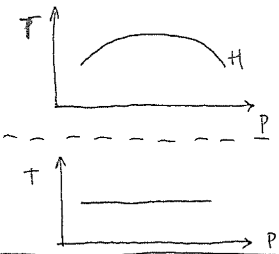
$$\boxed{U_f + P_f V_f = P_i V_i + U_i}$$

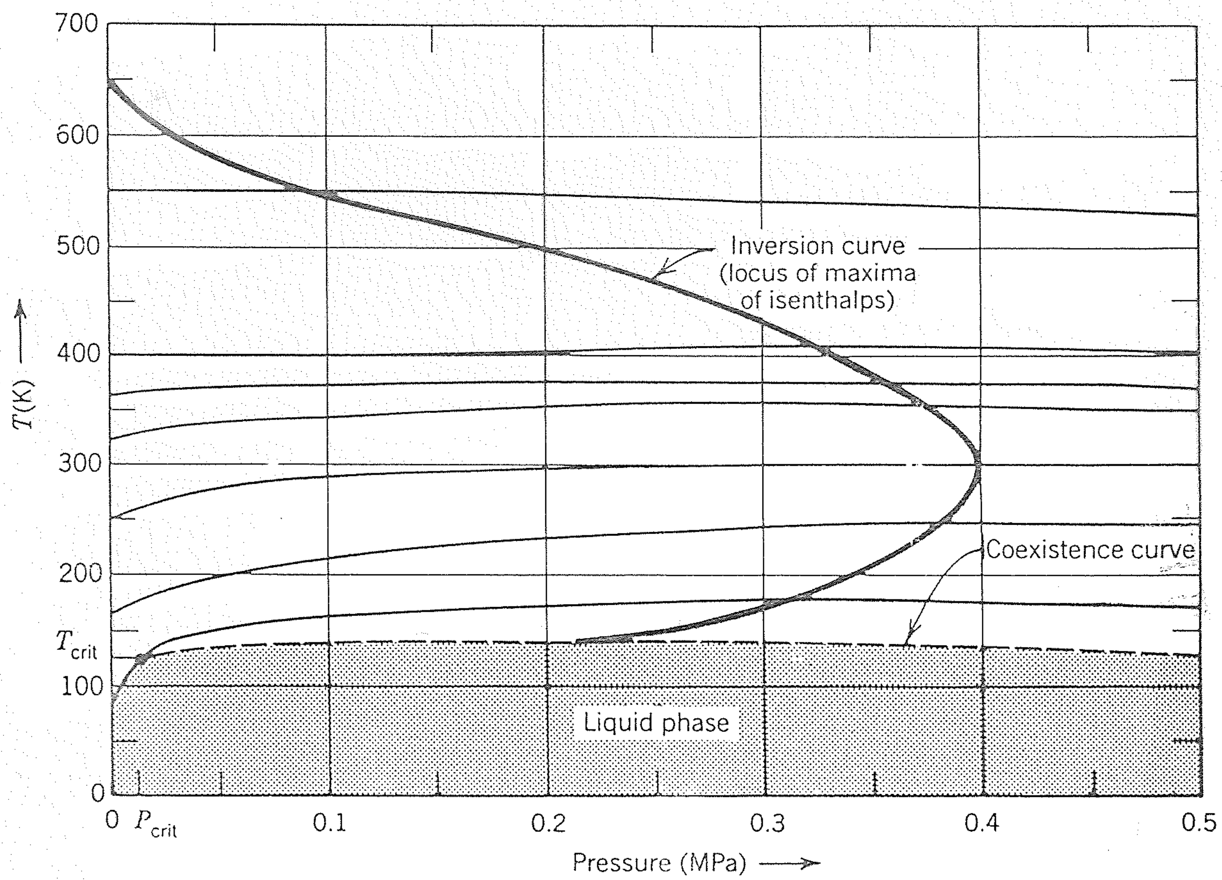
$$\boxed{\Delta H = 0 \Rightarrow H_f - H_i = 0 \Rightarrow H_f = H_i}$$

- Temperatura jaitsi nahi dugu
- Sistemari dagokion Z aldagai termodinamikoa aldatuko dugu (Z hozketa-parametroa)

$$\left.\right\} \boxed{\left(\frac{\partial T}{\partial Z}\right)_{\square}}$$

SISTEMA HIDROSTATIKOETAN : (P, V, T, N)

V HOZKETA-PARAMETROA	P HOZKETA-PARAMETROA
$S = kte$ $\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} = -\frac{\left(\frac{\partial P}{\partial T}\right)_V}{\frac{T}{T}\left(\frac{\partial S}{\partial T}\right)_V} = -\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V$ $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{k_T}$ $\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_V}\frac{\alpha}{k_T}}$	$S = kte$ $\left(\frac{\partial T}{\partial P}\right)_S = -\frac{\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_P} = -\frac{\left(\frac{\partial S}{\partial P}\right)_T}{\frac{T}{T}\left(\frac{\partial S}{\partial T}\right)_P} = +\frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P$ $\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \frac{T}{C_P}V\alpha}$
$U = kte$ $\left(\frac{\partial T}{\partial V}\right)_U = -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V}$ $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_V - P$ $\left(\frac{\partial U}{\partial T}\right)_V = C_V$ $\boxed{\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]}$	$H = kte$ $\left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P}$ $\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - V = T\left(\frac{\partial V}{\partial T}\right)_P - V$ $\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = C_P$ $\boxed{\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]}$
$\boxed{\left(\frac{\partial T}{\partial V}\right)_U = \left(\frac{\partial T}{\partial V}\right)_S + \frac{P}{C_V}}$	$\boxed{\left(\frac{\partial T}{\partial P}\right)_H = \left(\frac{\partial T}{\partial P}\right)_S - \frac{V}{C_P}}$
	
	



700
600
500
400
300
200
T_{crit}
100
0
T(K)
0
P_{crit}
0.1
0.2
0.3
0.4
0.5
Pressure (MPa)
Inversion curve
(locus of maxima
of isenthalps)
Coexistence curve
Liquid phase

TERMODINAMIKAREN HIRUGARREN PRINTZIPIOAREN HIRU ENUNTZIATU

(1) - PLANCK (1919)

BARNE-OREKAN DAGOEN SISTEMAN,
EDOZEIN MEKANISMOREKIN LOTUTA DAGOEN ENTROPIARAKO EKARPENA
NULUA DA $T=0$ TENPERATURA ABSOLUTUAN

(2) - NERNST (1912)

PAUSO-KOPURU FINITOZ OSATUTAKO PROZESUAREN BIDEZ, EZINEZKOA DA
$T=0$ LERRO ISOTERMANORAINO JAISTEA

EDOZEIN PROZESU FINITOREN BIDEZ EZINEZKOA DA TENPERATURA ABSOLUTUAREN ZEROA LORTZEA

(3) - NERNST/SIMON (1906)

BARNE-OREKA EGONKORRETAN DAUDEN SISTEMETARAKO PROZESU ISOTERMANOETAN,
ZEINTZUETAN Z PARAMETROA $Z_1 \longrightarrow Z_2$ ALDATU DEN,
ONDOKOA BETETZEN DA

$$\lim_{T\to 0} \Delta S_T = \lim_{T\to 0} \left[S(T,Z_2) - S(T,Z_1) \right] = 0$$

(IV) - POSTULATUA

EDOZEIN SISTEMAREN ~~TENPERATURA~~ ENTROPIA NULUA DA ONDOKOA BETETZEN DUEN EGOERAN:

$$\left(\frac{\partial U}{\partial S}\right)_{V,N,\ldots} = 0 \qquad (T=0)$$

HIRUGARREN PRINTZIPIOAREN ONDORIO FISIKOKIMIKOAK

(1) - POSIBLEA DA ENTROPIAREN BALIO ABSOLUTUAK LORTZEA

POSIBLEA DA ZENBAIT KONSTANTEREN BALIOAK LORTZEA

(2) - BERO-AHALMENA

$$C = T\left(\frac{dS}{dT}\right)_{\boxtimes}$$

$\boxtimes$ ZENBAIT PARAMETRO (INTENTSIBO, ESTENTSIBO) KONSTANTE

$$\left.\begin{array}{l}\Delta S \to 0 \\ T \to 0\end{array}\right\} \Rightarrow C \to 0 \text{ BAINA } T \to 0 \text{ BAINO ARINAGO}$$

(3') - ZABALKUNTZA-KOEFIZIENTEA (SISTEMA HIDROSTATIKOA)

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

PROZESU ISOTERMANOETAN ENTROPIAREN MALDA ZERORANTZ DOA

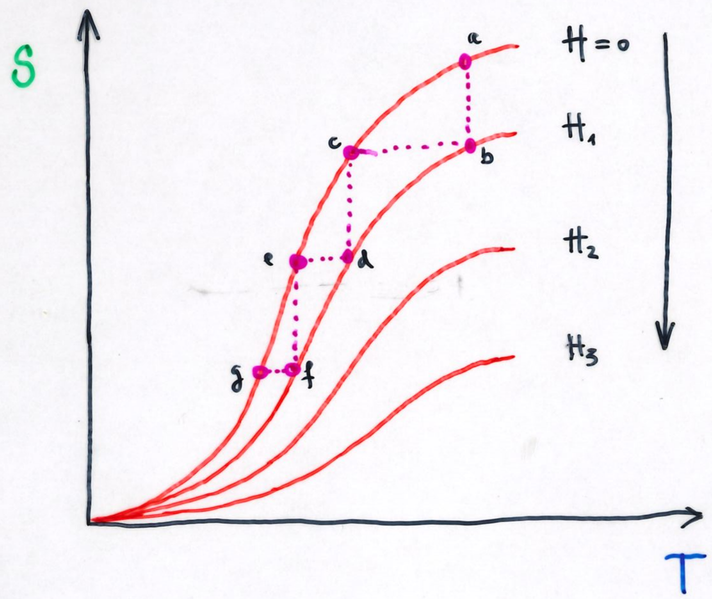
(3'') - "ZABALKUNTZA - KOEFIZIENTEA" (SISTEMA MAGNETIKOA)

$$\left(\frac{\partial m}{\partial T}\right)_{H_0} = \left(\frac{\partial S}{\partial H}\right)_T$$

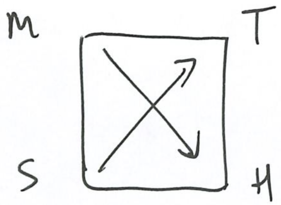
PROZESU ISOTERMANOETAN ENTROPIAREN MALDA ZERORANTZ DOA

(3) - ZABALKUNTZA-KOEFIZIENTEA EDOZEIN SISTEMATAN : OROKORRA

$$\left(\frac{\partial S}{\partial Z_i}\right)_T = \left(\frac{\partial z}{\partial T}\right)_{Z_i}$$



S
T
a
b
c
d
e
f
g
H = 0
H₁
H₂
H₃



$* \quad \left(\frac{\partial M}{\partial T}\right)_H = \left(\frac{\partial S}{\partial H}\right)_T$ Maxwell-en erlazioa

$* \quad \left(\frac{\partial M}{\partial T}\right)_H < 0$ experimentalki betetzen sisteme paramagnetikoetan

$\Rightarrow \boxed{\left(\frac{\partial S}{\partial H}\right)_T < 0}$ ①

zeinua finkatuta

$* \quad S = S(H,T) \rightarrow dS = \left(\frac{\partial S}{\partial H}\right)_T dH + \left(\frac{\partial S}{\partial T}\right)_H dT$

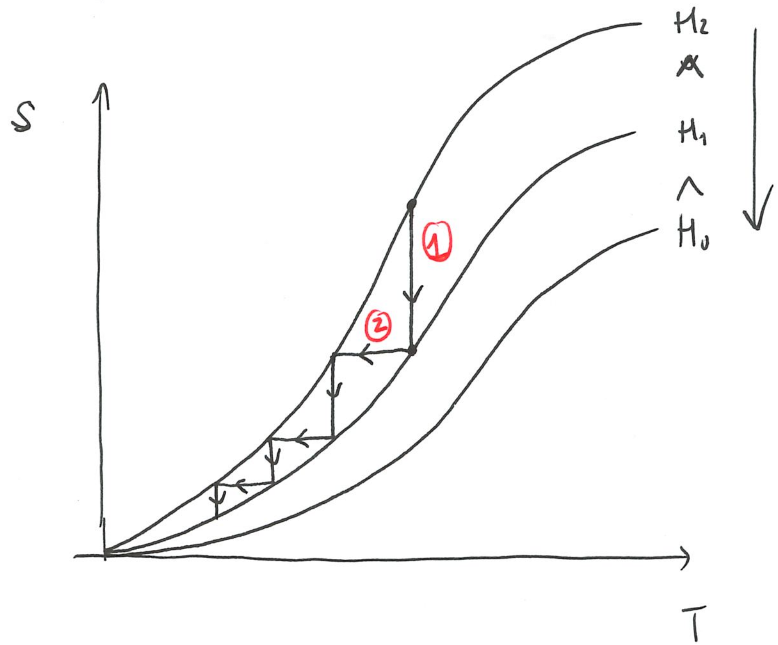
$dS = 0 \qquad 0 = \left(\frac{\partial S}{\partial H}\right)_T dH + \left(\frac{\partial S}{\partial T}\right)_H dT \Rightarrow \left(\frac{\partial T}{\partial H}\right)_S = -\frac{\left(\frac{\partial S}{\partial H}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_H}$ beraz bagenekien, jakina!

$\left(\frac{\partial T}{\partial H}\right)_S = -\frac{\left(\frac{\partial S}{\partial H}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_H} = -\frac{T}{C_H}\left(\frac{\partial S}{\partial H}\right)_T$

$\boxed{\left(\frac{\partial T}{\partial H}\right)_S > 0}$ zeinua finkatuta ②

- hozketa-prozesua aurrera eramateko
- azpiprozesuen konbinazioak temperatura jaitsiaraziko du

$\Downarrow$ ondorioak :



① - Temperatura konstante mantenduz : B-larekin kontaktuan

$H > 0 \Rightarrow S < 0$ ordenatu dugu

② - Adiabatikoki isolatu : b-i areagandik isolatu

$H < 0$ (lehengoa esaterako) $\Rightarrow T < 0$