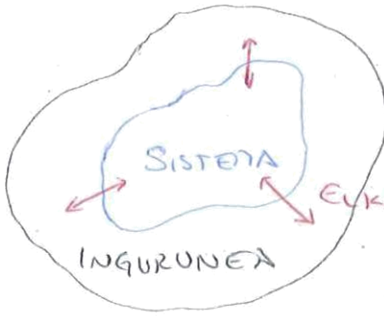

NO SEAS
RATA
ДЛЯ СЧАСТЬЯ НАРОДОВ!

OINARRIZKO KONTZEPTUAK

SISTEMA ∧ SISTEMAREN DESKRIPZIOA



↳ Idealki kenduko dugu

Bi irizpide daude:

MAKROSKOPIKOA

- Ez dago partikularik
-
-
-

MIKROSKOPIKOA

- Partikula osagaileak

LOTURA: Makroskopikoak erabiltzen dituen magnitude neurgarri urriak mikroskopikoak erabiltzen dituen ezaugarri askoren DENBORAKO BATAZBESTEKOAK dira.

(ALTERNATIBOA ↴

$\delta Q = TdS$ → ASKATASUN GRADU BERDINAREKIN LOTUAK

↳ ESTENTSIBOA

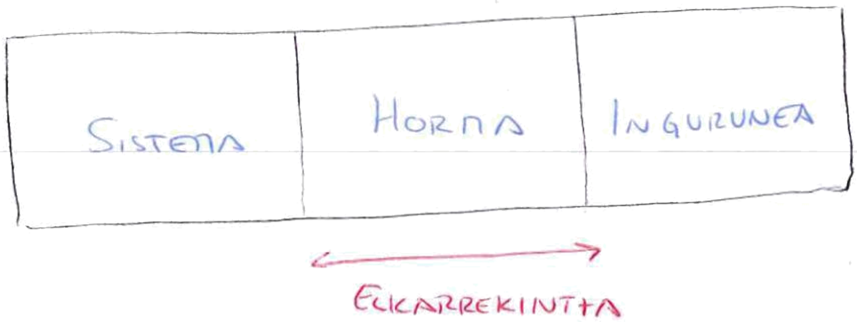
OREKA - EGOERA

- KOORDENATU TERMODINAMIKO INDEPENDIENTEAK

  $\{x, y, z, \ldots\}$ balioak ezagutu behar dira

- OREKA EGOERA OROKORRA

  $\{x, y, z, \ldots\}$ balio FINKOAK dituzte



ϕ; EZ DAGO / 1; BADAGO

HORMA MOTA $\longleftrightarrow$ ELKARREKINTZA MOTA

↳ Askatasun graduei lotuta "isolamendu partziala"

Zero Printzipioa: Tenperatura

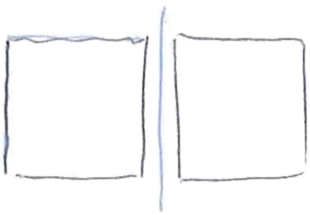
Oreka Termikoa

Elkarrekintza termikoa

Bai

Horma Diatermoa

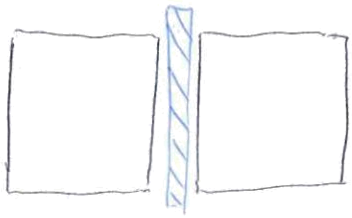
Isolamendu ϕ



Ez

Horma Adiabatikoa

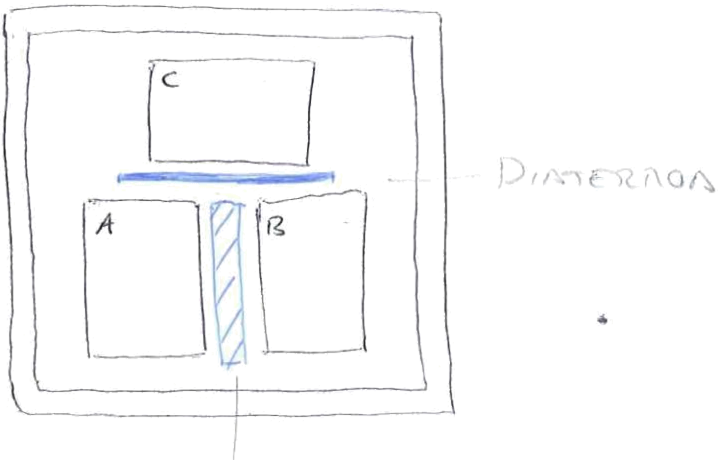
Isolamendua (1)



Oreka termikoa:

Horma diatermikoaren bidez "loturiko" bi sistemak lortuko duten egoera ALDAEZINA

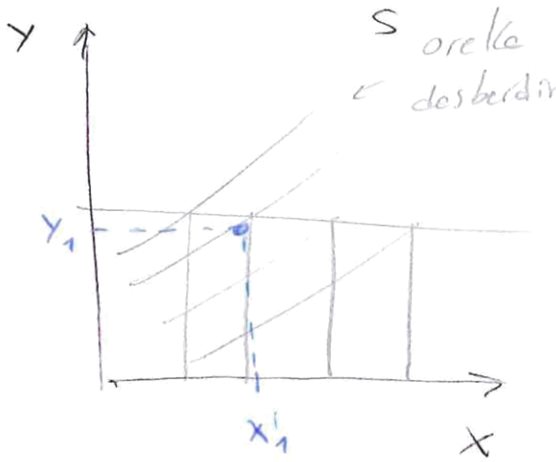
a)

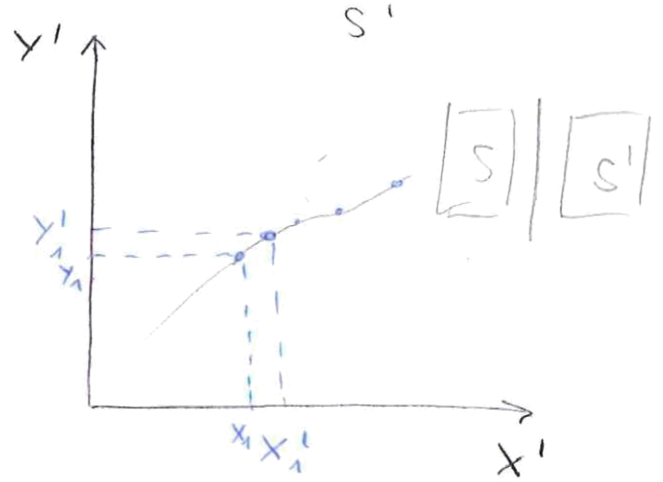


Experientziak dio: Adiabatikoa

$$\left.\begin{array}{l}\text{A-C oreka termikoan}\\ \text{B-C oreka termikoan}\end{array}\right\}\ \text{A-C oreka termikoan}$$

a) ESPERIENTZIAN OINARRITUTAKO "METODOA" T DEFINITZEKO





Lortu dezakegu S'-ren oreka termikoa S-ren oreka termikoarekin bat egiten duena.

S'-ren konfigurazio espazioan lortu dezakegu puntu segida bat zeinen haien artean oreka termikoan dauden → LERRO ISOTERMIKOA

Lerro isotermiko asko egin daitezke oreka termiko desberdinen funtzioan.

TENPERATURA: Bi sistemen artean komuna (oreka termikoa "ziurtatzen" du)

b) MATEMATIKAN OINARRITUTAKO METODOA

$\{A, B, C\}$ sistemak

$\{A, C\}$ OREKA TERMIKOA

$$f_{AC}(X_A, Y_A; X_C, Y_C) = 0$$
$$\Downarrow$$
$$Y_C = g_{AC}(X_A, Y_A; X_C)$$

$\{B, C\}$ OREKA TERMIKOA

$$f_{BC} = (X_B, Y_B; X_C, Y_C) = 0$$
$$\Downarrow$$
$$Y_C = g_{BC}(X_B, Y_B; X_C)$$

$$g_{AC}(X_A, Y_A ; X_C) = g_{BC}(X_B, Y_B ; X_C)$$

$\{A, B\}$ OREKA TERMIKOAN

$$f_{AB}(X_A, Y_A ; X_B, Y_B) = 0$$

$$g_{ABC}(X_A, Y_A ; X_B, Y_B, X_C) = 0 \Rightarrow X_C \text{ SOBERAN}$$

$h_A(X_A, Y_A) = h_B(X_B, Y_B) \rightarrow$ Bi sistemetan berdina

Bi balioak finkatuta $\rightarrow h_A$ finkatuta $\rightarrow T$ finkatuta

Edozein sistema definitu daiteke aldagai independenteen funtzioan definitutako T funtzioa

OREKAN:

$$h_A(X_A, Y_A) = h_B(X_B, X_B) = h_C(X_C, Y_C) = T$$

OROKORREAN

$$t = h_A(X_A, Y_A, Z_A, \dots) = \dots = h_i(X_i, Y_i, Z_i, \dots) = \dots$$

Oreka termikoan badaude:

- Tenperatura berean daude
- Funtzioak balio bakarra (eta komuna) du
- Hauxe da lerro isotermoaren sortaren balioa

Balioa finkatzeko tenperatura-eskala definitu behar da.

TENPERATURA ESKALA / NEURKETA

- BALIOA FINKATZEKO PROZEDURA OROKORRA

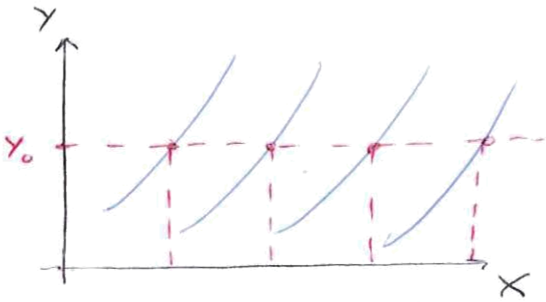
1.- Sistema mota → Gasa
2.- Sistema konkretua → Gas ideala
3.- Aldagai termodinamikoa.
4.- Funtzio termometrikoa → Aldagaia aldatu, zein da T?
5.- Puntu finkoak → Balio arbitrarioak eleitu: 0°C – 100°C

1.- SISTEMA MOTA

$$S = S(X, Y, Z, \dots) \qquad \{X, Y, Z\}$$

2.- SISTEMA KONKRETUA $\quad S(X, Y)$

3.- ALDAGAIA



X da aldagai termometrikoa $\{X; Y_0\}$

4.- $\theta(X) = aX$ FUNTZIO TERMOMETRIKOA

a?

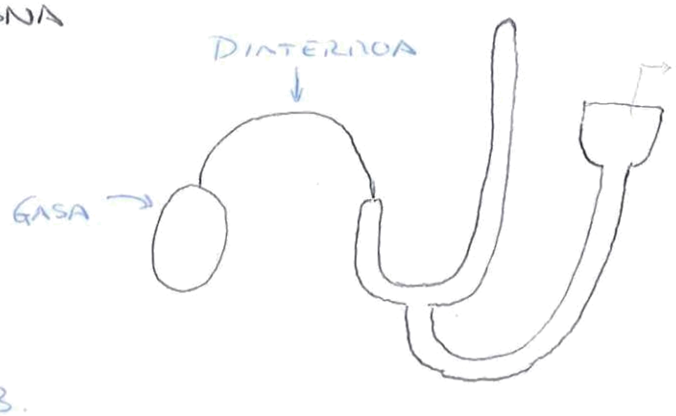
5.- PUNTU FINKOAK
arbitrarioki:

Finkatu X_i
Finkatu $\theta = \theta(X_i)$ $\Rightarrow$ a FINKATU $a = \dfrac{\theta_i}{X_i}$

$$\theta = \left[\frac{\theta_i}{X_i}\right] X$$

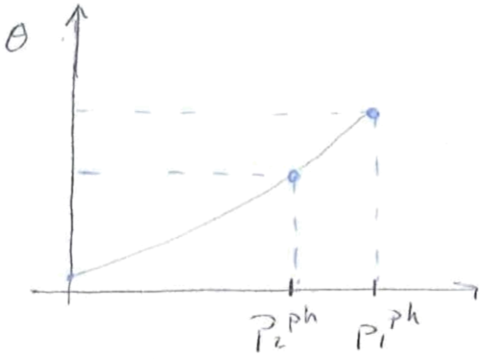
GAS IDEALEN TENPERATURA ESKALA

a) TRESNA



Finkatu punto finko bat

Presioa behatu



ADB.

1. N_2 sartu $\rightarrow m_1, V$

2. H_2O egoera hirukoitzean [puntu finkoa]
demagun $T = 273{,}16 K$ ↳ Erreferentziarako hartzen den E.T non T finkoa den.

3. Horma diatermo batekin lotu

4. Presioaren balioa behatu

$$P_1^{ph} \Rightarrow \theta = a X \quad \text{non} \quad a = \frac{273{,}16}{P_1^{ph}}$$

5. [Aldatu puntu finkoa $\rightarrow$ lortu beste P]

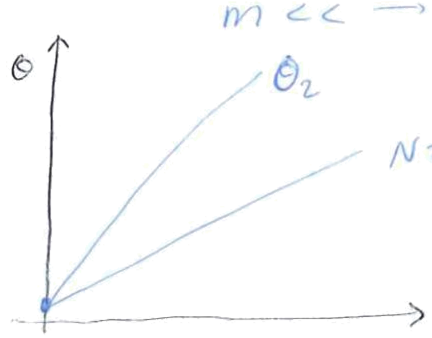
$$P_1^1 \rightarrow \theta^1 = \frac{273{,}16}{P_1^{ph}} P_1^1$$

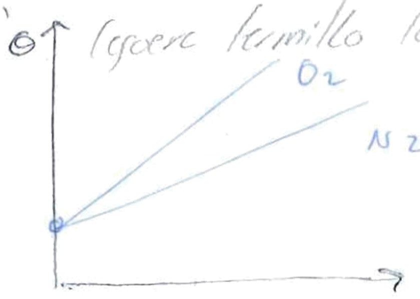
•) Aldatu $m_1 \geq m_2 \Rightarrow P_2^{ph}$ desberdina
V KTE — txikiagoa —

• $m << \longrightarrow \theta <<$ (baina konkretua)

•) Aldatu $N_2 \rightarrow O_2$ $\Rightarrow$ Bi gasekin limitea berdina
$m << \rightarrow \theta <<$

Beste batekoko E.T $\Rightarrow$

① 

② 

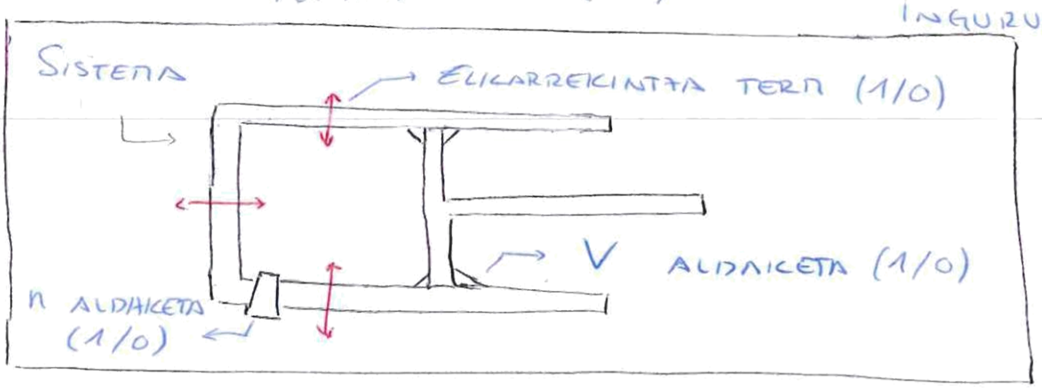
EGOERA EKUAZIOA

SISTEMA BAKUNA / SISTEMA HIDROSTATIKOA

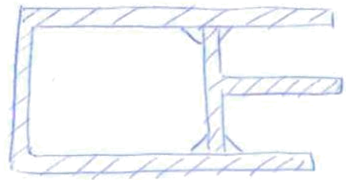
3 ASKATASUN GRADU → Askatasun gradu bakoitzeko aldagai independente bakoitza (bi aldagai termodinamiko)

- Mekanikoa (V, P) [est., in.]
- Kimikoa (μ, n) [pot. kim.]
- Termikoa (T, S) [entropia]

INGURUNEA → 2 oreka mota



Sistema isolatua



⇒ Unibertso bilakatu

3 oreka moduak beteten badira ⇒ OREKA TERMODINAMIKOA

SISTEMAREN DESKRIPZIOA: Oreka termodinamikoko egoeretan baino ezin da egin [magnitude t.d. finkoak eta berdinak sistema osoan]. Denborak ez du garantizatzen.

PROZESU KUASIESTATIKOA: Aldaketa infinituki motel gertatzen dela asumituz, gure sistema transformatzen den bitartean OREKA EGOERA batean izango dugu beti. [IDEALA]
Oreka termodinamikoen segida.
Sistema isten duten materialek elkarpen energetikorik ez dutela kontsideratuko dugu.

Soilik egoerak definituko dituzte

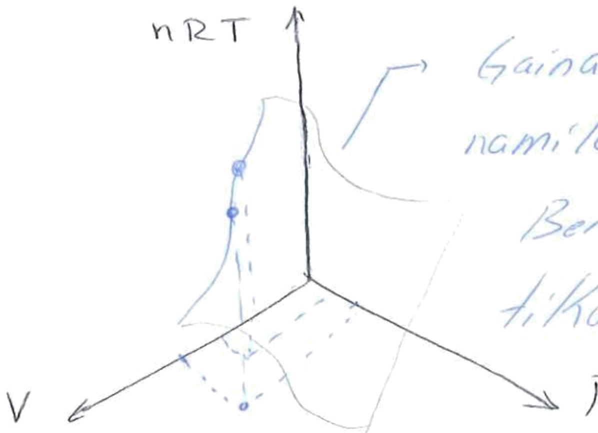
EGOERA-EKUAZIOA: Aldagai termodinamikoen arteko lotura $f(X, Y, Z, \dots) = 0$ oreka egoera definituko dituena.

Ez dira independienteak. Portaera mekanikoa adierazten du.

Askatasun gradu bakoitzari egoera ekuazio bat dagokio. "Ask. grad. mekanikoak eg. ek."

"Y eta X-en arteko lotura ⇒ Egoera ek.

$$p = p(V, T) \iff V = V(p, T) \iff T = T(V, p)$$



Gainazalean oreka termodinamikoko puntuak.

Beraz, prozesu kuasiestatikoak gainazaleko bi puntuen artean gertatzen dira.

- EGOERA EKUAZIOAREN ADIERAZPEN DIFERENTZIALA:

[OREKA-] EGOERAREN ALDAKETA

Egoera ekuazioa adierazteko (sistema hidrostatikoetan)

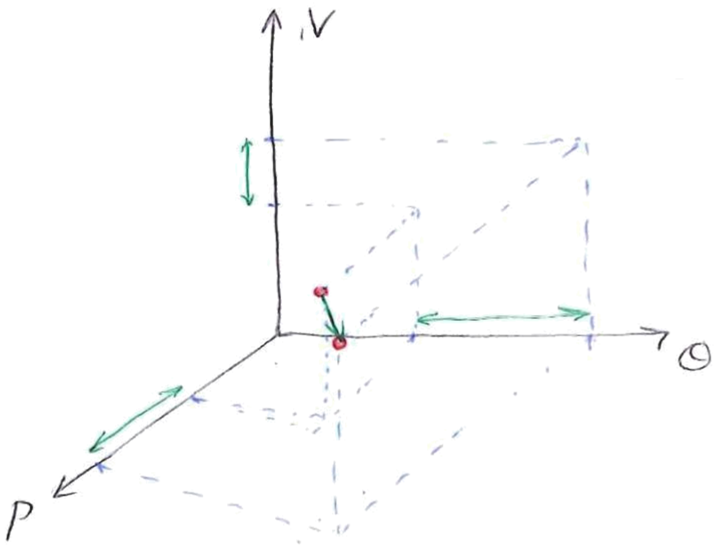
$V = V(p, \Theta)$ → Tenperatura esperimentala

$$\boxed{(P_0, \Theta_0)\ V_0} \longrightarrow \boxed{(P_1, \Theta_1)\ V_1}$$

$V_1 \to V_0 + dV$ → Egoera batetik bestera infinitesimalki.

Onartuko dugu definitute dagoela →

$$\boxed{dV = \left(\frac{\partial V}{\partial P}\right)_\Theta dP + \left(\frac{\partial V}{\partial \Theta}\right)_P d\Theta}$$



$$V = V(\Theta, P, N) =$$
$$= V(\Theta; P)$$
$$N \Rightarrow KTE$$

⊗ nola ko

nola aldatzen den V p ktea bada T aldatzean erlatiboki

$$dV = \left(\frac{\partial V}{\partial \Theta}\right)_P d\Theta + \left(\frac{\partial V}{\partial P}\right)_\Theta dP$$

$$\Downarrow \qquad\qquad \Downarrow$$

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial \Theta}\right)_{P,N} \qquad K_T = \ominus\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$$

KAPPA T

ZABALTZE KOEFIZIENTEA — KONPRIMIGARRITASUN ISOTERMOA

V nola aldatzen den T kte denean p aldatzen bada erlatiboki

$$dV = V\alpha\, dT - V K_T\, dP$$

$$dT = \frac{1}{V\alpha} dV + \frac{K_T}{\alpha} dP$$

$$dP = \frac{1}{\alpha} dT - \frac{1}{V\alpha} dV$$

ERLAZIOAK

- $$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y}$$

- $$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

$$\left(\frac{\partial T}{\partial P}\right)_V = -\frac{\left(\frac{\partial V}{\partial P}\right)_\Theta}{\left(\frac{\partial V}{\partial \Theta}\right)_P} = \frac{K_T}{\alpha} \qquad \left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{\left(\frac{\partial V}{\partial \Theta}\right)_P} = \frac{1}{V\cdot\alpha}$$

kte → bada dT gabe → $V_0(T_0, \Theta_0)$ behar

α eta K_T neurtu $\xrightarrow{int.}$ egoera ekuazioa lortu

ADIBIDEAK

1) $p \cdot V = nRT$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

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

$$\alpha = \frac{p}{nRT}\cdot\frac{nR}{p} \longrightarrow \alpha = \frac{1}{T}$$

$$k_T = \cancel{-}\frac{\cancel{p}}{nRT}\cdot\frac{\cancel{-}nRT}{p^{\cancel{2}}} \longrightarrow k_T = \frac{1}{p}$$

2) $p(V-b) = nRT$

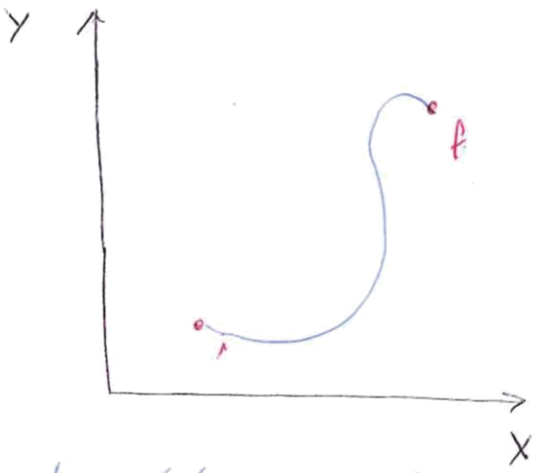
$$V = \frac{nRT}{p} + b \Rightarrow \begin{array}{l} \alpha = \frac{1}{T} \\ k_T = \frac{1}{p} \end{array}$$

3) $pV = nRT\left(1 + \frac{B}{V}\right)$ CGIN

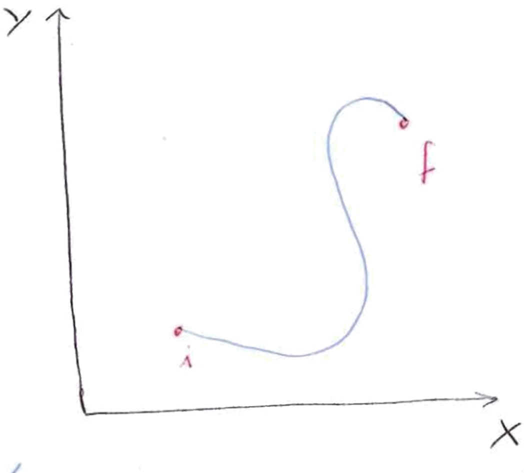
$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \Rightarrow \alpha = \frac{-1}{V}\,\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} = -\frac{1}{V}\cdot\frac{1}{\left(\frac{\partial T}{\partial V}\right)_p}$$

$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \Rightarrow k_T = -\frac{1}{V}\cdot\frac{1}{\left(\frac{\partial p}{\partial V}\right)_T} = -\frac{1}{V}\,\frac{\left(\frac{\partial T}{\partial p}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_p}$$

2 ASKATASUN GRADU



1 ASKATASUN GRADU



· {Y, X} aldagai independiente

· Planoko edozein puntu: oreka egoera

· Kurba: PROZESU KUASIESTATIKOA
Sistemari buruzko informazioa planoko puntuetan

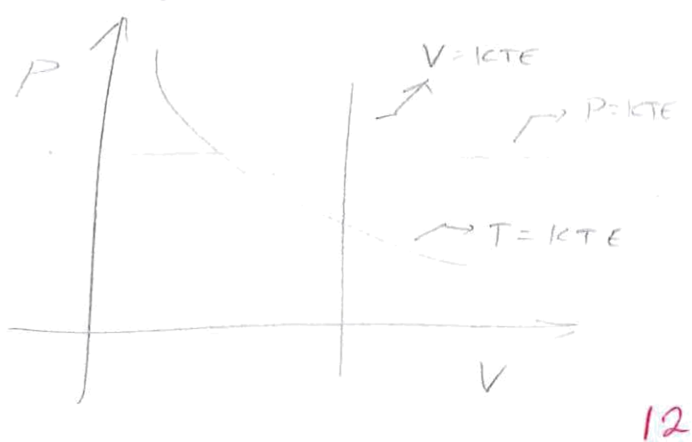
· {Y, X} aldagai deskribatzaile

· Planoko edozein puntu: EZ oreka egoera

· Kurba: EGOERA EKUAZIOA
sistemari buruzko inf. soilik kurbako puntuetan
[Kurbako edozein bi punturen arteko prozesu kuasiestatikoa]

PROZESU KUASIESTATIKOA:

Benetako existentzia fisikorik gabeko prozesua sistemari dagozkion oreka-egoeren, espazioko puntuen segidak osatutako lerro jarraitua. Hasierako eta bukaerako oreka egoerak lotuko dituena.



Lehenengo Printzipioa

Lana

LANA: Sistema bat indar baten eraginpean desplazatu gero. (ESKALARRA)

Sistema hidrostatikoa: $m = kte \wedge$ 2 aldagai independente.

↳ Printzipioz lan mekanikoa soilik.

INDAR MEKANIKOA

aldaketa infinitesimala

$$\Rightarrow \delta W = \vec{F} \cdot d\vec{r}$$

DESPLAZAMENDU ARRUNTA

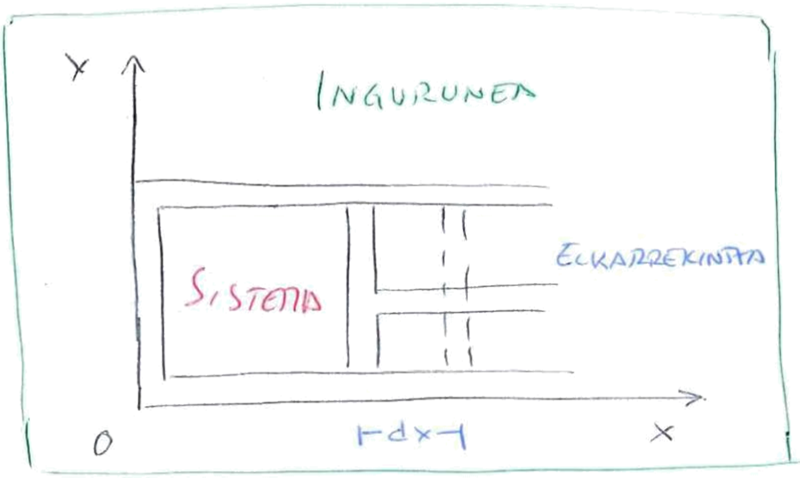
- Sistemak lana ematen badu → NEGATIBOA
- Sistemari lana ematen badiogu → POSITIBOA
- Lana ez da inoiz diferentzial zehatza ($\cancel{dW}$) — aldaketa finitua
- Ez dago sistema bati dagokion lana ← Ez da sistemaren propietatea
- Ez dago sistema bati dagokion $W = W(X, Y, \ldots)$
- Lana ibilbidearekiko menpekoa.

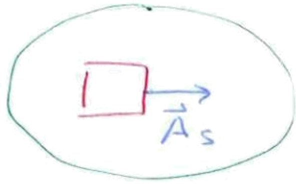
KASU BEREZIA

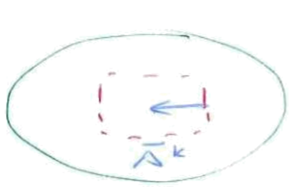
Lan mekaniko adiabatikoa

$$W^{ad} = \Delta U \rightarrow \text{sistemaren propietatea}$$

Bakarrik existitzen diren funtzioak







$$\delta W^s = -\underset{\text{SISTEMA}}{p^s}\, dV^s$$

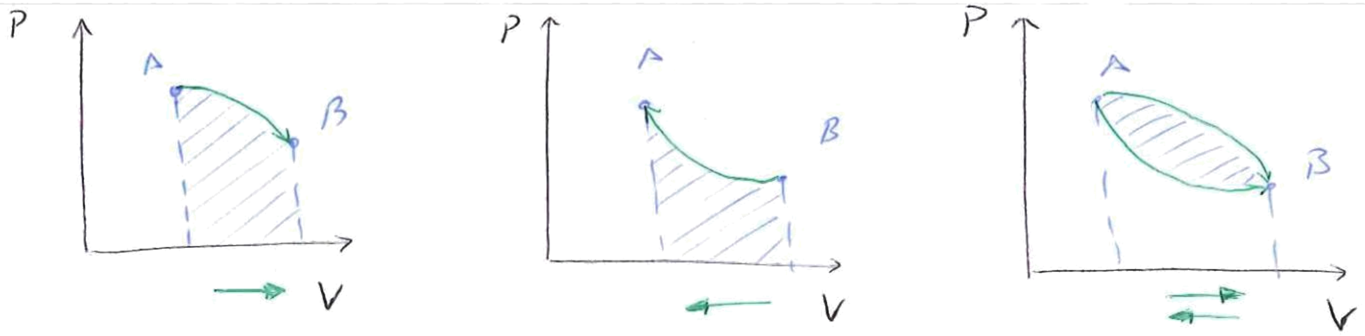
$$\delta W^s = -\underset{\text{INGURUNEA}}{p^k}\, dV^s$$

$\Rightarrow$ Sistema eta ingurunearen artean $p^s = p^k$ kontsideratuko dugu.

$$\Rightarrow \boxed{\delta W = -p\,dV} \rightarrow W = -\int_a^b -p\,dW$$

Ibilbidea ezagutu behar dago.

"Sistemak lana kanporatzen du"



$dV > 0$	$dV < 0$	$dV = 0$
AZALERA > 0	AZALERA < 0	AZALERA $\gtrless 0$
LANA < 0	LANA > 0	LANA $\lessgtr 0$

FUNTZIOEN PROPIETATEAK

$$z = z(x,y) \Rightarrow \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$$

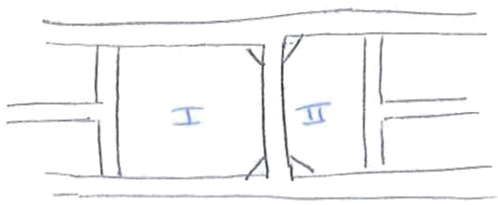
$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Ask. Gradua	Intentsiboa	Estentsiboa	δW
Mekanikoa	P	V	$-p\,dV$
Termikoa	T	S	$T\,dS$
Kimikoa	μ	N	$\mu\,dN$
Magnetikoa	B, H	M	$B\,dM$
Elektrikoa	E	P	$E\,dP$
Elastikoa	Z	L	$Z\,dL$
	X	Y	$X\,dY$

LANA OROKORREAN

* DESPLAZAMENDU OROKORTUA
  Y INDAR OROKORTUA $\Rightarrow \delta W = \vec{Y} \cdot d\vec{X}$

Sistemari dagokion askatasun-gradu berberarekin loturiko aldagai konjugatuak



→ SISTEMA KONPOSATUA

Horma adiabatikoa:
4 askatasun gradu
(bakoitzerako termikoa eta mekanikoa, edb)

Horma diatermoa: 3 askatasun gradu
(bakoitzerako mekanikoa + elkarrekin termikoa)

SISTEMA KONPOSATUA: Azpisistema bakoitzak ekarpen independentea emango dute. Zenbait askatasun-gradu badu, berauek ekarpen bana emango dute.

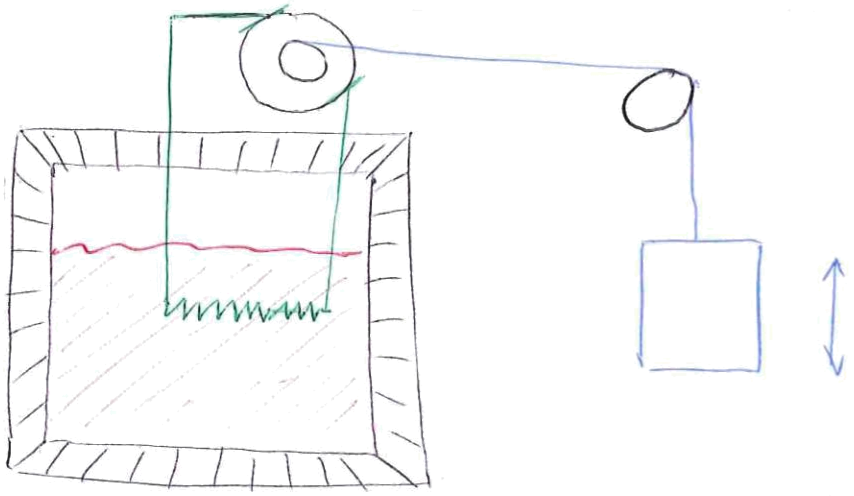
Beraz, [lan mekanikoa kontuan hartuz]

$$\boxed{\delta W_{OSOA} = \sum_{i=1}^{n} \delta W_i} = \sum_{i=1}^{n} \vec{Y}_i \, d\vec{X}_i$$

Sistemak termikoki edo mekanikoki (edo biak) lotu daitezke ingurunearekin.

Baina ez da beharrezkoa kontaktu termikoa izatea (egoera termikoa aldatzeko (mekanikoki alda daiteke, adb.). Beste askatasun graduekin berdin gertatzen da.

OINARRIZKO BEREIZKETA: SISTEMA - INGURUNEA



SISTEMA: Ura + erresistentzia

Lan mekanikoak sistema aldatu (adiabatikoa)

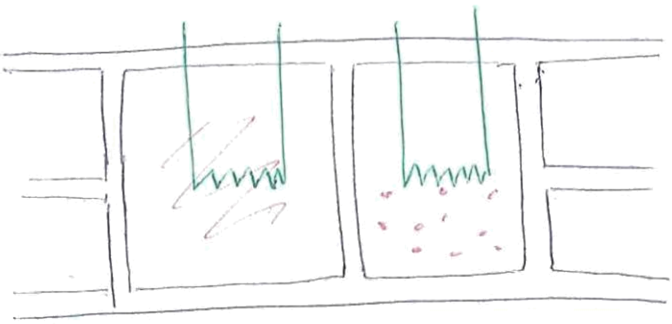
SISTEMA: Ura

Sistemaren egoera lotura termikoaren bidez aldatuko dugu, lana mekanikoa izanik. (diatermoa) Bero transferentzia dago.

LAN ADIABATIKOA

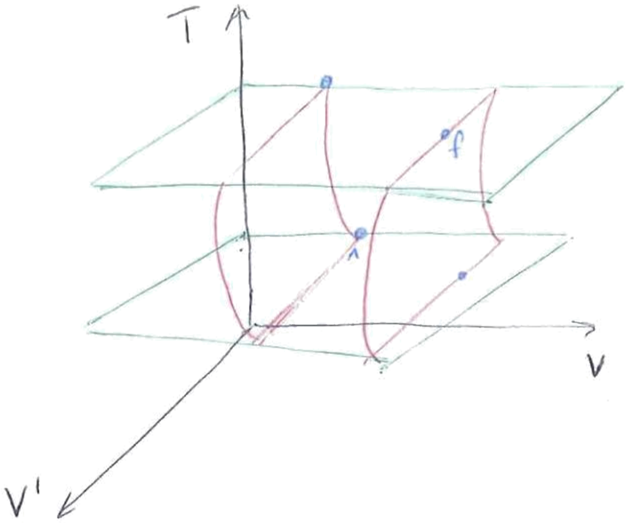
ESPERIMENTALKI ikusi da: Lana adiabatikoa izanda, sistema i egoeratik f egoerara eraman badugu, ibilbidea edozein izanda, egindako lana beti berdina izango da.
=> Lan adiabatikoak ez du ibilbidearekiko menpekotasunik => dW => Sistemaren propietatea da => $W^{ad} = \Delta U$

* BEROAREN DEFINIZIO KALORIMETRIKOA: Bi sistemen arteko tenperatura-diferentziari esker (soilik) bataletik bestera transferituko bero



P, V, T
P', V', T' $\Rightarrow \{V, V', T\}$

SISTEMA KONPOSATUA



$$\boxed{W^{ad}_{i\text{-}f} = U_f - U_i}$$

BARNE-ENERGIA

Quasiestatikoki → poliki-poliki; edozein puntutan orekan

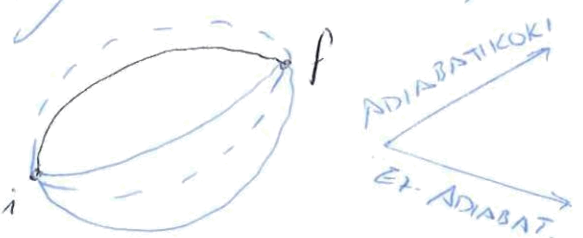
Sin rozamiento → Energia barreiaketarik gabe

$U = U(X, Y) \iff X = X(U, Y) \iff Y = Y(U, X)$

→ Barne energia sistemaren aldagaia izan daiteke

LORTU NAHI DUGUNA:

Masa konstanteko sistema hidrostatikoko energiaren adierazpena.



$W^{ad}_{i\to f} = \Delta U$

$W^{ez\text{-}ad}_{i\to f}(1) \neq W^{ez\text{-}ad}_{i\to f}(2) \ldots$

$\Downarrow$

Sistemaren propietatea ← ΔU_{if} berdina

$\Delta U_{if} \neq W^{ez\text{-}ad}_{i\to f} \Rightarrow \boxed{\Delta U_{if} - W_{i\to f} = Q_{if}}$

Zeinu aldaketak

$$\Delta U - W = Q \rightarrow \Delta U = W + Q \rightarrow dU = \delta W + \delta Q$$

Bi diferentzial ez zehatzen baturak diferentzial zehatz bat eraikitzen du.

$$\boxed{\delta Q = dU - \delta W^{mek}}$$

$$dU = \delta Q + \sum_{i=1}^{n} Y_i dX_i$$ → Sistemaren energiaren aldaketarako aldakuntza gradu termikoa eta besteko guztiak erabiltzen dira.

$$\delta Q = dU - \delta W^{mek} \xrightarrow{\text{SIST HIDROST.}} \delta Q = dU + p\,dV$$

Bero ITURRIA

- Masa oso handiko sistema
- Egoera termikoa finko mantentzen du (T = KTE), edozein bero truke izan arren.
- → irudia $\quad Q = \int_{\theta_i}^{\theta_f} C_\theta \, d\theta$
- Adibidez: termometro klinikorako iturria gorputza
- Tenperatura konstanteko prozesuak adierazteko erabiliko dugu.

Bero AHALMENA

$$C = \lim_{(\theta_f - \theta_i) \to 0} \frac{Q}{\theta_f - \theta_i}$$

$$c_\theta = \frac{C_\theta}{m}$$

Bero transferentzian sistemaren portaera

$$C_{\square} = \left[\frac{\delta Q}{dT} \right]_{\square}$$

Ze modutan ematen diogun beroa sistemari

C_V] → Beroa bolumena konstante utziz kalkulatuta
[V-rekiko menpekotasuna izan dezake → C_V']

Masa kte., sistema hidros.; $(\underbrace{C_p, C_v}, \underbrace{\alpha, k_T})$

Askatasun gradu bakoitzeko bi koefiziente experimental.

Bikoteen arteen erlazioa dago [ADB: $C_p - C_v = T\frac{V\alpha^2}{k_T}$]

$$\delta Q = dU + p\,dV$$

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + p\,dV =$$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\Big|_T + p\right) dV$$

$$\frac{1}{dT}\delta Q\Big|_V = \left[\left(\frac{\partial U}{\partial T}\right)_V \frac{dT}{dT} + \left(\frac{\partial U}{\partial V}\Big|_T + p\right)\overset{\to 0}{\frac{dV}{dT}}\right]_V$$

def ↓

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V}$$

Bolumena konstante izanik, energiaren aldaketa bero moduan soilik atera dezake.

$$\frac{1}{dT}\delta Q\Big|_p = \left[\left(\frac{\partial U}{\partial T}\right)_V \frac{dT}{dT} + \left(\frac{\partial U}{\partial V}\Big|_T + p\right)\frac{dV}{dT}\right]_p$$

$$C_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

$$C_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] V\alpha$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_V}{V\alpha} - p$$

$T, (Y, X)$

$C_X = \frac{\partial Q}{\partial T}\Big|_X$

"α" $= \frac{1}{X}\left(\frac{\partial X}{\partial T}\right)_Y$

"k_T" $= -\frac{1}{X}\left(\frac{\partial X}{\partial Y}\right)_T$

$$\delta Q = C_v\, dT + \left[\frac{C_p - C_v}{V\alpha} - p + p\right] dV$$

$$\boxed{\delta Q = C_v\, dT + \frac{C_p - C_v}{V\alpha}\, dV} \rightarrow$$ T, V aldagai independientetzat hartuta

Berdina egin baina T ∧ P aldagai independientetzat hartuz

$$\delta Q = dU + p\, dV$$

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp + p\left[\left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp\right]$$

$$\left.\frac{\delta Q}{dT}\right|_p = \left[\left(\frac{\partial U}{\partial T}\right)_p \overset{1}{\frac{dT}{dt}} + \left(\frac{\partial U}{\partial p}\right)_T \overset{0}{\frac{dp}{dt}} + p\left[\left(\frac{\partial V}{\partial T}\right)_p \overset{1}{\frac{dT}{dT}} + \left(\frac{\partial V}{\partial p}\right)_T \frac{dp}{dT}\right]\right]_p$$

$$\left.\frac{\delta Q}{dT}\right|_p = p\left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial T}\right)_p$$

$$C_p = \left.\frac{\delta Q}{dT}\right|_p \quad \wedge \quad \frac{1}{V}\left(\frac{dV}{dT}\right)_p = \alpha$$

$$C_p = pV\alpha + \left(\frac{\partial U}{\partial T}\right)_p$$

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

$$\left.\frac{\delta Q}{dT}\right|_V = \left[\left(\frac{\partial U}{\partial T}\right)_p \overset{1}{\frac{dT}{dt}} + \left(\frac{\partial U}{\partial p}\right)_T \frac{dp}{dT}\right|_V + p\left[\overset{0}{\left(\frac{\partial V}{\partial T}\right)\frac{dT}{dT}} + \overset{0}{\left(\frac{\partial V}{\partial p}\right)\frac{dp}{dT}}\right]\right]_V$$

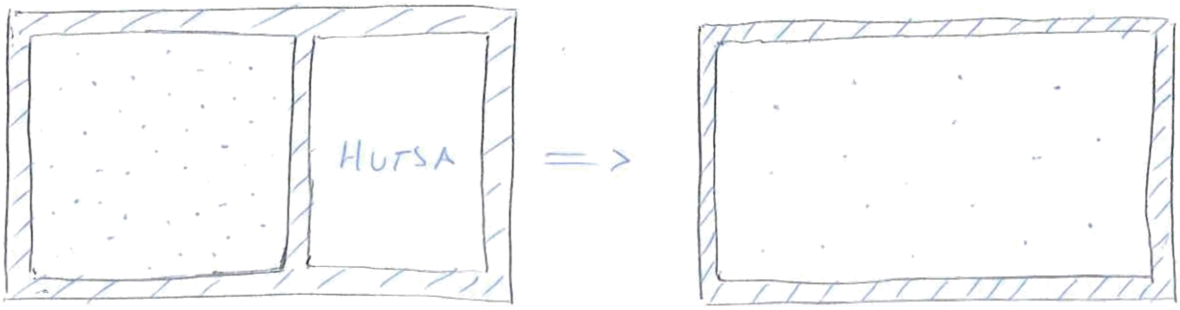
$$C_v = C_p - V\alpha p + \left(\frac{\partial U}{\partial p}\right)_T \frac{\alpha}{k_T}$$

$$\left(\frac{\partial U}{\partial p}\right)_T = \frac{C_v - C_p}{\alpha} k_T + V k_T p$$

GAS IDEALA

ESPANTSIO ASKEA

$N = KTE$



$$Q = \Delta U - W$$

Sistema adiabatikoki isolatua $\Rightarrow Q = 0$

Kontaktu mekanikorik ez duenez ingurunearekin $\Rightarrow W = 0$

$$Q = W = 0 \Rightarrow \Delta U = 0 \Rightarrow U_i = U_f$$

$dU \overset{?}{=} 0 \rightarrow U = KTE \rightarrow$ Prozesu kuasiestatikoa

Kasu honetan prozesua finitua denez ezin da (tarteko egoerak ez daude oreka termodinamikoan)

GAS IDEALAREN KONTZEPTUAREN DEFINIZIOA

• $U = U(T, V)$ $\qquad dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

(nahi dugulako)

Definituko dugu sistema bat non

$$dU = 0 \wedge dT = 0 \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = 0$$

Hau da, barne energiak ez du menpekotasunik bolumenarekiko Tenperatura kte bada.

ADB: Bero iturri bat erabiliz sistema $T = KTE$ mantentzen badugu, edozein bolumenean barne energia berdina da.

• $U = U(T,P) \qquad dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$

Definituko dugu sistema bat non

$dT = 0 \wedge dU = 0 \Rightarrow dU = \left(\frac{\partial U}{\partial P}\right)_T = 0$

Tenperatura konstantean, barne energiak ez du menpekotasunik presioarekiko, hau da, presioa edonolakoa izanda, sistema bero iturri batera lotuta badago barne energiak balio finkoa izango du.

$$\text{GAS IDEALA} \begin{cases} \boxed{P \cdot V = nRT} & \rightarrow \text{MEKANIKOA} \\ \left(\frac{\partial U}{\partial P}\right)_T = 0 \\ \left(\frac{\partial U}{\partial V}\right)_T = 0 \end{cases} \Bigg\} \boxed{U = U(T)} \rightarrow \text{TERMIKOA}$$

$$C_P - C_V = TV \frac{\alpha^2}{k_T}$$

$$\alpha = \frac{1}{T} \qquad k_T = \frac{1}{P} \quad \Rightarrow C_P - C_V = \cancel{T} V \cdot \frac{\frac{1}{T^{\cancel{2}}}}{\frac{1}{P}} = nR$$

MAYER-EN EKUAZIOA $\rightarrow \boxed{C_P - C_V = nR}$

$C_P \wedge C_V$ txikiak izanik $\Rightarrow C_P - C_V = R$

Gas ideala sistema hidrostatikoa denez $\Rightarrow$

$\left(\frac{\partial U}{\partial T}\right)_V = C_V \quad \wedge \quad U = U(T)$ denez $\Rightarrow$

$$C_V = \frac{dU}{dT} \overset{\text{integratu}}{\Rightarrow} \boxed{U = C_V T + K}$$

Gas idealetan zuzenean badakigu barne energia zein den [baita edozein sistematan zeinean $U = U(T)$ betetzen den $\Rightarrow U = C_x T + K$]

LEHENENGO PRINTZIPIOA GAS IDEALEN KASUAN

$$Q = \Delta U - W \Rightarrow \delta Q = dU - \delta W$$

Sisteme hidrostatikoa $\rightarrow \delta W = -p\,dV$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V \Rightarrow \left[\frac{\delta Q}{dT} = \frac{dU}{dT} + p\frac{dV}{dT}\right]_V$$

$$\left[\frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_V \frac{dT}{dT} + \left\{\left(\frac{\partial U}{\partial V}\right)_T + p\right\}\frac{dV}{dT}\right]_V$$

$$\frac{\delta Q}{dT} = C_v + p\frac{dV}{dT} \Rightarrow \boxed{\delta Q = C_v\,dT + p\,dV}$$

(T, V)

$$\boxed{\delta Q = C_p\,dT - V\,dp} \leftarrow (T, P)$$

$$\delta Q = C_v\,dT + p\,dV \Rightarrow dV = V\alpha\,dT - Vk_T\,dp$$

$$\alpha = \frac{1}{T} \quad k_T = \frac{1}{P} \Rightarrow dV = \frac{V}{T}dT - \frac{V}{P}dp$$

$$p\,dV = p\frac{V}{T}dT - \frac{V}{\cancel{P}}\cancel{p}\,dp \Rightarrow \delta Q = C_v\,dT + \frac{pV}{T}dT - V\,dp$$

$$\Rightarrow \delta Q = (C_v + nR)\,dT - V\,dp \Rightarrow \delta Q = C_p\,dT - V\,dp$$

Izan prozesu kuasiestatikoa gas idealetan non

$$\delta Q = 0 \Rightarrow \begin{cases} 0 = C_v\,dT + p\,dV \\ 0 = C_p\,dT - V\,dp \end{cases} \Rightarrow \begin{cases} C_v\,dT = -p\,dV \\ C_p\,dT = V\,dp \end{cases}$$

$$\Rightarrow \gamma = \frac{C_v}{C_p} = -\frac{V}{P}\frac{dP}{dV} \rightarrow \text{INDIZE ADIABATIKOA}$$

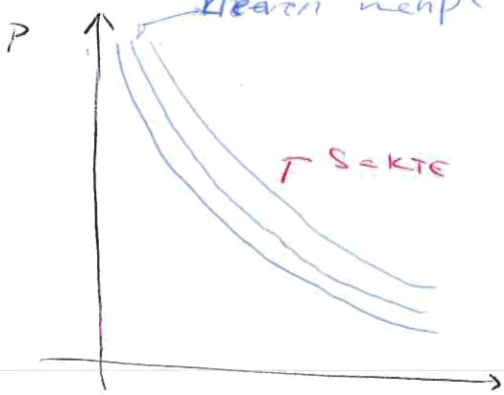
Gas idealetan C_p, C_p konstanteak.

$$\frac{dP}{P} = -\gamma\frac{dV}{V} \rightarrow$$ Gas idealen prozesu adiabatiko eta kuasiestatikoari dagokion P, V kurbaren ekuazioa emango digu.

$$\boxed{pV^{\gamma} = KTE}$$

ZABALTZE ASKEA (EZ DA KUASI)

Prozesu adiabatiko kuasiestatikoari dagokion forma P-V diagraman.
(gas idealetan)



- P-T-ren diagraman lortu nahiko baganu:

$$0 = C_p\,dT - V\,dp$$

$$C_p\,dT = V\,dp$$

Egoera ekuazioa bete beher denez: $PV = nRT$

$$C_p\,dT = \frac{nRT}{P}dp \rightarrow \frac{C_p}{nRT}\,dT = \frac{dP}{P}$$

$$\frac{C_p}{nR}\ln T = \ln p \Rightarrow T^{\frac{C_p}{nR}} = PK$$

$$\leftarrow \quad \boxed{\frac{1}{P}T^{\frac{C_p}{nR}} = KTE} \rightarrow TP^{\frac{1-\gamma}{\gamma}} = KTE$$

- V-T-ren kasuan:

$$0 = C_v\,dT + p\,dV \rightarrow C_v\,dT = -p\,dV$$

$$PV = nRT \rightarrow C_v\,dT = -\frac{nRT}{V}dV \rightarrow$$

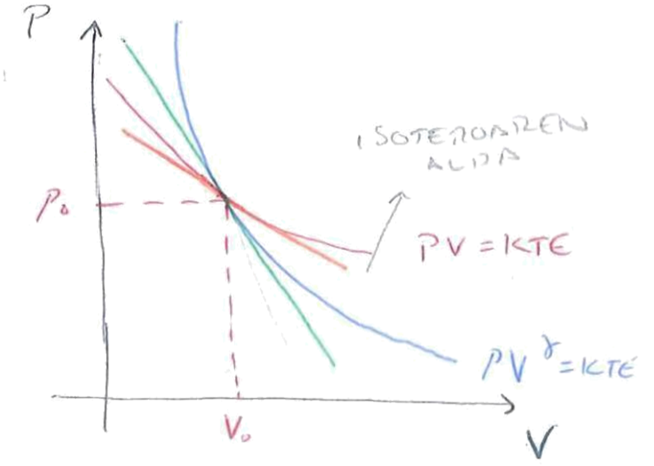
$$\frac{C_v}{nRT}\,dT = -\frac{dV}{V} \rightarrow T^{\frac{C_v}{nR}} = \frac{1}{V}K$$

$$\leftarrow \quad \boxed{T^{\frac{C_v}{nR}}V = KTE} \rightarrow TV^{\gamma-1} = KTE$$

Ozeen egoerak definitzen ditute, homogetik denek betiken dute $PV = nRT$

Prozesu honetan energia ez da barreiatzen eta, beraz, itzulgarriak dira.

Nola finkatu konstantearen balioa?



Prozesu adiabatikoa:

$$\delta Q = 0$$

$$pV^{\gamma} = KTE$$

$$(p_0, V_0)$$

$$pV^{\gamma} = p_0 V_0^{\gamma}$$

Zein da malda?

$$\frac{dp}{p} = -\gamma \frac{dV}{V} \Rightarrow \frac{dp}{dV} = -\gamma \frac{p}{V}$$

$$\gamma = \frac{C_p}{C_v} \qquad C_p - C_v = nR > 0 \rightarrow \quad \gamma > 1$$

Prozesua kuasiestatikoa eta isotermoa gas idealetan:

$$T = KTE \quad ; \quad PV = nRT \Rightarrow \quad PV = KTE$$

$$d(PV) = 0 \rightarrow \quad p\,dV + V\,dp = 0$$

$$\Rightarrow p\,dV = -V\,dp \Rightarrow \frac{dp}{dV} = -\frac{p}{V}$$

PROZESU POLITROPIKOAK

GAS IDEALETAN $\Rightarrow$ $PV^{j} = KTE \quad ; \forall j$

$j = 1 \Rightarrow pV^{j} = pV = KTE \rightarrow$ ISOTERMOA

$j = 0 \Rightarrow pV^{0} = p = KTE \rightarrow$ ISOBAROA

$j = \infty \Rightarrow pV^{\infty} = V = KTE \rightarrow$ ISOKOROA

$j = \gamma \Rightarrow pV^{\gamma} = KTE \rightarrow$ ADIABATIKOA

LANA

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

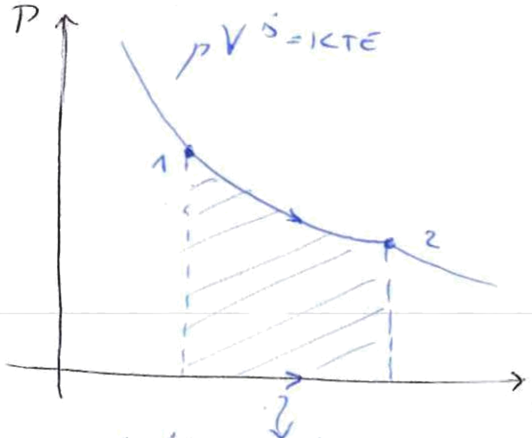
$$pV^{j} = C \Rightarrow p = \frac{C}{V^{j}} \Rightarrow \delta W = -\frac{C}{V^{j}}\,dV$$

$$\Rightarrow \quad W = -c \int \frac{1}{V^{\gamma}}\, dV$$

Ibilbidea ezaguna dugunez P-V diagraman integral ez-zehatzak kalkula daitezke.

$$W = \frac{1}{\gamma - 1}\left(p_2 V_2 - p_1 V_1\right)$$

$$W = \frac{1}{\gamma - 1}\, nR\left(T_2 - T_1\right)$$



zabaltzen da $\Rightarrow$ $W < 0$

BARNE-ENERGIA

$$U = U(t) \Rightarrow dU = C_v\, dT$$

$$\Delta U = C_v \Delta t$$

$$\Delta U = C_v (T_2 - T_1) \qquad \Delta U = C_v\, nR\, (T_2 - T_1)$$

BEROA

$$Q = nR\,(T_2 - T_1)\left[C_v - \frac{1}{\gamma - 1}\right]$$

$$Q = \frac{T_2 - T_1}{\gamma - 1}\left[\gamma C_v - C_p\right]$$

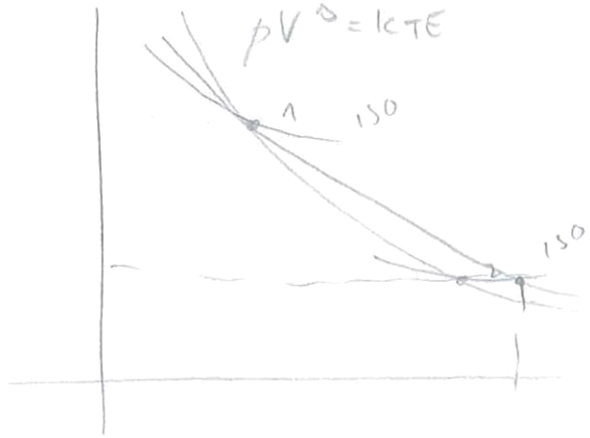
$$Q = \frac{T_2 - T_1}{\gamma - 1}\, nR\left[\gamma C_v - C_p\right]$$

GAS IDEALETAN prozesua edozein modutan gertatzen bada ere $\Delta U = C_v \Delta T$ ibilbidearen independentea da beti.

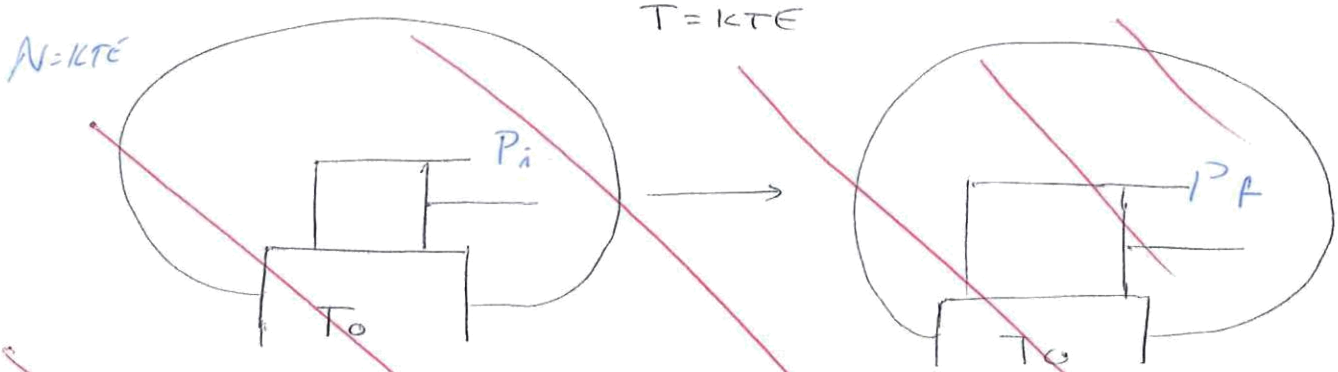
$$V = KTE \quad \Rightarrow \quad Q = \Delta U = C_v \Delta T$$

Prozesua adiabatikoa => Ez da berorik trukatzen (egoera termikoa aldatu daiteke!! $\Delta T \neq 0$)
Prozesu adiabatikoa bada ezinezkoa da puntu (P_0, V_0) berera ailegatzea

Hobetu (oraindik!!!)



LAN PROZEDUREN ARIKETAK GAS IDEALETAN



- Horma diatermoz inguratutako gas ideala dugu, T_0 tenperaturako bero-iturri batekin ukipen termikoan eta hasierako P_i presioko presio-iturriarekin ere kontaktuan. Iturriaren presioa P_f baliorainoko kuasiestatikoki aldatu da. Lortu ondokoak:

1. Transferitutako lana
2. Trukaturiko bero-kantitatea
3. Barne-energiaren aldaketa

} Kuasiestatikoa izanik kalkula daiteke

BARNE-ENERGIA

Prozesua kuasiestatikoa $\Rightarrow T = kte \Rightarrow \Delta U = 0$

ΔU sistemaren propietatea denez (egoera-funtzioa da) ez du ibilbidearekiko menpe-kotasunik.

KUASIESTATIKOKI $\begin{cases} dT = 0 \\ \Delta T = 0 \end{cases}$ edonola ere $\Rightarrow \Delta U = 0$

EZ-KUASIESTATIKOKI $\begin{cases} dT \neq 0 \\ \Delta T = 0 \end{cases}$

Planteatutako prozesua ez-kuasiestatikoa bada $\Rightarrow$ ez dira egoerak lotuta $\Rightarrow$ ez daude definituta
$\Rightarrow$ Ezin izango lirateke beroa eta lana kalkulatu (ezta lehenengo printzipioarekin ere)

LANA

Kasu honetan mekanikoa da: $\delta W = -p\,dV$
Gas ideala denez, egoera ekuazioa betetzen da: $PV = nRT = nRT_0 = kte$

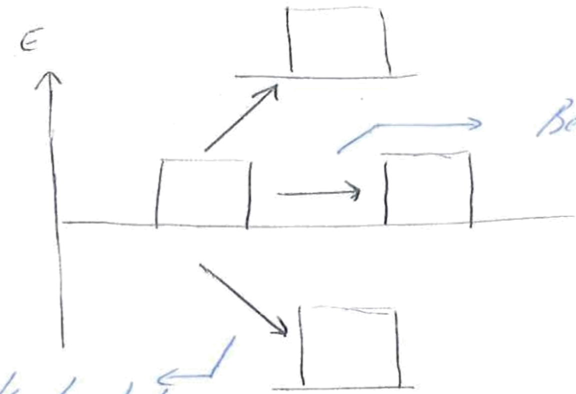
$$\int \delta W = -\int p(V)\,dV = -\int_f^i \frac{nRT_0}{V}\,dV$$

$$W = -nRT_0 \ln \frac{V_f}{V_i}$$

$\Rightarrow W = -nRT_0 \ln \frac{P_i}{P_f} < 0 \rightarrow$ Sistemak egin du lan pistoia altxatzeko. Hala ere, zabaltzean energia galtzen du baina bero

2. PRINTZIPIOA: ENTROPIA

Lehenengo printzipioak dio sistema isolatua badago energia kontserbatuko dela, baina ez du ezer esaten energia bereko egoeren aldaketari buruz. Bigarren printzipioak bereizketa hori egiten du: zer prozesu gertatzen diren berez eta zeintzuk ez.



Berezkoa (?)

Isolamendua kendu behar

$$\Delta S^{unibertso} \geq 0$$

$$\Delta S^{unib.} \equiv \Delta S^{sist} + \Delta S^{ing}$$

Oreka beretik:

$$\Delta S^{sist} = -\Delta S^{ing}$$

$\Delta S^{u} = 0 \rightarrow$ ITZULGARRIA

$\Delta S^{u} > 0 \rightarrow$ ITZULEZINA

IZADIKO ASIMETRIA

i) LANA $\longrightarrow$ BEROA TRANSFORMAZIOAK

1) %100 errendimendua

...egoera aldatu gabe

...berriro ("ad infinitum")

...tzen dira eta beti gerta

...de.

⊕ => W, Q sisteman sartu => $\Delta U > 0$

⊖ => W, Q sistematik atera => $\Delta U < 0$

... TRANSFORMAZIOAK

...aldi berean aurreko baldintzak

...gerta daitezkeen transformazioak.

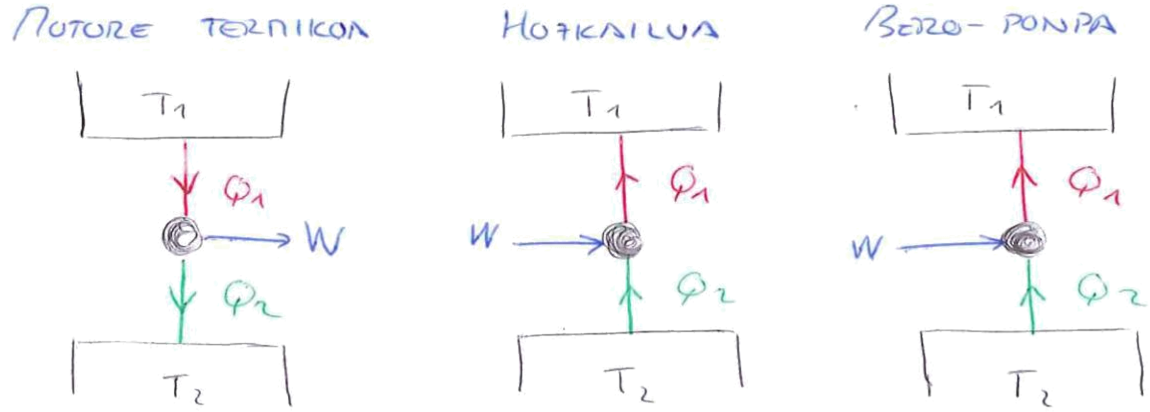
"Eskua sartu" behar dugu beroa lana bihurtzeko. Aldi berean hiru baldintzak betetzeko motorrak behar dira.

$$\text{LANA} \;\cancel{\rightleftarrows}\; \text{BEROA}$$
$$+ \text{bal}$$

$$\text{LANA} \;\rightleftarrows\; \text{BEROA}$$
$$+ \text{bal}$$

ZIKLOAK ETA MAKINA TERMIKOAK

$Q \rightarrow W$ prozesuek orokorrean sistemaren egoeraren aldaketa bat dakar. Horregatik, zenbait prozesu behar dira non sistema behin eta berriro hasierako egoerara itzultzen den; hau da, ZIKLOAK.



— Berezkoa — — Ez berezkoa —

$$Q = \Delta U - W \xrightarrow{\text{1. PRINTZIPIOA}} Q = -W$$

xurgatu

$$Q = Q_1 + Q_2 \Longrightarrow \boxed{Q = |Q_1| - |Q_2| = |W|}$$

askatu

MOTORE TERMIKOA: Ingurunera lana ematen dio behin eta berriro ziklo berdina osatuz.

ERRENDIMENDU TERMIKOA

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

$$\varepsilon_h = \frac{|Q_2|}{|W|} = \frac{|Q_2|}{|Q_1|-|Q_2|} = \frac{1}{\frac{|Q_1|}{|Q_2|}-1}$$

$Q_1 \rightarrow$ XURGATUA

$Q_2 \rightarrow$ ASKATUA

$$\varepsilon_p = \frac{|Q_1|}{|W|} = \frac{|Q_1|}{|Q_1|-|Q_2|} = \frac{1}{1-\frac{|Q_2|}{|Q_1|}}$$

Inoiz ez da $\varepsilon_p = 0$ izango ezlekine ezin delako inoiz beroa oso osorik lane bihurtu

"EL SISTEMA ESTÁ COBRANDO"

2. PRINTZIPIOAREN BI ENUNTZIATU

Printzipioa bakarra da baina zenbait modutan azaldu daiteke asimetria hori.

1. CLAUSIUS-EN ENUNTZIATUA

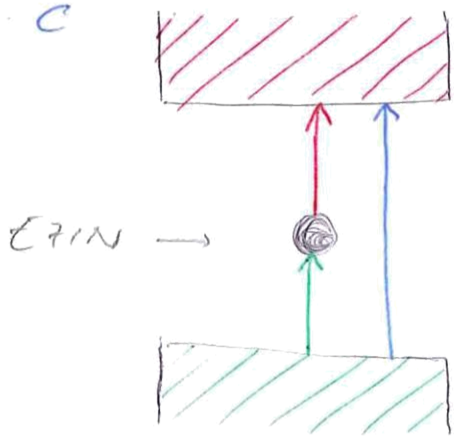
Ez dago prozesurik zeinearen ondorio bakarra gorputz hotzetik gorputz berora bero-transferentzia den.

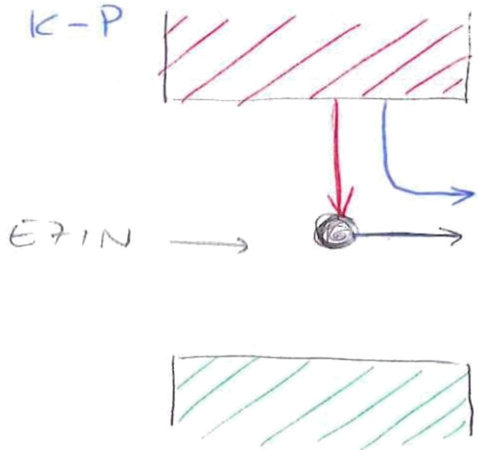
Beste modiko eragina beher da.

2. KELVIN-PLANCK-EN ENUNTZIATUA

Ez dago prozesurik zeinearen ondorio bakarra gorputz berotik hartutako bero guztia lan bihurtzea den.

Sistemak beti hartzen du zerbait (~~%100~~ ezlekine)



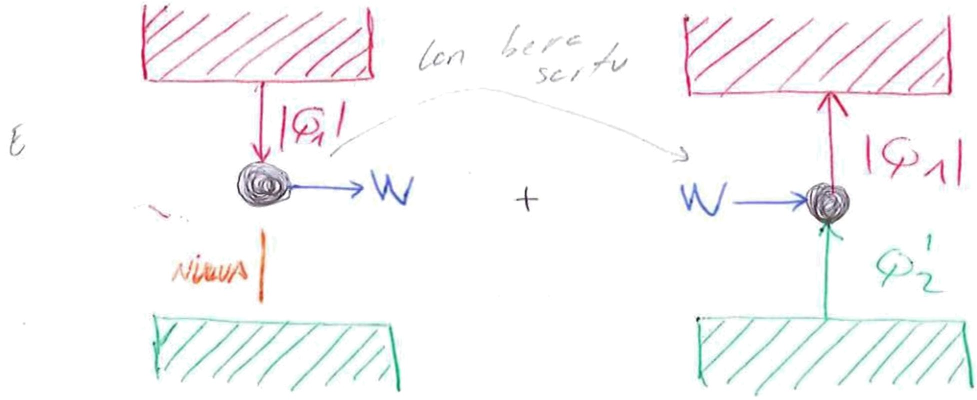


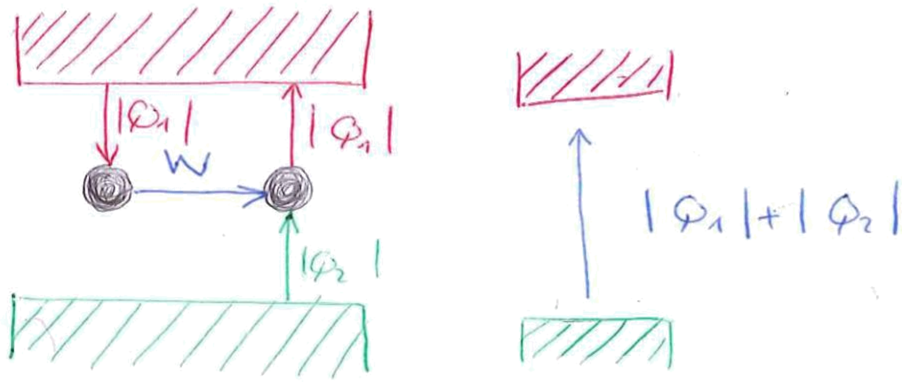
ENTROPIA: Askatasun gradu termikoari lotutako aldagai estentsiboa. $\boxed{\underbrace{\delta W^T}_{\text{LAN TERMIKOA}} = TdS = \delta Q}$

ENUNTZIATUEN ARTEKO BALIOKIDETASUNA

$$C \Longleftrightarrow K-P$$

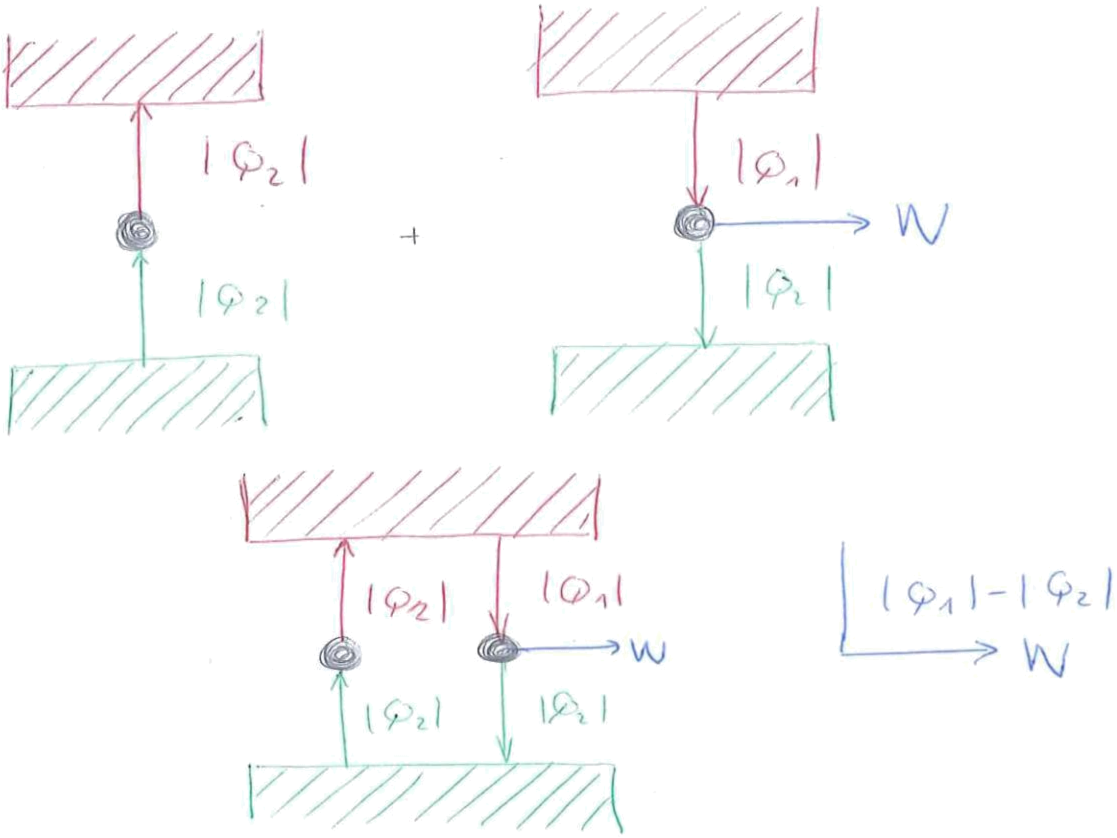
i) $C \Rightarrow K-P$; EZ $K-P \Rightarrow$ EZ C



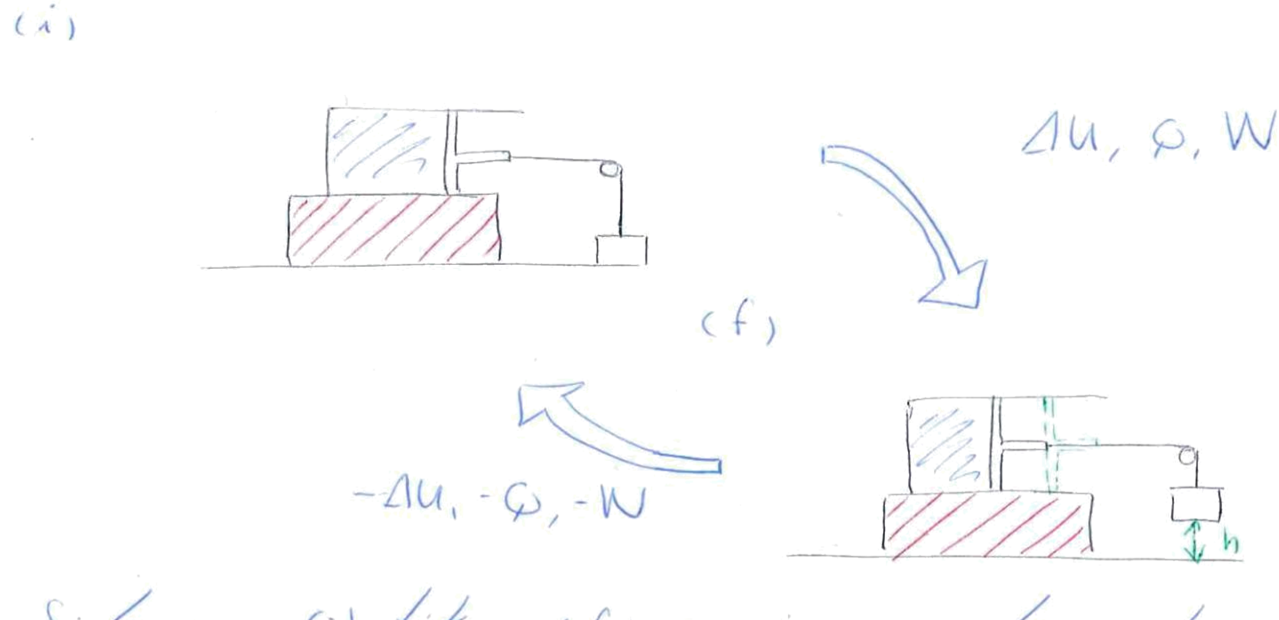


Sistema osoak egiten duena $|Q_2|$ beroa iturri hotzetik berora pasatzea da $\Rightarrow$ Clausius-en enuntziatua ez da betetzen

ii) K-P ⟹ C ; ET C ⟹ ET K-P



ITZURGARRITASUNA



Sistema (i)-tik (f)-ra igaro ostean berriro hasierako oreka egoerara gainontzeko unibertsoan aldaketak sorrarazi gabe bueltatu badaiteke prozesua ITZULGARRIA da.

Berez gertatzen diren prozesu guztiak

ez dira itzulgarriak.

NOIZ DA PROZESU BAT ITZULGARRIA?

- Energia barreiatzen ez denean
- Prozesua kuasiestatikoa denean

(biak batera bete behar dira)

BIGARREN PRINTZIPIOAREN ONDORIOAK

1. Benetako prozesuak (espontaneoak) ITZULEZINAK dira.
2. GAINAZAL ADIABATIKO ITZULGARRIEN existentzia

Caratheodory-ren enuntziatua:
Edozein sistemaren edozein oreka-egoeraren inguruan prozesu adiabatiko itzulgarrien bidez lotu ezin diren oreka-egoerak daude.

i) Osagai bakarreko sistema

$\{t, Y, X\}$ non $Y = Y(t, X)$

$$\delta Q = dU - \delta W = dU - Y dX$$

$$dU = \left(\frac{\partial U}{\partial t}\right)_X dt + \left(\frac{\partial U}{\partial X}\right)_t dX$$

$$\delta Q = \left(\frac{\partial U}{\partial t}\right)_X dT + \left[\left(\frac{\partial U}{\partial X}\right)_t - Y\right] dX$$

Prozesu adiabatikoan $\Rightarrow$ $\delta Q = 0$

$$\left(\frac{\partial U}{\partial t}\right)_X dT + \left[\left(\frac{\partial U}{\partial X}\right)_t - Y\right] dX = 0$$

$$\left(\frac{\partial U}{\partial t}\right)_X dT = \left[Y - \left(\frac{\partial U}{\partial X}\right)_t\right] dX$$

$$\left[\frac{dT}{dX}\right]_{ad} = \frac{Y - \left(\frac{\partial U}{\partial X}\right)_t}{\left(\frac{\partial U}{\partial t}\right)_X} \Rightarrow \boxed{\sigma = \sigma(t, X) = KTE}$$

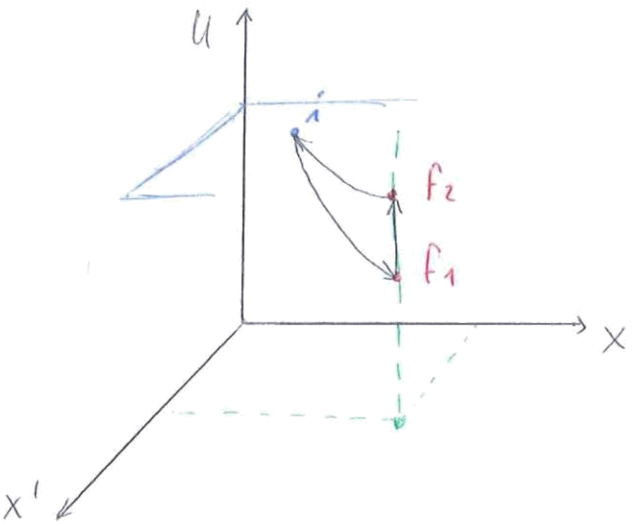
Prozesu adiabatiko itzulgarriak σ gainazal batean daude. Hasierako egoera desberdina izanik aurrekoarekin gurutzatzen ez den beste gainazal batean egongo da.

iii) Aldagai anitzeko sistema

3.A.G. $\{t, Y, X, Y', X'\} \Rightarrow Y = Y(t, x) \quad Y' = Y'(\tau, x)$

$$\delta Q = dU - Y dX - Y' dX'$$

FROGATU: Edozein sistematan posible dela gainazal adiabatikoko funtzioa lortzea.



$i \to f_1 \Rightarrow$ Adiabatiko itzulgarria

$i \to f_2 \Rightarrow$ Adiabatiko itzulgarria

$f_1 \to f_2 \Rightarrow Q$ xurgatu

- Prozesu adiabatiko itzulgarrietan $Q = 0$ baina $W = ?$
$(i \to f_1 \wedge f_2 \to i)$
- $f_1 \to f_2$ (X, X') Kte $\Rightarrow W = 0 \wedge Q = \eta$
- Prozesu osoan ez dago barne energiaren aldaketarik hasierako egoerara bueltatzen delako $(i \to f_1 \to f_2 \to i)$

$$\Rightarrow Q = \Delta U - W = 0 \Rightarrow Q = W$$

EMAITZA: Sistemak ziklo bat osatu du non ondorio bakarra beroa xurgatu eta lanean bihurtzea izan den.
$\Rightarrow$ Kelvin-Planck-en enuntziatuaren aurka

Beraz: $f_1 \wedge f_2$ egoerak ezin dira lortu prozesu adiabatikoen itzulgarrien bitartez (i-tik)

$\Rightarrow$ i-tik hasita prozesu adiabatiko itzulgarrien bitartez X, X'-ko zuzeneko puntu BAKARRA lortu daiteke.

[NOTA: Prozesu honetan bero trukaketa bakarra dago, φ ez da batura aljebraikoa, horregatik ~~Σ~~]

3 aldagai independenteen arteko lotura lortu dugu!!

Hiru aldagai independenteko (t, X, X') sisteme batean, i puntutik prozesu adiabatiko itzulgarrien bidez lortu daitezkeen oreka egoerak hartzen dituen GAINAZAL ADIABATIKO ITZULGARRIA honela adierazi daiteke

$$\sigma(t, X, X') = \text{KTE}$$

3. $\delta\varphi$-ren FAKTORE INTEGRATZAILEA

$$\delta\varphi = dU - Y dX - Y' dX' \qquad \begin{cases} U = U(T, X, X') \\ Y = Y(T, X, X') \\ Y' = Y'(T, X, X') \end{cases}$$

$$\sigma = \sigma(T, X, X') = \text{kte} \longrightarrow T = T(\sigma, X, X')$$

Ordezkatuz

$$\delta\varphi = \left(\frac{\partial U}{\partial \sigma}\right)_{X,X'} d\sigma + \left[\left(\frac{\partial U}{\partial X}\right)_{\sigma,X'} - Y\right] dX + \left[\left(\frac{\partial U}{\partial X'}\right)_{\sigma,X} - Y'\right] dX'$$

↳ Sistemak trukatzen duen beroa

Prozesua itzulgarria $\Rightarrow$ $d\sigma = 0$

Prozesua adiabatikoa $\Rightarrow$ $\delta\varphi = 0$

Prozesu adiabatiko itzulgarrietan:

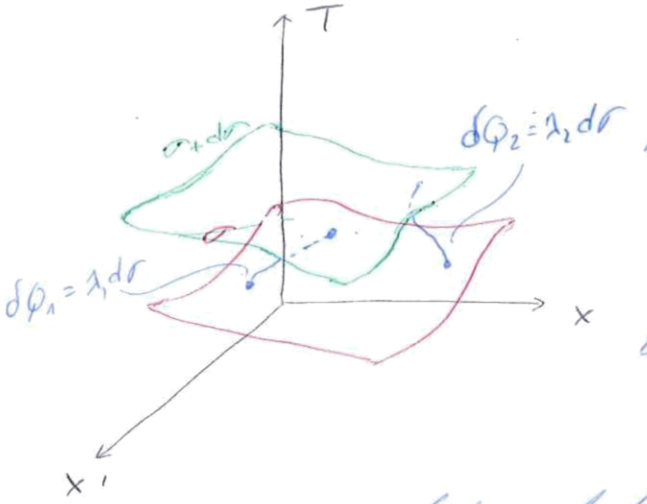
$$\left[\left(\frac{\partial u}{\partial x}\right)_{\sigma,x'} - y\right]dx + \left[\left(\frac{\partial u}{\partial x'}\right)_{\sigma,x} - y'\right]dx' = 0$$

$\underset{0}{\shortparallel}$ ← Behar da → $\underset{0}{\shortparallel}$

$$\left(\frac{\partial u}{\partial x}\right)_{\sigma,x'} = y \quad \text{eta} \quad \left(\frac{\partial u}{\partial x'}\right)_{\sigma,x} = y'$$

$$\Rightarrow \boxed{\delta \varphi = \left(\frac{\partial u}{\partial \sigma}\right)_{x,x'} d\sigma} \quad \text{beteko da}$$

$$\lambda \equiv \left(\frac{\partial u}{\partial \sigma}\right)_{x,x'} \Rightarrow \delta\varphi = \lambda\, d\sigma \;;\; \lambda = \lambda(\sigma, x, x')$$



- Edozein prozesurentzat gainazal baten gainean: $\delta\varphi = 0$
- Gainazal bakoitzeko puntu bat lotzen duen prozesuetan bero transferentzia dago: $\delta\varphi = \lambda d\sigma$
- Bi gainazalak lotzen dituzten prozesu orok $d\sigma$ berdina dute baina λ-ren balio desberdinekin.

FAKTORE INTEGRATZAILEAREN ESANGURA FISIKOA

BERO-ITURRIA

	SISTEMA NAGUSIA	ERREFERENTZIA-SISTEMA
ALD. INDP.	t, x, x'	$T, \hat{x}, \hat{x}'$
G. A. IG.	$\sigma = \sigma(T, x, x')$	$\hat{\sigma} = \hat{\sigma}(T, \hat{x}, \hat{x}')$
FAKT. INT.	$\lambda = \lambda(T, \sigma, x)$	$\hat{\lambda} = \hat{\lambda}(\sigma, T, X)$

SISTEMA KONPOSATUA

SISTEMA KONPOSATUA:

$$\{t, \sigma, x, \hat{\sigma}, \hat{x}\}$$

$$\bar{\sigma} = \bar{\sigma}(t, \sigma, x, \hat{\sigma}, \hat{x})$$

$$\bar{\lambda} = \bar{\lambda}(t, \sigma, x, \hat{\sigma}, \hat{x})$$

Bero iturritik $\delta\bar{\varphi}$-ko bero transferentzia egongo da bi sistemen artean banatuta.

$$\delta\bar{\varphi} = \delta\varphi + \delta\hat{\varphi}$$

$\delta\varphi = \lambda d\sigma$

$$\bar{\lambda} d\bar{\sigma} = \lambda d\sigma + \hat{\lambda} d\hat{\sigma}$$

$$d\bar{\sigma} = \frac{\lambda}{\bar{\lambda}} d\sigma + \frac{\hat{\lambda}}{\bar{\lambda}} d\hat{\sigma}$$

$$\bar{\sigma} = \bar{\sigma}(\sigma, \hat{\sigma}) \Rightarrow d\bar{\sigma} = \left(\frac{\partial\bar{\sigma}}{\partial\sigma}\right)_{\hat{\sigma}} d\sigma + \left(\frac{\partial\bar{\sigma}}{\partial\hat{\sigma}}\right)_{\sigma} d\hat{\sigma}$$

$$\bar{\sigma} = \bar{\sigma}(t, \sigma, x, \hat{\sigma}, \hat{x}) \Rightarrow$$

$$d\bar{\sigma} = \left(\frac{\partial\bar{\sigma}}{\partial t}\right)_{m} dt + \left(\frac{\partial\bar{\sigma}}{\partial\sigma}\right)_{n} d\sigma + \left(\frac{\partial\bar{\sigma}}{\partial x}\right)_{n} dx + \left(\frac{\partial\bar{\sigma}}{\partial\hat{\sigma}}\right)_{n} d\hat{\sigma} + \left(\frac{\partial\bar{\sigma}}{\partial\hat{x}}\right)_{n} d\hat{x}$$

$$\left(\frac{\partial\bar{\sigma}}{\partial t}\right) dT = \left(\frac{\partial\bar{\sigma}}{\partial x}\right) dx = \left(\frac{\partial\bar{\sigma}}{\partial\hat{x}}\right) d\hat{x} = 0$$

$$\Rightarrow d\bar{\sigma} = \left(\frac{\partial\bar{\sigma}}{\partial\sigma}\right)_{t,x,\hat{\sigma},\hat{x}} d\sigma + \left(\frac{\partial\bar{\sigma}}{\partial\hat{\sigma}}\right)_{t,\sigma,x,\hat{x}} d\hat{\sigma}$$

$$\left(\frac{\partial\bar{\sigma}}{\partial\sigma}\right)_{t,x,\hat{\sigma},\hat{x}} = f_1(t, \sigma, \hat{\sigma}, x, \hat{x});$$

$$\left(\frac{\partial\bar{\sigma}}{\partial\hat{\sigma}}\right)_{t,x,\sigma,\hat{x}} = f_2(t, \sigma, \hat{\sigma}, x, \hat{x})$$

$$\frac{\lambda}{\bar{\lambda}} = \frac{\lambda(t, \sigma, x)}{\bar{\lambda}(t, \sigma, \hat{\sigma}, x, \cancel{\hat{x}})} = \left(\frac{\partial\bar{\sigma}}{\partial\sigma}\right)_{\hat{\sigma}} d\sigma = g_1(\sigma, \hat{\sigma})$$

$$\Rightarrow \bar{\lambda} = \bar{\lambda}(t, \sigma, \hat{\sigma}, x)$$

$$\frac{\hat{\lambda}}{\bar{\lambda}} = \frac{\lambda(t, \hat{\sigma}, \hat{x})}{\bar{\lambda}(t, \sigma, \hat{\sigma}, \cancel{x}, \hat{x})} = \left(\frac{\partial \bar{\sigma}}{\partial \hat{\sigma}}\right)_{\sigma} d\sigma = g_2(\sigma, \hat{\sigma})$$

$$\Rightarrow \bar{\lambda} = \bar{\lambda}(t, \sigma, \hat{\sigma}) \quad \begin{cases} \lambda = \lambda(t, \sigma) \\ \hat{\lambda} = \lambda(t, \hat{\sigma}) \end{cases}$$

(berdina $\bar{\lambda}$ hiruekin ginen)

Azkenik,

$$\frac{\lambda}{\bar{\lambda}} = \frac{\lambda(t, \sigma)}{\bar{\lambda}(t, \sigma, \hat{\sigma})} = g_1(\sigma, \hat{\sigma})$$

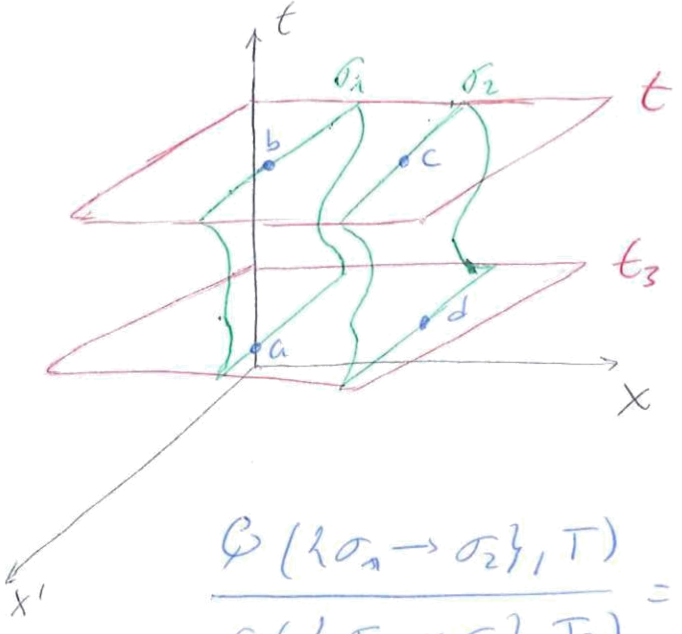
$$\frac{\hat{\lambda}}{\bar{\lambda}} = \frac{\hat{\lambda}(t, \hat{\sigma})}{\bar{\lambda}(t, \sigma, \hat{\sigma})} = g_2(\sigma, \hat{\sigma}) \quad \Rightarrow \quad \boxed{\begin{aligned} \lambda(t, \sigma) &= \phi(t) f_1(\sigma) \\ \hat{\lambda}(t, \hat{\sigma}) &= \phi(t) f_2(\hat{\sigma}) \\ \bar{\lambda}(t, \sigma, \hat{\sigma}) &= \phi(t) f(\sigma, \hat{\sigma}) \end{aligned}}$$

$$\boxed{\delta Q = \phi(t) f(\sigma) d\sigma} \quad ; \quad \phi(t) \text{ unibertsala}$$

↳ T absolutua

4. KELVIN TENPERATURA ESKALA

Izan $\{\tau, x, x'\}$ edozein sistema



$$Q = \phi(t) \int_{\sigma_1}^{\sigma_2} f(\sigma) d\sigma$$

$$\frac{Q}{Q_3} = \frac{\phi(t)}{\phi(t_3)}$$

$$\frac{Q(\{\sigma_1 \rightarrow \sigma_2\}, T)}{Q_3(\{\sigma_1 \rightarrow \sigma_3\}, T_3)} = \frac{T}{T_3}$$

$$\boxed{T = 273{,}16 \left[\frac{Q}{Q_{PH}}\right] K}$$

5. ENTROPIA FUNTZIOAREN EXISTENTZIA

$$\delta\varphi = \lambda d\sigma \quad \text{non} \quad \lambda = \phi(t) f(\sigma)$$

$$\delta\varphi = \phi(t) f(\sigma) d\sigma$$

$$\frac{\varphi'}{\varphi} = \frac{T'}{T} \rightsquigarrow \frac{\delta\varphi'}{\delta\varphi} = \frac{T'}{T} \; ; \quad T = k\phi(t)$$

$$\frac{\delta\varphi^{IG}}{T} = \frac{\delta\varphi'}{T'} = \frac{\phi(t) f(\sigma) d\sigma}{k\phi(t)} = \frac{1}{k} f(\sigma) d\sigma$$

$$\frac{\delta\varphi^{IG}}{T} = \frac{1}{k} f(\sigma) d\sigma = dS \equiv \text{ENTROPIA}$$

$$\delta\varphi^{IG} = dU - \delta W \Rightarrow dS = \frac{(dU - \delta W)^{IG}}{T}$$

- Sistemaren propietatea da
- Egoera funtzioa
- Aldagaien funtzioa

$$\oint \frac{\delta\varphi}{T} \leq 0 \quad \begin{cases} < 0 \Rightarrow \text{Itzulezina (ez da "entropia")} \\ = 0 \Rightarrow \text{Itzulgarria} \equiv \Delta S = 0 \end{cases}$$

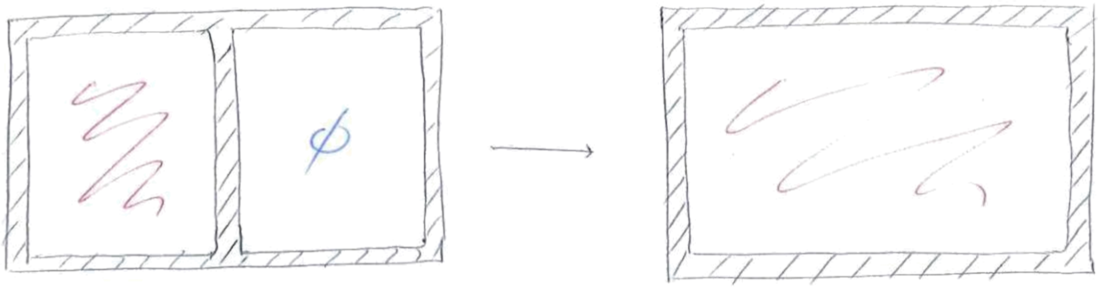
Adi!! $dS = \frac{\delta\varphi^{IG}}{T} \neq \frac{\delta\varphi}{T} \rightarrow$ Itzulgarria izan behar

$$dS = \frac{(dU - \delta W)^{IG}}{T} \Rightarrow \int_i^f dS = \Delta S_{if} = \int_i^f \frac{\delta\varphi^{IG}}{T}$$

Egoera funtzioa $\Rightarrow$ Ibilbidearen independentea

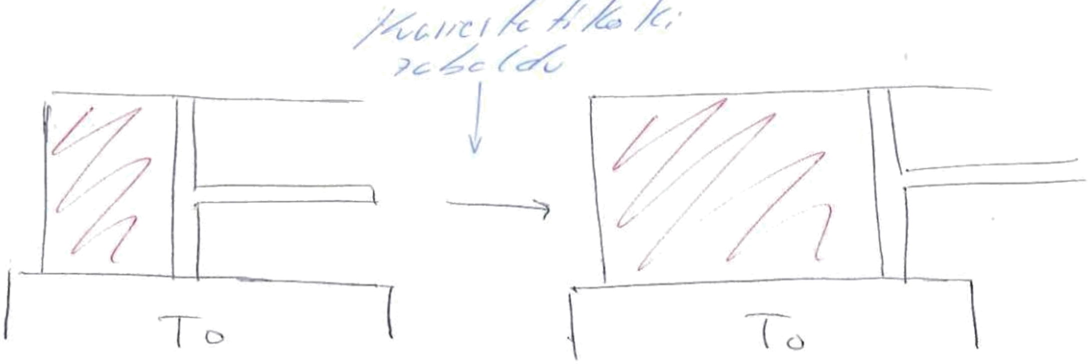
ADIBIDEA

Gas idealaren zabaltze askea. Ez da prozesu itzulgarria $\Rightarrow \Delta S$ kalkulatzeko beste prozesu bat lortu



(V_0, T_0, p_0) $\qquad$ $(2V_0, T_0, \frac{p_0}{2})$

Hasiera eta amaierako oreko egoera berdinak dituen prozesu bat asmatuko dugu entropia kalkulatzeko.



(V_0, T_0, p_0) $\qquad$ $(2V_0, T_0, p_0/2)$

$$dS = \frac{\delta Q^{IG}}{T} = \frac{(dU - \delta W)^{IG}}{T} =$$

GAS IDEALA: $\delta W = -p\,dV \wedge dU = C_V\,dT$

$$= (C_V\,dT + p\,dV)\cdot\frac{1}{T}$$

$$dS = \cancel{\frac{C_V}{T}}^{\,T=kte} dT + \frac{p}{T}dV = \frac{p}{T}[dV]_T \overset{PV=nRT}{=} \frac{nR}{V}dV$$

$$dS_{if} = nR\ln\frac{V_f}{V_i} = nR\ln 2$$

OROKORREAN:

$$dS = \frac{C_X}{T}dT + \frac{1}{T}\cdot\frac{C_Y - C_X}{\left(\frac{\partial X}{\partial T}\right)_Y}dX$$

Sistema baten beroa prozesu kuasiestatikoan

$$\delta Q = C_x\, dT + \frac{C_x - C_y}{\left(\frac{\partial x}{\partial T}\right)_x} dX$$

$S = S(T, X)$ → Egoera funtzioa

$\delta Q \longrightarrow \delta Q(T, X)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_X dT + \left(\frac{\partial S}{\partial X}\right)_T dX$$

$$T \cdot \left(\frac{\partial S}{\partial T}\right)_X = C_x \qquad T \cdot \left(\frac{\partial S}{\partial T}\right)_x = C_y$$

$$T\left(\frac{\partial S}{\partial T}\right)_X = C_x = \left(\frac{\partial Q}{\partial T}\right)_x$$

$$C_x = \left(\frac{\partial u}{\partial T}\right)_X \Rightarrow T\left(\frac{\partial S}{\partial T}\right)_X = \left(\frac{\partial u}{\partial T}\right)_X$$

ADIBIDEA 2:

i) $T_0 \longrightarrow T_1$: ΔS?

Ezin dugu zuzenean kalkulatu kuasiestatikoa ez delako.

ii) $T_0 \longrightarrow \frac{T_1 - T_0}{2} \xrightarrow{\text{Kuasiestatikoki}} T_1$; m, c

$$\Delta S^u = \Delta S^{ing} + \Delta S^{sist}$$

$$dS^{sist} = \frac{mc}{T} dT \Rightarrow \Delta S^{sist} = mc \ln \frac{T_f}{T_i}$$

$$\Delta S = mc \cdot \left[\ln \frac{T_1 - T_0}{2 T_0} + \ln \frac{T_1 \cdot 2}{T_1 - T_0} \right] = mc \ln \frac{T_1}{T_0}$$

i)-ko prozesuan entropia berdina izango litzateke.

Itzulgarria denez $\Rightarrow \Delta S^u = 0 \Rightarrow \Delta S^{ing} = -\Delta S^{sist}$

$$\Delta S^u = \sum_{j=1}^{n} \Delta S_j^{sist} + \Delta S^{ing}$$

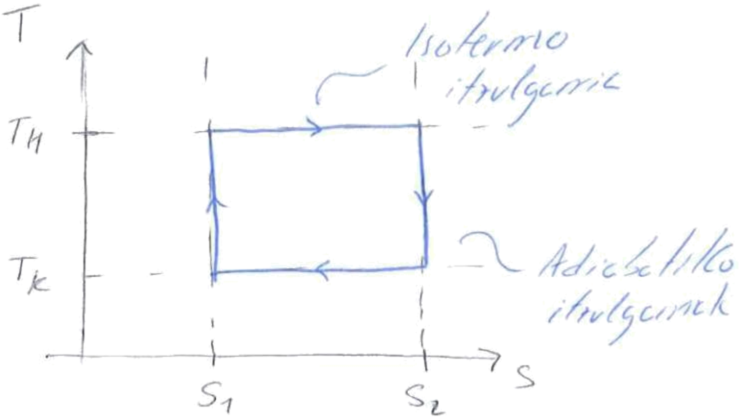
CARNOT-EN ZIKLOA

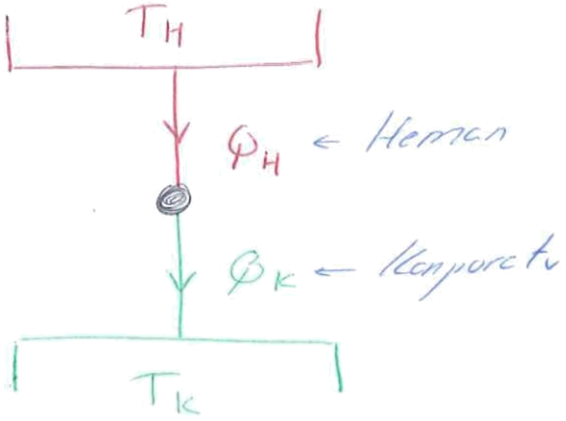
Bi lerro isotermo itzulgarri
Bi lerro adiabatiko itzulgarri } osaturiko zikloa

BI BERO ITURRI:

· Xurgatutako beroa, goi tenperaturan dagoen bero-iturritik

· Kanporatutako beroa, behe tenperaturan dagoen bero-iturrira.



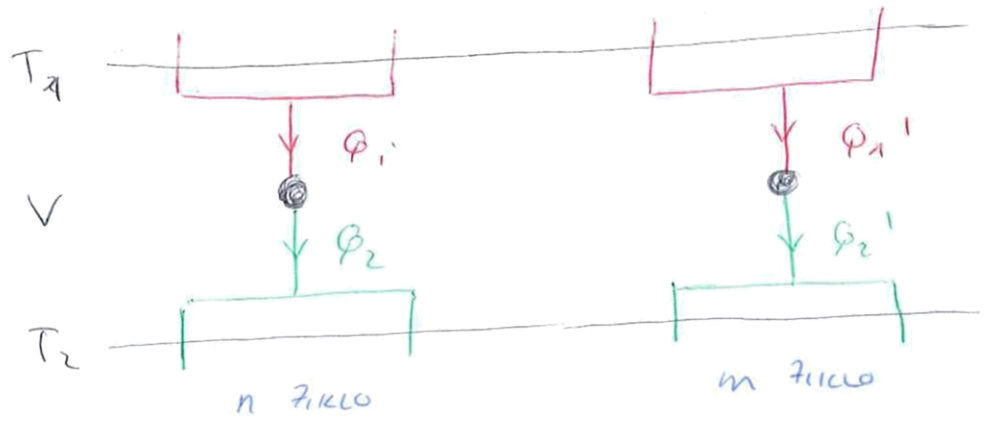


Guztira zikloa itzulgarria da eta

$$\eta_c = 1 - \frac{T_c}{T_H}$$

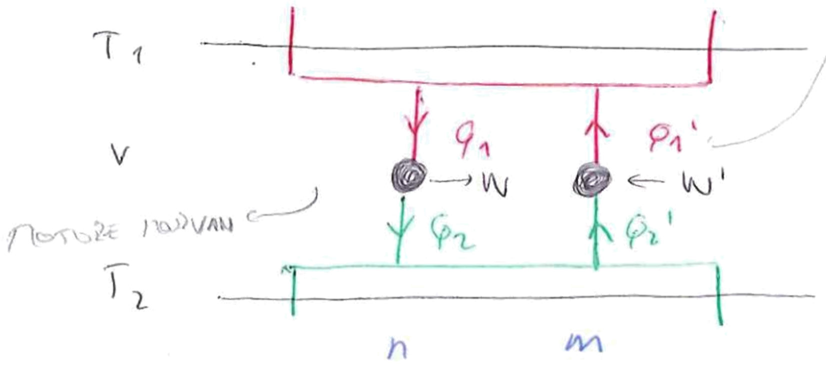
(1)- CARNOT-EN MOTOREAREN ETEKINAK EZ DAUKA SISTEMAREKIKO MENPEKOTASUNIK

Bi sistema Carnot-en zikloarekin



Ondorioztuko dugu: $n|\varphi_2| = m|\varphi_2'|$

BIAK AKOPLATUKO DITUGU:



$\varphi_1'' \neq 0$

$W'' \neq 0$

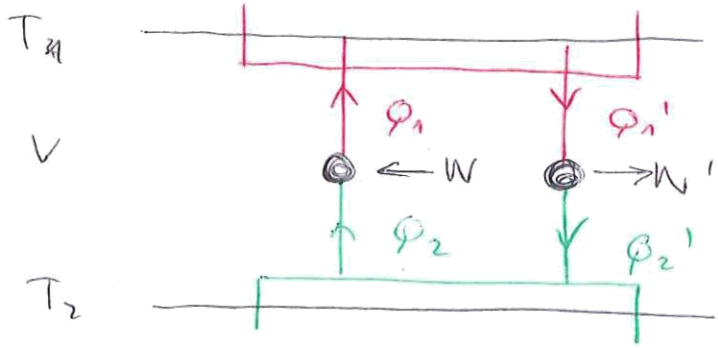
$\varphi_2'' = 0$

$\uparrow$

Guk aukeratu

$[n\varphi_2 + m\varphi_2' = 0]$

ALDERANTZIZ AKOPLATUZ GERO:



$\varphi_1'' \neq 0$

$W'' = 0$

$\varphi_2'' = 0$

$$\varphi_{1_1}'' > 0 \quad ; \quad \varphi_{1_2}'' < 0 \quad \Rightarrow \quad \varphi_1'' = 0$$

Lehenengo zikloari 1.P aplikatu:

$$n\varphi_1 + m\varphi_1' = \Delta U - W''$$

$$n\varphi_1 + m\varphi_1' = -W''$$

$$n\varphi_1 + m\varphi_1' > 0 \longrightarrow \text{EZINEZKOA} \quad (2.P)$$

Beraz, $n\varphi_1 + m\varphi_1' \leq 0$

Bigarren zikloari 1.P aplikatuz gero (itzulgarriak):

$$n\varphi_1 + m\varphi_1' \geq 0$$ → Alderantziz egin dugulako prozesua

$n\varphi_2 + m\varphi_2' = 0$

$$n\varphi_1 + m\varphi_1' = 0$$

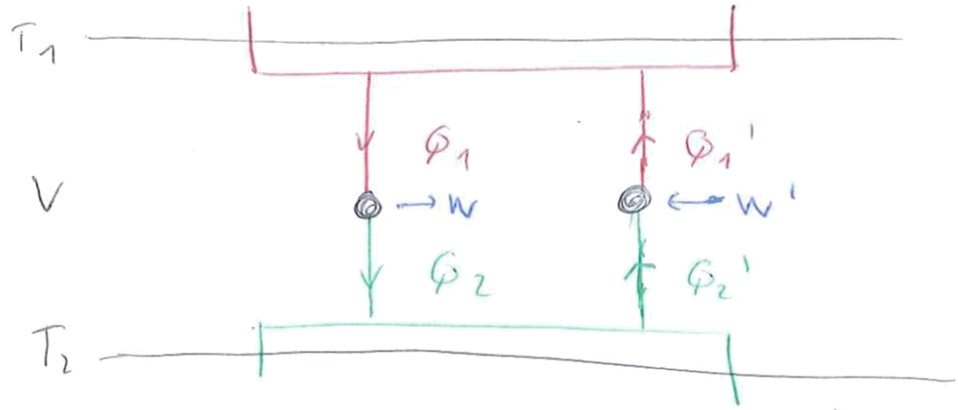
Orduan $\Rightarrow$ $\boxed{\dfrac{\varphi_2}{\varphi_1} = \dfrac{\varphi_2'}{\varphi_1'}}$ → Aukera bakarra da biak bat dadin; hau da, itzulgarriak izan dadin.

(2) - CARNOT-EN MOTOREAK FINKATURIKO TENPERATUREN ARTEKO ETEKIN MAXIMOA

$$\eta_c = \frac{|W|}{|Q_1|} = \frac{|Q_1| - |Q_2|}{|Q_1|} = 1 - \frac{|Q_2|}{|Q_1|}$$

$$\eta^* = 1 - \frac{|Q_2'|}{|Q_1'|}$$

$$\eta > \eta^* \Rightarrow \frac{|Q_2|}{|Q_1|} \leq \frac{|Q_2'|}{|Q_1'|}$$

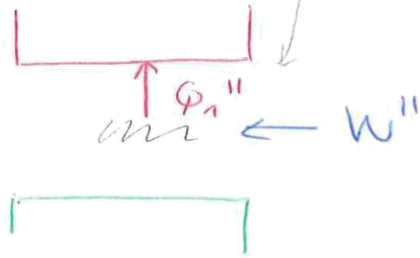


2. Printzipioa bete dadin ziklikoki prozesu [illegible] de

$Q_1'' < 0$

$W'' \neq 0$

$Q_2'' = 0$



Dakigunez:

$$-n|Q_2| = -m|Q_2'| \Rightarrow n|Q_2| = m|Q_2'|$$

$nQ_1 + mQ_1' \leq 0 \Rightarrow$ $n|Q_1| \leq m|Q_1'| \Rightarrow n|Q_1| \leq m|Q_1'|$

$nQ_1 \leq -mQ_1'$

$(-)$

$$\Rightarrow \frac{|Q_2|}{|Q_1|} \leq \frac{|Q_2'|}{|Q_1'|}$$ Frogatu dugu.

CLAUSIUS-EN TEOREMA

$$\oint \frac{dQ}{T} \leq 0 \begin{cases} = 0 & \text{ITZULGARRIA} \\ < 0 & \text{ITZULEZINA} \end{cases} \left[dS \neq \frac{dQ}{T} \right]$$

Ez da ezer orduan.

ENTROPIA ENERGIAREN FUNTZIOA

Guztiz isolatutako sistemaren barruan, prozesu itzulezin bat gertatzen bada entropiaren aldaketa positiboa da, itzulgarria bada nulua da.

$$\Delta S^{u} \geq \phi \begin{cases} =0 & , \text{ ITZULGARRIA} \\ >0 & , \text{ ITZULEZINA} \end{cases}$$

$$\Delta S^{u} = \Delta S^{sis} + \Delta S^{ing}$$

I.G. $\Rightarrow -\Delta S^{sis} = \Delta S^{ing} \Rightarrow$ KONPENTSATUAK DAUDE

I.E.

$\Delta S^{ing} < 0 \quad \Delta S^{sis} < 0$

$\Delta S^{ing} < 0 \quad \Delta S^{sist} > 0$

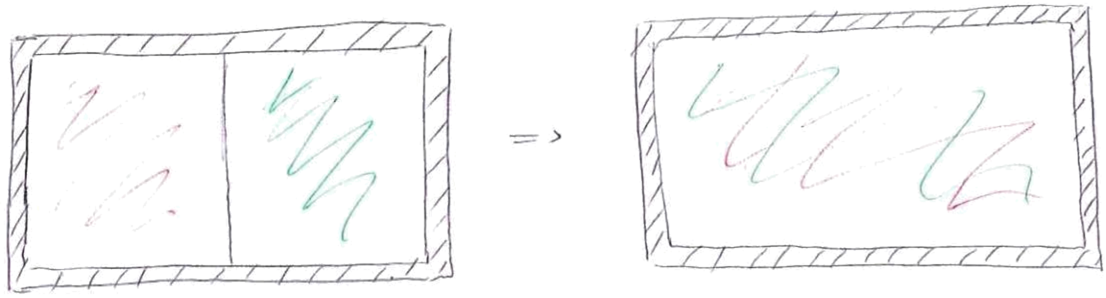
$\Delta S^{ing} > 0 \quad \Delta S^{sis} < 0 \Rightarrow$ Ez dugu horren informaziorik

$\Delta S^{ing} > 0 \quad \Delta S^{sis} > 0$

Prozesua itzulgarria izateko eskua sartu behar dugu sistemak galtzen duen entropia inguruneak irabazten duen berdina izateko.

Helburua → Berezko prozesuak erabili ditzakegu berezkoak ez diren prozesuak abiarazteko. Horrela, unibertsoaren entropia aldaketa positiboa da

ADIBIDEA



Biak gas idealak => Ez dute elkar ikusiko

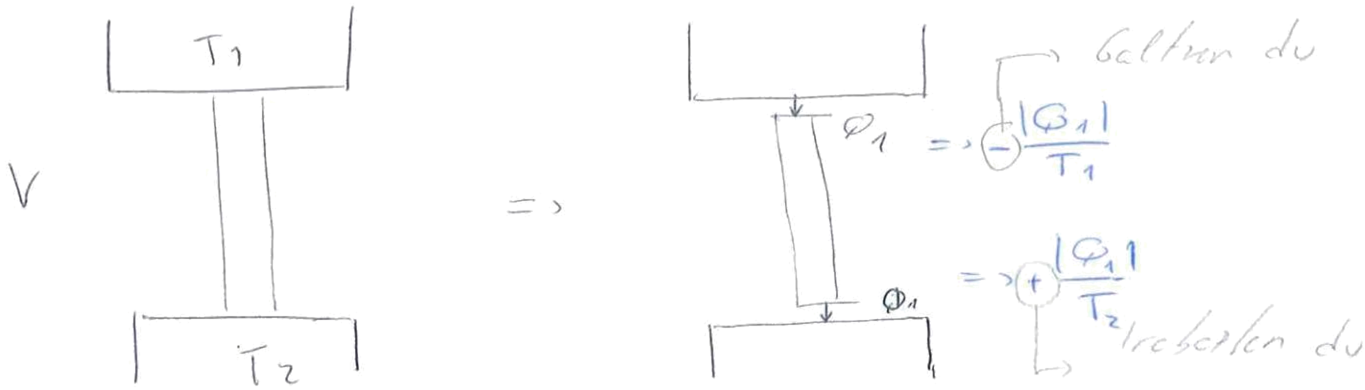
Bi zabalkuntza aiko egongo dira (gas bakoitzak bat)

$$V_1 = V_1' = V \Rightarrow V_2 = V_2' = 2V$$

Beraz, $\Delta S_{ing} = 0$ $\quad \Delta S_{sist} = 2R\ln 2$ $\Rightarrow \Delta S_u = 2R\ln 2 > 0$

[Hasierako egoerak berdinak badira]

ADIBIDEA$_2$:



$$\Delta S^u = \Delta S^{sist} + \Delta S^{ing}$$

$$i = f \Rightarrow \Delta S^{sist} = 0$$

$ING = U - SIST \longrightarrow$ Bero iturriak dira ingurunea

$\Delta S^{ing} = \frac{Q}{T} \leftarrow$ Bero iturriak xurgatzen duen beroa

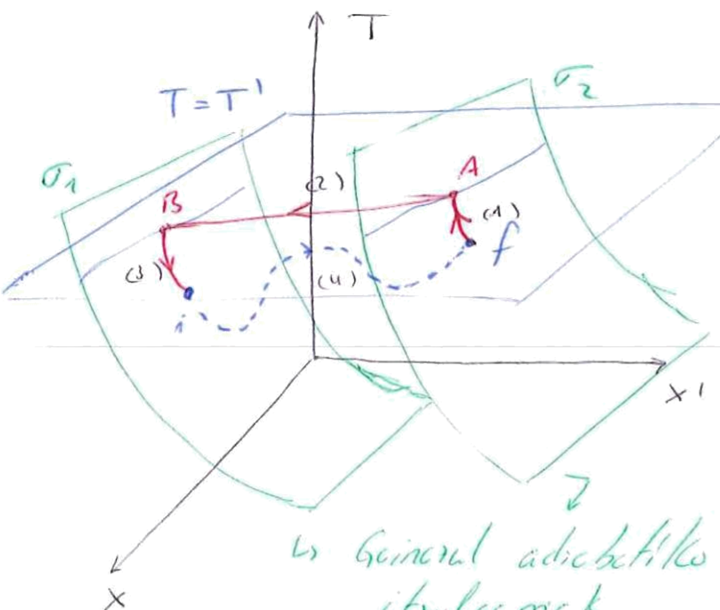
Bere ikuspuntutik oso energia txikia doa: $dS^{ing} = \frac{\delta Q^{ing}}{T}$

$$\Rightarrow \Delta S^{ing} = \frac{1}{T}\int \delta Q^{ing}$$

$$\Delta S^{ing} = -\frac{|Q_1|}{T_1} + \frac{|Q_1|}{T_2} \overset{T_1 > T_2}{>} 0$$

FROGATU: Edozein prozesu adiabatiko itzulezinetan unibertsoaren entropiak gora egiten du.

3. AG-ko sistema : $\{T, x, x'\}$



$i \to f$ adiabatiko itzulezina

$\Rightarrow \Delta S^{unib}_{i\to f} > 0$

ZIKLOAN:

$(Q = \Delta U - W)^z$

$Q^z = \Delta U^z - W^z$

- Bero truke bakarra (2)-n [Besteak definizioz adiabatikoak]
- Zikloa denez $\Delta U^z = 0$

$Q^z = \cancel{0} - W^z$

- 2.P dela eta $Q^z < 0$ izan behar da

ENTROPIAREN KALKULUA

$\Delta S^u = \Delta S_{i\to f} + \Delta S_{f\to A} + \Delta S_{A\to B} + \Delta S_{B\to i}$

- Edozein prozesu adiabatiko itzulgarrietan $\Delta S = 0$

$\Rightarrow \Delta S_{f\to A} = \Delta S_{B\to i} = 0$

- Ziklo bat denez $\Delta S^z = 0$

$\Rightarrow \Delta S_{i\to f} + \Delta S_{A\to B} = 0 \Rightarrow \Delta S_{i\to f} = -\Delta S_{A\to B}$

• $\Delta S_{A\to B}$ prozesu isotermo itzulgarria $\Rightarrow \Delta S = \frac{Q}{T}$

$$\Rightarrow \Delta S_{A\to B} = \frac{Q_{A\to B}}{T'} < 0 \quad (2.P)$$

Beraz, $\Delta S_{i\to f} = -\frac{Q_{A\to B}}{T'} > 0$ ∎

LAN MAXIMOAREN TEOREMA

Zer baldintzatan lortuko dugu lan maximoa?

KUANTITATIBOKI

ΔU_s, ΔS_s finkoak; amaiera egoera finkoak

$$(-\Delta U_s) = Q_{BI} + W_{LI}$$

MINIMIZATU: minimizatu

$$\Delta S_u = \Delta S_s + \Delta S_{BI} \Rightarrow \Delta S_u = \Delta S_s \Rightarrow \Delta S^u = 0$$

finko — Itzulgarria

Prozesua itzulgarria izatean lan maximoa lortzen da.

Zein da bere forma?

$$Q = \Delta U - W$$

$$(Q = \Delta U - W)^{sist} \Rightarrow (-\Delta U)^{sist} = -(Q+W)^{sist} = -Q^{sist} - W^{sist}$$

$$(-\Delta U)^{sist} = Q^{BI} + W^{LI}$$

$$\Delta S^u = \Delta S^{sist} + \Delta S^{ing} = \Delta S^{sist} + \Delta S^{BI}$$

Carnotek eta ... ([illegible])

$$\delta W^{LI} \leq dU + T^{BI} dS$$

$$\delta W^{LI} = \underbrace{-TdS}_{-\delta Q} - \delta W + T^{BI} dS$$

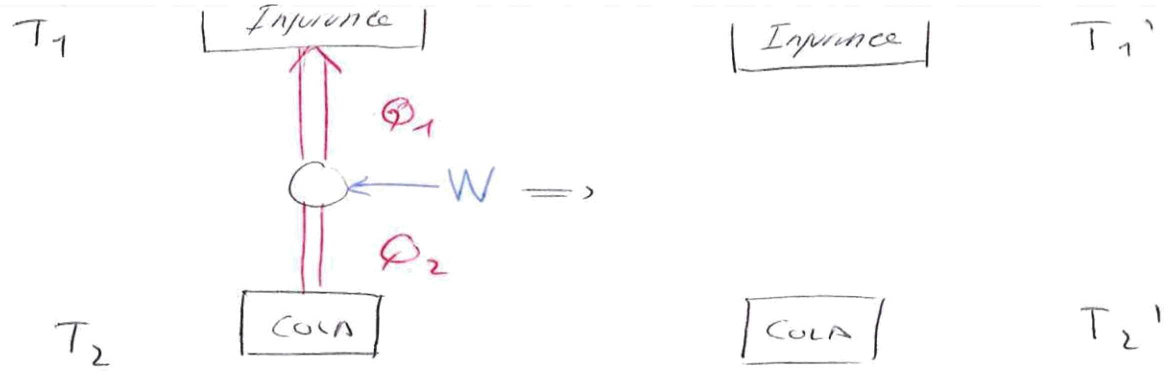
→ Berdintza hartzen prozesua itzulgarria dela suposatu dugu

Lan erabilgarria

$$\boxed{\delta W^{LI} = -\delta W + TdS\left(1 - \frac{T^{BI}}{T}\right)}$$

Sistemak jasotzen eman dezakena ← ↳ Tenperatura altutik eragindakoa

ADIBIDEA$_1$



Cola hertu nahi dugu

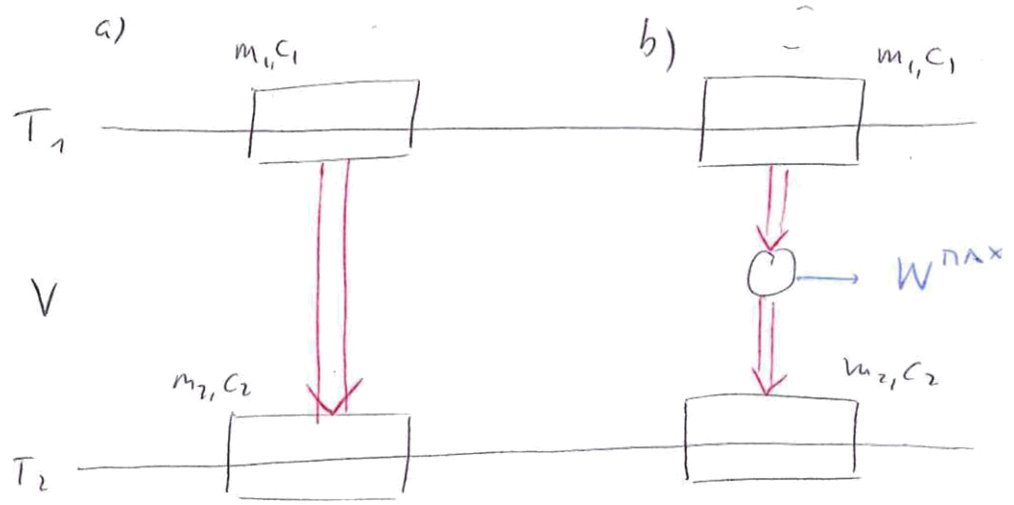
$T = T_1'$; $T_1 = T_2$; $T_2' - T_1' = \Delta T$

Prozesua ez da berezkoa izango eta bai itzulgarria, horrenbestez bi azpisistemen arteko entropia ezin da aldatu ($\Delta S = 0$)

$$\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0$$

$$\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2'} = \frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2 + dT_2} = 0$$

ADIBIDEA$_2$:



a) Biek amaieran T_f tenperatura berdina izango dute.

Bero trukaketa berezko prozesua da eta itzulezina; beraz, $\Delta S^u > 0$

Bukaerako egoera finkatzeko digun ekuazioa:

$$Q = Q_1 + Q_2 = 0$$

$$Q_i = \int_{T_i}^{T_f} C_i \, dT_i$$

$$Q_1 = \int_{T_1}^{T_f} C_1 \, dT_1 = C_1 (T_f - T_1) < 0$$

$$Q_2 = \int_{T_2}^{T_f} C_2 \, dT_2 = C_2 (T_f - T_2) > 0$$

$$Q = C_1 (T_f - T_1) + C_2 (T_f - T_2) = 0 \quad \left[C_1 = C_2 \Rightarrow T_f^{FG} = \frac{T_1 + T_2}{2} \right]$$

$$T_f \cdot (C_1 + C_2) = C_1 T_1 + C_2 T_2 \Rightarrow T_f^{IE} = \frac{C_1 T_1 + C_2 T_2}{C_1 + C_2}$$

$$\Delta S_i = \int_{T_i}^{T_f} \frac{C_i}{T_i} dT_i$$

$$\Delta S_1 = \int_{T_1}^{T_f} \frac{C_1}{T_1} dT_1 = C_1 \ln T \Big|_{T_1}^{T_f} = C_1 \ln \frac{T_f}{T_1}$$

$$\Delta S_2 = \int_{T_2}^{T_f} \frac{C_2}{T_2} dT_2 = C_2 \ln T \Big|_{T_2}^{T_f} = C_2 \ln \frac{T_f}{T_2}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = C_1 \ln \frac{T_f}{T_1} + C_2 \ln \frac{T_f}{T_2} > 0$$

b) Biek amaieran T_f tenperatura bera izango dute. Eskuz sortzen dugunez lan maximoa lortzeko prozesua ez da berezkoa eta itzulgarria da.

Beraz, $\Delta S^u = 0$ eta $\varphi_1 + \varphi_2 = W^{max} < 0$ → sistematik atera

$$\Delta S_i = \int_{T_i}^{T_f} \frac{c_i}{T_i}\, dT^i \qquad \Delta S_1 + \Delta S_2 + \cancel{\Delta S^{ing}}^{\,0} = 0$$

$$\Delta S_1 = c_1 \ln \frac{T_f}{T_1} \qquad \Delta S_2 = c_2 \ln \frac{T_f}{T_2}$$

$$\Delta S^u = \Delta S_1 + \Delta S_2 = c_1 \ln \frac{T_f}{T_1} + c_2 \ln \frac{T_f}{T_2} = 0$$

$$c_1 \ln T_f - c_1 \ln T_1 + c_2 \ln T_f - c_2 \ln T_2 = 0$$

$$(c_1 + c_2) \ln T_f - c_1 \ln T_1 - c_2 \ln T_2 = 0$$

$$(c_1 + c_2) \ln T_f = c_1 \ln T_1 + c_2 \ln T_2$$

$$\ln T_f = \frac{c_1 \ln T_1 + c_2 \ln T_2}{c_1 + c_2} \qquad \left[c_1 = c_2 \Rightarrow T_f^{EQ} = \sqrt{T_1 T_2} \right]$$

$$T_f^{IG} = e^{\frac{c_1 \ln T_1}{c_1 + c_2}} \cdot e^{\frac{c_2}{c_1 + c_2} \ln T_2} = \left(T_1^{c_1} \cdot T_2^{c_2} \right)^{\frac{1}{c_1 + c_2}}$$

$$\varphi_1 = c_1 (T_f - T_1) \qquad \varphi_2 = c_2 (T_f - T_2)$$

$$W^{max} = c_1 (T_f - T_1) + c_2 (T_f - T_2) =$$

$$= T_f (c_1 + c_2) - T_1 c_1 - T_2 c_2 =$$

$$= (c_1 + c_2) \left(T_1^{c_1} \cdot T_2^{c_2} \right)^{\frac{1}{c_1 + c_2}} - T_1 c_1 - T_2 c_2 < 0$$

→ Lana ateratzen da.

c) Errepikatu aurreko arriketak non $C \neq KTE$,

$C_i = \frac{C_{0i}}{T}$ den.

1. Itxulerina

$$Q_1 = \int_{T_1}^{T_f} C_i \, dT_i = \int_{T_1}^{T_f} \frac{C_0^i}{T_i} dT_i = C_0^i \ln \frac{T_f}{T_i}$$

$$Q = Q_1 + Q_2 = C_0^1 \ln \frac{T_f}{T_1} + C_0^2 \ln \frac{T_f}{T_2} = 0$$

$$\ln T_f (C_0^1 + C_0^2) = C_0^1 \ln T_1 + C_0^2 \ln T_2$$

$$\ln T_f = \frac{C_0^1 \ln T_1}{C_0^1 + C_0^2} + \frac{C_0^2 \ln T_2}{C_0^1 + C_0^2}$$

$$T_f^{IE} = \left(T_1^{C_0^1} \cdot T_2^{C_0^2}\right)^{\frac{1}{C_0^1 + C_0^2}}$$

Beroek trukatzeko modua esango digu bukaerako oreka termikoko tenperatura zein den. Ezin da jakin bakarrik prozesuaren izaerarekin. (C behar digu)

2. Itzulgarria

$$\Delta S_i = \int_{T_1}^{T_f} \frac{C_i}{T_i} dT_i = \int_{T_i}^{T_f} \frac{C_0^i}{T_i^2} dT_i = C_{0i} \cdot \left(\frac{1}{T_i} - \frac{1}{T_f}\right) =$$

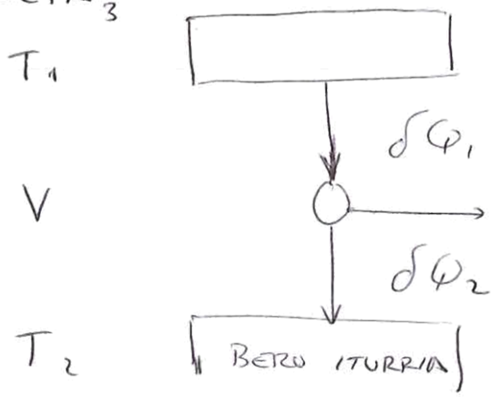
$$\Delta S^u = C_0^1 \cdot \frac{T_f - T_1}{T_1 T_f} + C_0^2 \cdot \frac{T_f - T_2}{T_2 T_f} = 0$$

$$C_0^1 \cdot (T_f - T_1) + C_0^2 (T_f - T_2) = 0$$

$$(C_0^1 + C_0^2) T_f = C_0^1 T_1 + C_0^2 T_2$$

$$T_f = \frac{C_0^1 T_1 + C_0^2 T_2}{C_0^1 + C_0^2}$$

ARIKETA 3



$C_p = a + bT$

$\delta W = \delta Q_1 + \delta Q_2$ $\quad -W = Q^1 + Q^2$

↳ Maximoa $\quad |W| = |Q^1| - |Q^2|$

Bero iturriko tenperatura aldatzen ez denez,

$$T_f = T_2$$

Beraz, ez da betebeharko $\Delta S^u = 0$ aplikatzea.
Baina lana lortuko bai.

$$dS^{BI} = \frac{\delta Q^{BI}}{T^{BI}} \Rightarrow \delta Q^{BI} = T^{BI} dS^{BI} \underset{\uparrow}{=} -T^{BI} dS_1^{u}$$

$$dS^u = dS_1 + dS_2^{BI} = 0$$

$$dS_1 = \frac{C_{p1}}{T_1} dT_1$$

Bero iturrien barnean ez dakigu nola trukatzen den beroa

$$\delta Q_2^{BI} = -T_2^{BI} dS_1 = -T_2^{BI} \cdot \frac{C_{p1}}{T_1} dT_1$$

$$\delta Q_1 = T_1 dS_1 = T_1 \frac{C_{p1}}{T_1} dT_1 = C_{p1} dT_1$$

$$Q_2^{BI} = -\int_{T_1}^{T_f = T_2} T_2 \left(\frac{a}{T_1} + b\right) dT_1 = -T_2 \cdot \Big[a \ln T + bT\Big]_{T_1}^{T_2} =$$

$$= -T_2 \cdot \left(a \ln \frac{T_2}{T_1} + b(T_2 - T_1)\right)$$

$$Q_1 = \int_{T_1}^{T_2} (a + bT)\, dT = aT + \frac{1}{2} bT^2 \Big|_{T_1}^{T_2} = a(T_2 - T_1) + \frac{1}{2} b (T_2^2 - T_1^2)$$

$$-W = Q_1 + Q_2 = (a - T_2 b)(T_2 - T_1) + \frac{1}{2} b (T_2^2 - T_1^2) - T_2 b \ln \frac{T_2}{T_1}$$

ARIKETA 4:

N sistema $\left.\begin{matrix} T^i \\ C^i \end{matrix}\right| i=1,\dots,N$ Horien arteko tenperatura diferentziak aprobetxatuz lana lortu nahi dugu, zein da oreka termikoko egoera? Eta ez badugu lanik ateratzen?

$\{T_1, \dots, T_N\}$

$\{c_1, \dots, c_n\}$

ITZULEZINA

- $\Delta S^u > 0 \Rightarrow \Delta S^u = \sum_{i=1}^{n} \Delta S_i > 0$

$$\Delta S_i = \int_{T_i}^{T_f^{IE}} dS_i = \int_{T_i}^{T_f^{IE}} \frac{\delta Q_i}{T} = \int_{T_i}^{T_f^{IE}} \frac{C_i}{T} dT$$

Onartuz $C_i = KTE$

$$\Delta S_i = C_i \ln \frac{T_f^{IE}}{T_i}$$

$$\Delta S^u = \sum_i^N C_i \ln \frac{T_f^{IE}}{T_i}$$

- $Q_{TOT} = 0 \Rightarrow Q_{TOT} = \sum_i^N Q_i = 0$

$$Q_i = \int_{T_i}^{T_f^{IE}} dQ = \int_{T_i}^{T_f^{IE}} C_i \, dT = C_i (T_f^{IE} - T_i)$$

$$Q_{TOT} = \sum_i^N C_i (T_f^{IE} - T_i) = 0$$

$$\sum_i^N C_i T_f^{IE} = \sum_i^N C_i T_i \Rightarrow T_f^{IE} = \frac{\sum_i^N C_i T_i}{\sum_1^N C_i}$$

ITZULGARRIA

- $\Delta S^u = 0 \Rightarrow \Delta S^u = \sum_i^N \Delta S_i = 0$

$$\Delta S_i = \int_{T_i}^{T_f^{IG}} dS = \int_{T_i}^{T_f^{IG}} \frac{\delta Q}{T} = \int_{T_i}^{T_f^{IG}} \frac{C_i}{T} dT = C_i \ln \frac{T_f^{IG}}{T_i}$$

$$\Delta S^u = \sum_i^N C_i \ln \frac{T_f^{IG}}{T_i} = 0 \Rightarrow T_f^{IG} = \left[\prod_i^N T_i^{C_i}\right]^{\frac{1}{\sum_i^N C_i}}$$

- $-W = \sum_i^N Q_i$

$$Q_i = \int_{T_i}^{T_f^{IG}} dQ_i = \int_{T_i}^{T_f^{IG}} C_i \, dT_i = C_i (T_f^{IG} - T_i)$$

$$-W = \sum_i^N C_i \left\{ \left[\prod_i^N T_i^{C_i}\right]^{\frac{1}{C_i}} - T_i \right\}$$

ENERGIA EZ-ERABILGARRIA

Edozein prozesu itzulezinak lanerako erabilgarria den energiaren partetik energia ez-erabilgarri bilakatzen du; hau da, ezin dugu lanerako inoiz ez erabili. (Energia "degradatzen" da)

Zenbatekoa da energia kantitate hau?

$$\boxed{E_{ez} = T \Delta S}$$

Askotan erantzunagoa da energia nuklearra ikustearena baina ≠ txikiagoten lan egiten dutelako.

FORMALISMO ALDAKETA

1. POSTULATUA: OREKA-EGOEREN DEFINIZIOA

Sistema bakunei (hidrostatikoei) dagozkien egoera bereziak existitzen dira. Makroskopikoki ondoko magnitudeez ezaugarritu daitezke:

U BARNE ENERGIA
V BOLUMENA
N_i OSAGAI KIMIKOEN MOL KOP

→ ESTENTSIBOAK

OREKA EGOERA LOTUAK: Kanpotik ezarjinen bakak finkatuta daude.
b/d kanp. helan, pistoia finko, geratu edb.

TERMODINAMIKAREN OINARRIZKO PROBLEMA

Hasierako oreka-egoera lotua — finkatuta — ⇒ barne loturen askapena ⇒ bukaerako egoera { lotua / Ez-lotua

2. POSTULATUA: ENTROPIA FUNTZIOAREN EXISTENTZIA

S, entropia funtzioa:

- Edozein sistema konposatuari dagokion parametro estentsibo guztien funtzioa da.
- Oreka-egoera guztietan definituta egongo da.
- Barne-loturarik ez dagoen kasuan, parametro estentsiboen balioek entropia MAXIMIZATUKO dute. Maximizazioa oreka egoera lotuetako burutu behar da.

[Barne-loturarik ez → berezko prozesua hasiera tu → prozesua itzulezina → Entropiak gora egin]

3. POSTULATUA: EZAUGARRIAK

- Azpisistemekiko batukorra
- Funtzio jarraia eta deribagarria (matematikoki: magnitude ohol.edb)
- Barne-energiaren funtzio monotono gorakorra

BATUIKORRA

a) $S = \sum_{n=1}^{N} S^n$

ESTENTSIBOA

b) 1. ORDENAKO FUNTZIO HOMOGENEOA: $S(\lambda U, \lambda V, \ldots) = \lambda S(U, V, \ldots)$

MONOTONO GORAKORRA

$$-\left(\frac{\partial S}{\partial U}\right)_{V,N_1,\ldots} > 0$$

JARRAITASUNA, DERIBAGARRITASUNA

$S(U, V, N_1, \ldots) \longrightarrow U(S, V, N_1)$ baliokideak

PROZESUEN ADIERAZPENA

$$U = U(S, V, N_1, \ldots, N_n)$$

(KONTUZ HORIEKIN

I. G.

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N_1,\ldots,N_n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N_1,\ldots,N_n} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V,\ldots,N_n} dN_1 + \cdots + \left(\frac{\partial U}{\partial N_n}\right)_{S,V,N} dN_n$$

Intentsiboak → $T(S,V,N)$ $\quad -p(S,V,N) \quad \mu(S,V,N)$ → FUNTZIOAK!!!

$$\Rightarrow \boxed{dU = TdS - pdV + \mu dN}$$

↳ EGOERA EK

[NOMENKLATURA

Sist elastikoa: $U = U(S, L, N)$; Sist elek: $U = U(S, \underline{P}, N)$ polarizazioa]

Baliokidea: $S = S(U, V, N)$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

Intentsiboak → $1/T \quad p/T \quad -\mu/T$ — FUNTZIOAK!!!

$$\Rightarrow \boxed{dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN}$$ → OINARRIZKO EK

1. PRINTZIPIOA → Lana (mek, kim, ...)

$$dU = TdS + \sum_{j}^{N} P_j dX_j$$

Elkarpen formikoa ↵ $\quad P_j dX_j \equiv Y_i dX_i$

Indar orokortua ↵ $\quad$ ↳ Desplazamendu orokortua

⇒ ENERGIAREN KONTSERBAZIOA

$$P_j = \left(\frac{\partial U}{\partial X_j}\right)_{X_0,\dots,X_n} \Rightarrow dU = TdS + \sum_{j=1}^{N} P_j\, dX_j$$

LOTURA

$$F_j = \left(\frac{\partial S}{\partial X_j}\right)_{X_0,\dots,X_n} \Rightarrow dS = \sum_{k=0}^{N} F_k\, dX_k \quad : \boxed{F_0 = \frac{1}{T_0}\ ;\ F_k = -\frac{P_k}{T}}$$

ADIBIDEAK: Kalkulatu egoera ekuazioak

i) $U = \left(\frac{v_0\Theta}{R^2}\right)\frac{S^3}{NV}$ [Adierazpen energetikoa]

$$T = \left(\frac{\partial U}{\partial S}\right)_{N,V} = \frac{v_0\Theta}{R^2}\, 3\, \frac{S^2}{NV}$$

ADI!! Ziurtatu 1.ord funtzio homog. dela: $\lambda S, \lambda V, \lambda N \longrightarrow \lambda U$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = +\frac{v_0\Theta}{R^2}\frac{S^3}{NV^2}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = -\frac{v_0\Theta}{R^2}\frac{S^3}{VN^2}$$

ii) $u = \left(\frac{v_0^{1/2}\Theta}{R^{3/2}}\right)\frac{s^{5/2}}{v^{1/2}}$ [Masa unitateko u adierazpena]

$$U(S,V,N) \xrightarrow[\lambda = \frac{1}{N}]{} u(s,v,1) \quad s, v \text{ molarrak}$$

· 2. aldagai independiente ditu

· 0 ordenako funtzio homogeneoa

$$T = \left(\frac{\partial u}{\partial s}\right)_v = T(s,v) = \left(\frac{v_0^{1/2}\Theta}{R^{3/2}}\right)\cdot\frac{5}{2}\frac{s^{3/2}}{v^{1/2}}$$

$$P = -\left(\frac{\partial u}{\partial v}\right)_s = P(s,v) = -\left(\frac{v_0^{1/2}\Theta}{R^{3/2}}\right)\cdot\frac{-1}{2}\cdot\frac{s^{5/2}}{v^{3/2}}$$

$$\frac{U}{N} = C\cdot\frac{(S/N)^{5/2}}{(V/N)^{1/2}} \Rightarrow U = C\cdot\frac{S^{5/2}}{V^{1/2}}\cdot\frac{N^{1/2}}{N^{5/2}}\, N$$

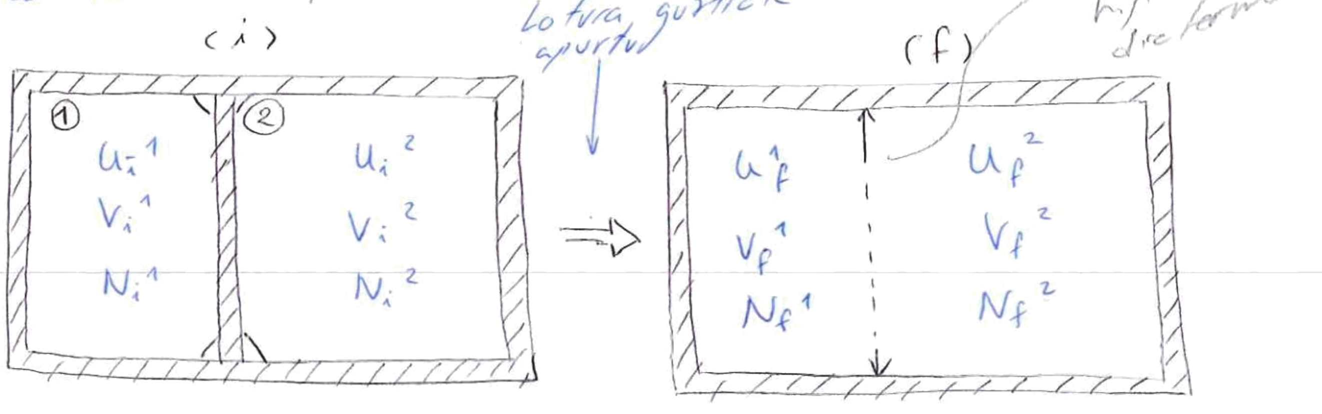
$$\Rightarrow U = C\cdot\frac{S^{5/2}}{V^{1/2}}\cdot\frac{1}{N}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = C\cdot\frac{S^{5/2}}{V^{1/2}}\cdot\frac{-1}{N^2}$$

TERMODINAMIKAREN OINARRIZKO PROBLEMAREN EBAZPENA:

PRINTZIPIO ESTREMALA

Oreka-egoera loturen dagoen sistema itxiak barne-loturaren bat askatuko zein oreka-egoeratan bukatuko du?



$$S = S(U, V, N)$$

$$S^1 = S^1(U^1, V^1, N^1)$$

$$S^2 = S^2(U^2, V^2, N^2)$$

Printzipio estremalak dio bukaerako egoeran lotura bat askatuta parametro estentsiboak aldatu egingo direla entropia maximizatuz; hau da, amaierako parametro estentsiboak taulatuko kantitatea entropia maximoa izatea lortuko dute eta momentu horretan parametro estentsiboek balio bera izango dute bi azpisistemetan.

ITXITURA BALDINTZAK

$$\left(\begin{array}{l} U = U_i^1 + U_i^2 = KTE \\ V = V_i^1 + V_i^2 = KTE \\ N = N_i^1 + N_i^2 = KTE \end{array}\right)_{i,f}$$

Entropia maximoa $\Rightarrow$ lehen deribatua nulua

$$S = S^1 + S^2$$

$$dS = dS^1 + dS^2 = 0$$

$$dS^1 = \left(\frac{\partial S^1}{\partial U^1}\right)_{V^1,N^1} dU^1 + \left(\frac{\partial S^1}{\partial V^1}\right)_{U^1,N^1} dV^1 + \left(\frac{\partial S^1}{\partial N^1}\right)_{U^1,V^1} dN^1$$

$$dS^2 = \left(\frac{\partial S^2}{\partial U^2}\right)_{V^2,N^2} dU^2 + \left(\frac{\partial S^2}{\partial V^2}\right)_{U^2,N^2} dV^2 + \left(\frac{\partial S^2}{\partial N^2}\right)_{U^2,V^2} dN^2$$

Printzipioz 6 aldagaien gradu izango lirateke baina termikoki, mekanikoki eta kimikoki lotuta daudenez, 3 aldagaien gradu izango dira.

Itxidura ekuazioetatik $\Rightarrow \begin{cases} dU^2 = -dU^1 \\ dV^2 = -dV^1 \\ dN^2 = -dN^1 \end{cases}$

$$dS = \left[\left(\frac{\partial S^1}{\partial U^1}\right)_{V^1,N^1} - \left(\frac{\partial S^2}{\partial U^2}\right)_{V^2,N^2}\right] dU^1 + \left[\left(\frac{\partial S^1}{\partial V^1}\right)_{U^1,N^1} - \left(\frac{\partial S^2}{\partial V^2}\right)_{U^2,N^2}\right] dV^1 + \left[\left(\frac{\partial S^1}{\partial N^1}\right)_{U^1,V^1} - \left(\frac{\partial S^2}{\partial N^2}\right)_{U^2,V^2}\right] dN^1$$

$$dS = \left[\left(\frac{1}{T}\right)^1 - \left(\frac{1}{T}\right)^2\right] dU^1 + \left[\left(\frac{P}{T}\right)^1 - \left(\frac{P}{T}\right)^2\right] dV^1 - \left[\left(\frac{\mu}{T}\right)^1 - \left(\frac{\mu}{T}\right)^2\right] dN^1 = 0$$

$$\left(\frac{1}{T}\right)^1 - \left(\frac{1}{T}\right)^2 = \left(\frac{P}{T}\right)^1 - \left(\frac{P}{T}\right)^2 = \left(\frac{\mu}{T}\right)^1 - \left(\frac{\mu}{T}\right)^2 = 0$$

$$\left(\frac{1}{T}\right)^1 = \left(\frac{1}{T}\right)^2 ; \left(\frac{P}{T}\right)^1 = \left(\frac{P}{T}\right)^2 ; \left(\frac{\mu}{T}\right)^1 = \left(\frac{\mu}{T}\right)^2$$

$$U = U^1 + U^2 = KTE \Rightarrow U_i^1 + U_i^2 = \boxed{U_f^1 + U_f^2}$$

$$V = V^1 + V^2 = KTE \Rightarrow V_i^1 + V_i^2 = \boxed{V_f^1 + V_f^2} \rightarrow \text{Ezezagunak}$$

$$N = N^1 + N^2 = KTE \Rightarrow N_i^1 + N_i^2 = \boxed{N_f^1 + N_f^2}$$

6 ezezagun ∧ 3 ekuazio ⇒ beste hiru behar:

$$\left[\begin{array}{l} \left(\frac{1}{T}\right)^1 = \left(\frac{1}{T}\right)^2 \\ \left(\frac{P}{T}\right)^1 = \left(\frac{P}{T}\right)^2 \\ \left(\frac{\mu}{T}\right)^1 = \left(\frac{\mu}{T}\right)^2 \end{array}\right]^f \Rightarrow \frac{1}{T}(U_f^1, V_f^1, N_f^1) = \frac{1}{T}(U_f^2, V_f^2, N_f^2)$$

EULER-EN EKUAZIOA

Dinamikako ekuazio 1. ordeneko ekuazio homogeneoa denez, Euler-en ekuazioa beteko du

$$U(\lambda S, \lambda V, \lambda N, \dots) = \lambda U(S, V, N, \dots)$$

$$\frac{d}{d\lambda}\left[U(\lambda S, \lambda V, \lambda N, \dots)\right] = \frac{d\lambda}{d\lambda} U(S, V, N, \dots) = U(S, V, N, \dots)$$

$$\frac{1}{d\lambda}\cdot\left(\frac{\partial U}{\partial(\lambda S)}\right)\left(\frac{\partial \lambda S}{\partial \lambda}\right) d\lambda + \dots + \left(\frac{\partial U}{\partial \lambda N}\right)\left(\frac{\partial \lambda N}{\partial N}\right) d\lambda =$$

$$= \left(\frac{\partial U}{\partial \lambda S}\right)\cdot S + \dots + \left(\frac{\partial U}{\partial \lambda N}\right)\cdot N =$$

$$\lambda = 0$$

$$= \left(\frac{\partial U}{\partial S}\right)\cdot S + \left(\frac{\partial U}{\partial V}\right)\cdot V + \dots + \left(\frac{\partial U}{\partial N}\right) N =$$

$$\boxed{\underbrace{T}_{\text{funtzioak}} \cdot S - p \cdot V + \sum_{k=1}^{N} \mu_k \cdot N_k = U(S, V, N, \dots)}$$

$$S = \frac{1}{T} U + \frac{P}{T} V - \frac{\mu}{T} N$$

GIBBS-DUHEM-EN ERLAZIOA

Parametro intentsiboak ez dira independenteak.

ERA FORMALEAN

$$U = U(S, V, N)$$

$$\cdot\frac{1}{N} \hookrightarrow u = u(s, v) \xrightarrow{\partial/\partial}$$

askatu

$$\left.\begin{array}{l} T = T(s, v) \\ P = P(s, v) \\ \mu = \mu(s, v) \end{array}\right\} \begin{array}{l} \rightarrow s = s(T, v) \\ \rightarrow v = v(s, P) \end{array} \Bigg\} \Rightarrow \mu = \mu(T, P)$$

EULER-EN EKUAZIOTIK ABIATUZ

$$U = T\cdot S - p\cdot V + \mu N$$

$$dU = d(T\cdot S) - d(p\cdot V) + d(\mu N)$$

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

$$dU = TdS \qquad - pdV \qquad + \mu dN$$

Bi.ts →

$$\begin{cases} U = U(S, V, N) \\ dU = \left(\frac{\partial U}{\partial S}\right)dS + \left(\frac{\partial U}{\partial V}\right)dV + \left(\frac{\partial U}{\partial N}\right)dN \\ dU = TdS - pdV + \mu dN \end{cases}$$

$$\Rightarrow \boxed{SdT - Vdp + Nd\mu = 0}$$

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dp = -s\,dT + v\,dp$$

Integratuz $\Rightarrow$ $\mu(T, p)$ lortu

ARIKETAK

1/ $\begin{cases} U = pV \\ P = BT^2 \end{cases}$ Lortu oinarrizko ekuazioa egoera ekuazioak hauek badira.

U aldagai moduan emanten digutenez, adierazpen entropikoa bilatuko dugu. Lortu $\frac{1}{T}$ eta $\frac{P}{T}$

$$p = \frac{U}{V} \rightarrow T^2 = \frac{U}{VB} \Rightarrow T = \frac{U^{1/2}}{V^{1/2}B^{1/2}} \Rightarrow \frac{1}{T} = \frac{V^{1/2}B^{1/2}}{U^{1/2}}$$

$$p = BT^2 \longrightarrow \frac{P}{T} = BT = \frac{BU^{1/2}}{V^{1/2}B^{1/2}} \Rightarrow \frac{P}{T} = \frac{B^{1/2}U^{1/2}}{V^{1/2}}$$

Molarrak bihurtu $(\cdot \frac{1}{N})$

$$\frac{P}{T} = B^{1/2}\frac{u^{1/2}}{v^{1/2}} \quad ; \quad \frac{1}{T} = B^{1/2}\frac{v^{1/2}}{u^{1/2}}$$

$$\begin{cases} d\left(\frac{1}{T}\right) = B^{1/2}\cdot\left[\frac{1}{2}v^{-1/2}u^{1/2} - \frac{1}{2}v^{1/2}u^{-3/2}du\right] \Big\}\cdot u \\ d\left(\frac{P}{T}\right) = B^{1/2}\cdot\left[\frac{1}{2}u^{-1/2}v^{1/2}du - \frac{1}{2}v^{-3/2}u^{1/2}\right] \Big\}\, v \end{cases}$$

$$B^{1/2}\left[-\frac{1}{2}u^{1/2}u^{-1/2}du+\frac{1}{2}v^{-1/2}u^{1/2}\right]$$

$$+\ B^{1/2}\left[\frac{1}{2}v^{1/2}u^{-1/2}du-\frac{1}{2}u^{1/2}u^{-1/2}\right]$$

$$d\left(\frac{\mu}{T}\right)=\phi+\phi=\phi \Rightarrow \frac{\mu}{T}=\left(\frac{\mu}{T}\right)_0$$

$$S=B^{1/2}\frac{V^{1/2}}{U^{1/2}}U+B^{1/2}\frac{U^{1/2}}{V^{1/2}}V-N\left(\frac{\mu}{T}\right)_0=$$

$$=B^{1/2}\left[2V^{1/2}U^{1/2}\right]-N\left(\frac{\mu}{T}\right)_0$$

21

$$T=3A\frac{S^2}{V}=3A\cdot\frac{1}{N}\frac{s^2}{v}$$

Lortu dinamiko ekuazioa

$$p=A\frac{S^3}{V^2}=A\cdot\frac{1}{N}\frac{s^3}{v^2}$$

Entropia aldagai modian dagoenez, adierazpen energetikoa bilatu behar dugu.

$$\left[dT=3A\cdot2\frac{S}{V}dS-3A\frac{S^2}{V^2}dV\right]\cdot(-s)$$

$$\left[dp=A\cdot3\frac{S^2}{V^2}dS-2A\frac{S^3}{V^3}dV\right]\cdot v$$

$$-s\,dT=-6A\frac{s^2}{v}ds+3A\frac{s^3}{v^2}dV$$

$$+\ v\,dp=3A\frac{s^2}{v}ds-2A\frac{s^3}{v^2}dV$$

$$d\mu=-s\,dT+v\,dp=-3A\frac{s^2}{v}dS+A\frac{s^3}{v^2}dV$$

$$d\mu=-3A\frac{s^2}{v}dS+A\frac{s^3}{v^2}dV$$

$$\mu=-A\frac{s^3}{v}+\mu_0=-A\cdot\frac{S^3}{V\cdot N^2}+\frac{\mu_0}{N}$$

INTEGRAZIOA

$$\mu_1=-A\frac{s^3}{v}+f(v)$$

$$\left(\frac{\partial\mu_1}{\partial v}\right)=+A\frac{s^3}{v^2}+f'(v)=A\frac{s^3}{v^2}\Rightarrow f'(v)=0$$

$$f(v)=k$$

$$U = TS - pV + \mu \cdot N =$$

$$= 3A \frac{S^2}{VN} S - A \frac{S^2}{V^2 N} V - \frac{AS^3}{VN^2} N + \frac{\mu_0}{N} N$$

$$U = (3A - A - A) \frac{S^3}{VN} + \mu = A \frac{S^3}{VN} + \mu_0 = U$$

Bste modu:

$$dU = Tds - pdV \rightarrow \text{OINARRIZKO EKUAZIO NOLABRRA}$$

$$dU = 3A \frac{S^2}{V} dS - A \frac{S^3}{V^2} dV$$

$$U_1 = A \frac{S^3}{V} + f(V)$$

$$\frac{\partial U_1}{\partial V} = -A \frac{S^3}{V^2} + f'(V) = -A \frac{S^3}{V^2} dV \Rightarrow f'(V) = 0$$

$$U = A \frac{S^3}{V} + U_0$$

$$\frac{U}{N} = A \frac{S^3}{V} \cdot \frac{1}{N^2} + \frac{U_0}{N}$$

$$U = A \frac{S^3}{V} \cdot \frac{1}{N} + U_0 \rightarrow \text{Aurrekoan lortutakoa}$$

PROPOSAMENAK

1) $U = \frac{3}{2} pV$

$U^{1/2} = BTV^{1/3}$

2) $U = \frac{1}{2} pV$

$T^2 = A \frac{U^{3/2}}{VN^{1/2}}$

* 3) GAS IDEALAK

$$\begin{matrix} pV = nRT \\ U = NC_vT \end{matrix} \rightarrow \begin{matrix} \frac{P}{T} = \frac{nR}{V} \Rightarrow \frac{P}{T} = \frac{R}{v} \\ \frac{1}{T} = \frac{NC_v}{U} \Rightarrow \frac{1}{T} = \frac{C_v}{u} \end{matrix} \Bigg\} \text{molarrak}$$

$$dS = \frac{1}{T} du + \frac{P}{T} dv$$

$$G.I \Rightarrow S = \frac{N}{N_0} S_0 + NR \ln \left[\left(\frac{U}{U_0}\right)^{c} \left(\frac{V}{V_0}\right) \left(\frac{N}{N_0}\right)^{-(c+1)} \right], \quad c = \frac{C_v}{nR}$$

$$VdW \Rightarrow S = NR \ln \left[(v-b) \left(u + \frac{a}{v}\right)^c \right] + Ns_0$$

AUKERAKO FORMULAZIOAK: BALIOKIDETASUNA

Edozein sistemaren kasuan, entropia beti aldagai naturaletan idatzita: $\left(\frac{\partial S}{\partial U}\right)_{\dots} > 0$ betetzen da.

KUALITATIBOKI $\Rightarrow$ $\underset{U=KTE}{S^{UNIB}_{max}} \iff \underset{S=KTE}{U^{SIST}_{min}}$

LEGENDRE-REN TRANSFORMAZIOAK

$$U = U(S,V,N)$$

$$U = U(T,V,N) = U\Big(\underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,N}}_{\text{Ez dago konpletua}}, V, N\Big)$$

ADD IND 1-EKO FUNTZ. $\Rightarrow Y = Y(\overset{EST.}{x})$

$\underset{INT.}{P} = \frac{dY}{dx}$ sartu nahi dugu

$\Big\} \; Y = Y(P)$

• Lehenengo hurbilketa txarra

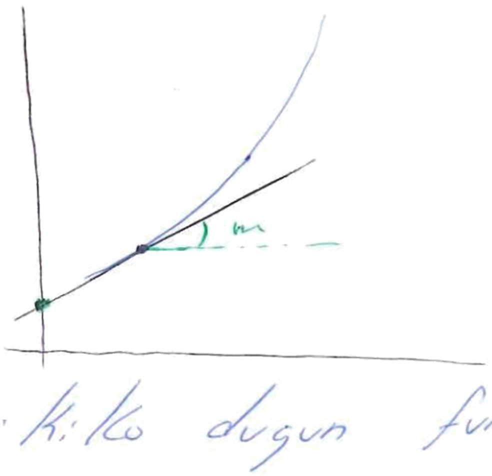
$P = \frac{dY}{dX} \Rightarrow P = P(X) \Rightarrow X = X(P)$

$Y = Y(X)$

$\Big\} \; Y = Y(X(P)) = Y(P)$

$\Rightarrow$ Informazio galera dago

• Hurbilketa ona



1.→ Sortu lerro ukitzailea

2.→ Ukitzailearen jatorriko ordenatua lortu

$Y = Y(x)$; $P = \frac{dY}{dx} \rightarrow x = X(P)$

Eraikiko dugun funtzioa: $\boxed{\Psi = Y(P) - X(P)P}$

$\Rightarrow Y(x) = Y(X(P)) = Y(P)$

$\Rightarrow X(P)\cdot P$

$\Big\} \Rightarrow \Psi(P)$

Demagun bi aldagai independente ditugula

$$Y = Y(x_1, x_2)$$

$$P_1 = \left(\frac{\partial Y}{\partial x_1}\right)_{x_2} \quad ; \quad P_2 = \left(\frac{\partial Y}{\partial x_2}\right)_{x_1}$$

notazioa

$$Y[P_1] \equiv \Psi(P_1, x_2) = Y(P_1, x_2) - P_1 \, x_1(P_1, x_2)$$

$$Y[P_1, P_2] \equiv \Psi(P_1, P_2) = Y(x_1(P_1, P_2), x_2(P_1, P_2)) + \\ - P_1 \cdot x_1(P_1, P_2) - P_2 \cdot x_2(P_1, P_2)$$

ADIBIDEA

$$Y = \frac{1}{10} x^2 \Rightarrow \Psi(P)?$$

$$P = \frac{dY}{dx} = \frac{1}{5} x \Rightarrow x(P) = 5P$$

$$Y = Y(x(P)) = \frac{1}{10}(5P)^2 = \frac{5}{2} P^2$$

$$\Psi = Y(P) - P \cdot x(P) = \frac{5}{2} P^2 - P \cdot 5P = \frac{-5}{2} P^2$$

$$Y(x) = \frac{1}{10} x^2 \Longleftrightarrow \Psi(P) = -\frac{5}{2} P^2$$

PROPOSAMENA: $Y = A e^{Bx} \Rightarrow \Psi(P)?$

TERMODINAMIKARA ERAMANDA:

$$U = U(S, V, N)$$

$G(T, p, N) = U[T, p] \rightarrow$ GIBBS-EN ENERGIA ASKEA

$F(T, V, N) = U[T] \rightarrow$ HELMHOLTZ-EN ENERGIA ASKEA

$H(S, p, N) = U[p] \rightarrow$ ENTALPIA

$(T, V, \mu) = U[T, \mu]$

Definizioz:

$$F = U[T] = U(T, S, V) - T S(T, V, N)$$

$$H = U[p] = U(S, P, N) + p V(S, p, N)$$

$$G = U[T, p] = U(T, p, N) - T S(T, p, N) + p V(T, p, N)$$

Adierazpen diferentziale

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

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

$$dH = TdS + Vdp + \mu dN$$

$$dG = -SdT + Vdp + \mu dN$$

- $U = U(S, V, N)$

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}, \quad p = -\left(\frac{\partial U}{\partial V}\right)_{S,N}, \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

- $F = F(T, V, N)$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

- $H = H(S, p, N)$

$$T = \left(\frac{\partial H}{\partial S}\right)_{p,N}, \quad V = \left(\frac{\partial H}{\partial p}\right)_{S,N}, \quad \mu = \left(\frac{\partial H}{\partial N}\right)_{S,p}$$

- $G = G(T, p, N)$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,N}, \quad V = \left(\frac{\partial G}{\partial p}\right)_{T,N}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,p}$$

NOTA

$$K = K(T, p, \mu) \Rightarrow \left(\frac{\partial K}{\partial T}\right)_{\underbrace{p,\mu}} \neq -S = S(T, \underbrace{p, N})$$

$\Rightarrow$ Ez dira berdinak!!

* 67. oir - propos - 3

GAS IDEALA (C-66)

$$\begin{cases} pV = NRT & \rightarrow \dfrac{p}{T} = \dfrac{NR}{V} \\ U = CNRT & \rightarrow \dfrac{1}{T} = \dfrac{CNR}{U} \end{cases}$$

GIBBS-DUHEM $\Rightarrow$ $\boxed{d\left(\frac{\mu}{T}\right) = u\,d\left(\frac{1}{T}\right) + v\,d\left(\frac{p}{T}\right)}$

$$d\left(\frac{\mu}{T}\right) = -\frac{CNR}{u^2}u\,du - \frac{NR}{v^2}v\,dv = -\frac{CNR}{u}du - \frac{NR}{v}dv$$

$$\frac{\mu}{T} = -cNR\ln\frac{u}{u_0} - NR\ln\frac{v}{v_0} + \left(\frac{\mu}{T}\right)_0$$

$$\text{EULER} \Rightarrow S = \left(\frac{1}{T}\right)U + \left(\frac{P}{T}\right)V - \left(\frac{\mu}{T}\right)N$$

$$S = \frac{cNR}{\cancel{U}}\cancel{U} + \frac{NR}{\cancel{V}}\cancel{V} + N^2R\ln\left(\frac{u}{u_0}\right)^c + N^2R\ln\frac{v}{v_0} + \left(\frac{\mu}{T}\right)_0 =$$

$$= NR(c+1) + NR\ln\left[\left(\frac{U}{U_0}\right)^c\left(\frac{V}{V_0}\right)\left(\frac{N}{N_0}\right)^{-(c+1)}\right] - \left(\frac{\mu}{T}\right)_0 N$$

$$S = N\left[R(c+1) - \left(\frac{\mu}{T}\right)_0\right] + NR\ln\left[\left(\frac{U}{U_0}\right)^c\left(\frac{V}{V_0}\right)\left(\frac{N}{N_0}\right)^{-(c+1)}\right]$$

VAN DER WAALS FLUID

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \Rightarrow \frac{P}{T} = \frac{R}{v-b} - \frac{a}{v^2T}$$

$$\frac{1}{T} = f(u,v)$$

$$ds = \frac{1}{T}du + \frac{P}{T}dv$$

ds perfect differential $\Rightarrow \frac{\partial^2 s}{\partial u \partial v} = \frac{\partial^2 s}{\partial v \partial u} \Rightarrow$

$$\frac{\partial}{\partial v}\left(\frac{1}{T}\right)_u = \frac{\partial}{\partial u}\left(\frac{P}{T}\right)_v = \frac{\partial}{\partial u}\left(\frac{R}{v-b} - \frac{a}{v^2T}\right)_v \Rightarrow$$

$$\frac{\partial}{\partial v}\left(\frac{1}{T}\right)_u = -\frac{a}{v^2}\frac{\partial}{\partial u}\left(\frac{1}{T}\right)_v \Leftrightarrow$$

$$\frac{\partial}{\partial(1/v)}\left(\frac{1}{T}\right)_u = -\frac{\partial}{\partial(u/a)}\left(\frac{1}{T}\right)_v \Rightarrow \frac{1}{T} = \frac{cR}{u + \frac{a}{v}}$$

$$\frac{P}{T} = \frac{R}{v-b} - \frac{acR}{uv^2 + av}$$

$$ds = \left(\frac{cR}{u + \frac{a}{v}}\right)du + \left(\frac{R}{v-b} - \frac{acR}{uv^2+av}\right)dv$$

$$s = cR\ln\left|u + \frac{a}{v}\right| + f(v)$$

$$\left(\frac{\partial s}{\partial v}\right)_u = cR \cdot \frac{1}{u+\frac{a}{v}} \cdot \frac{-a}{v^2} + f'(v) = -\frac{acR}{uv^2+av} + f'(v) =$$

$$= \frac{R}{v-b} - \frac{acR}{uv^2+av} \Rightarrow f'(v) = \frac{R}{v-b}$$

$$f(v) = R\ln(v-b) + K$$

$$s = cR\ln\left(u+\frac{a}{v}\right) + R\ln(v-b) + s_0 =$$

$$= R\ln\left[\left(u+\frac{a}{v}\right)^c (v-b)\right] + s_0 \Rightarrow$$

$$S = NR\ln\left[\left(u+\frac{a}{v}\right)^c (v-b)\right] + Ns_0$$

$$c_v = \left(\frac{\partial Q}{\partial T}\right)_v \underset{\substack{\uparrow \\ \delta Q = TdS}}{=} T\left(\frac{\partial S}{\partial T}\right)_v$$

$$U = U(S, V, N)$$

$$\Updownarrow$$

$$F = F(T, V, N) \rightarrow dF = -SdT - pdV + \mu dN$$

$$H = H(S, p, N) \rightarrow dH = TdS + Vdp + \mu dN$$

$$G = G(T, p, N) \rightarrow dG = -SdT + Vdp + \mu dN$$

$$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial H}{\partial N}\right)_{S,p} = \left(\frac{\partial G}{\partial N}\right)_{T,p}$$

PRINTZIPIO ESTREMALAK

- $S = S(U, V, N)$ max $\overset{T=KTE}{\Longrightarrow}$ $F \overset{SIST}{=} F(T, V, N)$ min
- $S = S(U, V, N)$ max $\overset{p=KTE}{\Longrightarrow}$ $H \overset{SIST}{=} H(S, P, N)$ min
- $S = S(U, V, N)$ max $\underset{T=KTE}{\overset{P=KTE}{\Longrightarrow}}$ $G \overset{SIST}{=} G(T, P, N)$ min

FRGA (G)

$$\Delta S_{osoa} = \Delta S_{sist} + \Delta S_{ing} < \begin{matrix} IE > 0 \\ IG = 0 \end{matrix}$$

$$Q_{osoa} = Q_{sist} + Q_{ing} = 0 \Rightarrow Q_{ing} = -Q_{sist}$$

$$T, p = kte \Rightarrow Q_{ing} = \Delta H_{sist}$$

$$Q_{ing} = T\Delta S_{ing} \Rightarrow \Delta S_{ing} = \frac{Q_{ing}}{T}$$

Def: $G = H - TS \Rightarrow \Delta G = \Delta H - T\Delta S$

$$\Rightarrow \Delta G = -T\Delta S_{osoa}$$

MAXWELL-EN ERLAZIOAK

$U \longrightarrow$ BARNE-ENERGIA

$H = U + P \longrightarrow$ ENTALPIA

$F = U - TS \longrightarrow$ HELMHOLTZ-EN FUNTZIOA

$G = U + PV - TS \longrightarrow$ GIBBS-EN FUNTZIOA

$$dz = M\,dx + N\,dy \qquad (z = z(x,y))$$

z DIFERENTZIAL ZEHATZA $\Rightarrow \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

$$dU = TdS - pdV + \dots \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

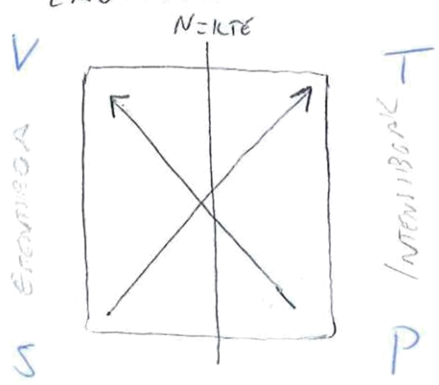
$$dH = TdS + Vdp + \dots \Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

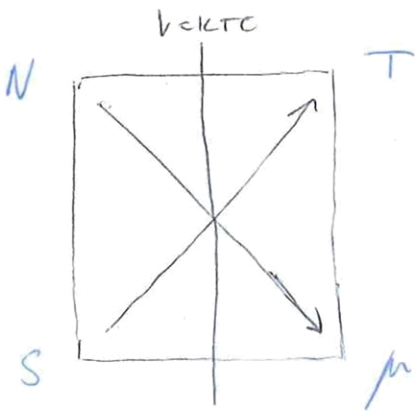
$$dF = -SdT - pdV + \dots \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

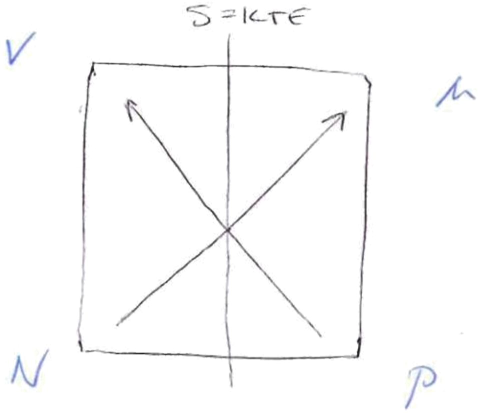
$$dG = -SdT + Vdp + \dots \Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

KONTUAN IZAN: $\left(\frac{\partial \boxtimes}{\partial \square}\right)_{\blacksquare} \Rightarrow \boxtimes = \boxtimes(\square, \blacksquare)$

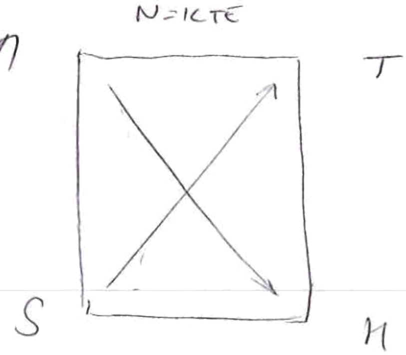
BORN-EN LAUKIA



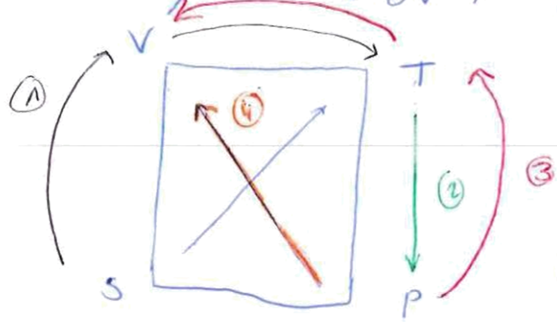




Bigarren deribatuen arteko baldintza horiek ahalbidetzen digu energia honek.

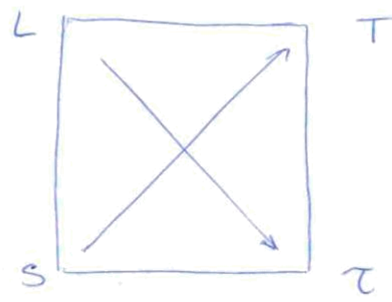


Demagun $\left(\frac{\partial S}{\partial V}\right)_T$ galdetzen digutela



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

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



$$\left(\frac{\partial S}{\partial L}\right)_\tau = -\left(\frac{\partial \tau}{\partial T}\right)_L$$

Adi! Gerick beti intentsibotik estentsibora mekanikoaren kasuan izan ohi ("ikur aldaketa")

- Koefiziente termodinamikoekin zuzenean:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

- Kasu "arraroetan": T sartu

$$\left(\frac{\partial S}{\partial V}\right)_P \overset{\downarrow}{=} \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P = \frac{C_P}{T}\cdot\frac{1}{V\alpha}$$

- Demagun $\left(\frac{\partial u}{\partial P}\right)_S$ eskatzen digutela

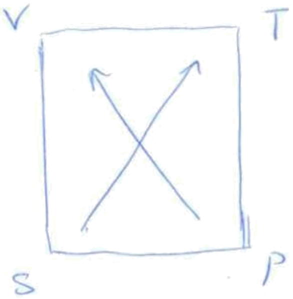
$u = u(S,V)$

$du = \left(\frac{\partial u}{\partial S}\right)_V dS + \left(\frac{\partial u}{\partial V}\right)_S dV$ idatzi beharrean, ⇒

$du = T\,dS - p\,dV$

$$\left(\frac{\partial u}{\partial P}\right)_S = \frac{\partial}{\partial P}\left[T\,dS - p\,dV\right]_S$$

$$\Rightarrow \left(\frac{\partial u}{\partial p}\right)_s = T \cancel{\left(\frac{\partial s}{\partial p}\right)_s}^{\,0} - p\left(\frac{\partial v}{\partial p}\right)_s$$



Berucen her

$$\left(\frac{\partial v}{\partial p}\right)_{s} = - \frac{\left(\frac{\partial s}{\partial T}\right)_v}{\left(\frac{\partial s}{\partial v}\right)_p} \overset{T \text{ arh}}{=} - \frac{\left(\frac{\partial s}{\partial T}\right)_v \left(\frac{\partial T}{\partial p}\right)_v}{\left(\frac{\partial s}{\partial T}\right)_p \left(\frac{\partial T}{\partial v}\right)_p} =$$

$$= - \frac{\frac{c_v}{\cancel{T}}\left(-\left(\frac{\partial v}{\partial p}\right)_T \Big/ \cancel{\left(\frac{\partial v}{\partial T}\right)_p}\right)}{\frac{c_p}{\cancel{T}} \cdot \frac{1}{\cancel{\left(\frac{\partial v}{\partial T}\right)_p}}} = + \frac{c_v}{c_p}\left(\frac{\partial v}{\partial p}\right)_T$$

$$\Rightarrow \left(\frac{\partial u}{\partial p}\right)_s = - \frac{c_v}{c_p}\, p \left(\frac{\partial v}{\partial p}\right)_T$$

- Demanem $\left(\frac{\partial p}{\partial u}\right)_s$

$$\left(\frac{\partial p}{\partial u}\right)_s = \frac{1}{\left(\frac{\partial u}{\partial p}\right)_s} = - \frac{c_p}{c_v} \cdot \frac{1}{p} \cdot \left(\frac{\partial p}{\partial v}\right)_T$$

- Demanem $\left(\frac{\partial s}{\partial p}\right)_u$

$$\left(\frac{\partial s}{\partial p}\right)_u = - \frac{\left(\frac{\partial u}{\partial p}\right)_s}{\left(\frac{\partial u}{\partial s}\right)_p} \qquad (\dots)$$

- Demanem $\left(\frac{\partial F}{\partial s}\right)_p$

$$dF = -S\,dT - p\,dV$$

$$\left(\frac{\partial F}{\partial s}\right)_p = - S\left(\frac{\partial T}{\partial s}\right)_p - p\left(\frac{\partial v}{\partial s}\right)_p = - S \cdot \frac{T}{c_p} - p\left(\frac{\partial T}{\partial p}\right)_s$$

$$\left(\frac{\partial T}{\partial p}\right)_s = - \frac{\left(\frac{\partial s}{\partial p}\right)_T}{\left(\frac{\partial s}{\partial T}\right)_p} = - \frac{-\left(\frac{\partial v}{\partial T}\right)_p}{\frac{c_p}{T}} = \frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p$$

$$\left(\frac{\partial F}{\partial s}\right)_p = - S \cdot \frac{T}{c_p} - p\frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p = - \frac{T}{c_p}\left(S + p\left(\frac{\partial v}{\partial T}\right)_p\right)$$

· Demagun $\left(\frac{\partial u}{\partial H}\right)_T$

$$\left(\frac{\partial u}{\partial H}\right)_T = T\left(\frac{\partial S}{\partial H}\right)_T - p\left(\frac{\partial V}{\partial H}\right)_T = T \cdot \frac{1}{\left(\frac{\partial H}{\partial S}\right)_T}$$

$$T\cancel{\left(\frac{\partial S}{\partial S}\right)_T}^{1} + V\left(\frac{\partial P}{\partial S}\right)_T = \hookleftarrow$$

Beste mota bat: AZIKETA

Sistema bati dagokion oinarrizko ekuazioa honelako hau da: $F = -A N^{2/3} V^{1/3} T^2$

Bolumena zortzi aldiz handitu duen espantsio adiabatiko itzulgarriak, nola aldatu da T?

TRADUCCIÓN: $\left(\frac{\partial T}{\partial V}\right)_S \Rightarrow \Delta T = \int \qquad \Rightarrow \Delta T$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} = -\frac{-\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V}{\left(\frac{\partial^2 F}{\partial T^2}\right)_V}$$

$$dF = -S\,dT - p\,dV = -\left(\frac{\partial F}{\partial T}\right)_V dT - p\,dV$$

$F = F(T, V, N)$

$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial}{\partial T}\left[-\left(\frac{\partial F}{\partial V}\right)_{T,N}\right]_p \Rightarrow$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial T \partial V} = -\frac{\partial^2 F}{\partial V \partial T}$$

$C_v = T\left(\frac{\partial S}{\partial T}\right)_V$

$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \Rightarrow C_v = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N}$

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{T}{C_V}\frac{\partial^2 F}{\partial V \partial T}$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = \frac{1}{-T\left(\frac{\partial^2 F}{\partial T^2}\right)_V} \cdot \frac{\partial^2 F}{\partial V \partial T} = - \frac{\frac{\partial^2 F}{\partial V \partial T}}{\left(\frac{\partial^2 F}{\partial T^2}\right)_V}$$

$$T(S,V) \Rightarrow dT = \underbrace{\cancel{\left(\frac{\partial T}{\partial S}\right)_V}}_{ADIAB}{}^{\to 0} dS + \left(\frac{\partial T}{\partial V}\right)_S dV$$

$$dT = \left(\frac{\partial T}{\partial V}\right)_S dV = - \frac{\frac{\partial^2 F}{\partial V \partial T}}{\left(\frac{\partial^2 F}{\partial T^2}\right)_V}$$

$$\int \left[dT = - \left(\frac{\frac{\partial^2 F}{\partial V \partial T}}{\left(\frac{\partial^2 F}{\partial T^2}\right)_V} \right) dV \right]_{V_0}^{8V_0}$$

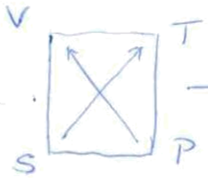
ARIKETA:

Kalkulatu $\left(\frac{\partial T}{\partial P}\right)_H$

$$\left(\frac{\partial T}{\partial P}\right)_H = - \frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = - \frac{T\left(\frac{\partial S}{\partial P}\right)_T + V\cancel{\left(\frac{\partial P}{\partial P}\right)_T}^{\to 1}}{T\left(\frac{\partial S}{\partial T}\right)_P + V\cancel{\left(\frac{\partial P}{\partial T}\right)_P}^{\to 0}} =$$

$H = H(S,P)$

$dH = TdS + VdP$



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

$$= - \frac{T\left(\frac{\partial S}{\partial P}\right)_T + V}{C_P} = - \frac{1}{C_P}\left[- T\left(\frac{\partial V}{\partial T}\right)_P + V \right] = \frac{V}{C_P}(T\alpha - 1)$$

ARIKETA:

Kalkulatu $\left(\frac{\partial T}{\partial V}\right)_h$ non $h = \frac{H}{N}$

$$\left(\frac{\partial T}{\partial V}\right)_h = - \frac{\left(\frac{\partial h}{\partial V}\right)_T}{\left(\frac{\partial h}{\partial T}\right)_V} = - \frac{T\left(\frac{\partial S}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T}{T\left(\frac{\partial S}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_V} =$$

BORN

$$\overset{|}{=} - \frac{T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T}{C_p - V\frac{\left(\frac{\partial h}{\partial T}\right)_V}{\left(\frac{\partial h}{\partial P}\right)_T}} = - \frac{T\frac{\alpha}{\kappa_T} - \frac{V}{V\kappa_T}}{C_V + V\frac{\alpha}{\kappa_T}} = - \frac{T\alpha - 1}{C_V\kappa_T + V\alpha}$$

ARIKETA:

Kalkulatu $\left(\frac{\partial s}{\partial f}\right)_p$ non $f = \frac{F}{N}$

$$\left(\frac{\partial s}{\partial f}\right)_p = \frac{1}{\left(\frac{\partial f}{\partial s}\right)_p} =$$

BORN ERABILTZEN SARTU

$$f = f(T, v) \longrightarrow df = -s\,dT - p\,dv$$

$$\left(\frac{\partial f}{\partial s}\right)_p = -s\left(\frac{\partial T}{\partial s}\right)_p - p\left(\frac{\partial v}{\partial s}\right)_p = -s\frac{1}{\left(\frac{\partial s}{\partial T}\right)_p} - p\left(\frac{\partial v}{\partial T}\right)_p \underbrace{\left(\frac{\partial T}{\partial s}\right)_p}_{= \frac{1}{\left(\frac{\partial s}{\partial T}\right)_p}} =$$

$$= -s\frac{T}{c_p} - p\,v\alpha\frac{T}{c_p} = -T\left(\frac{s}{c_p} + \frac{pv\alpha}{c_p}\right) =$$

$$= -\frac{T}{c_p}(s + pv\alpha) \Rightarrow \left(\frac{\partial s}{\partial f}\right)_p = -\frac{c_p}{T(s+pv\alpha)}$$

ARIKETA:

Frogatu $\left(\frac{\partial c_p}{\partial p}\right)_T = -Tv\left[\alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_p\right]$

$$\left(\frac{\partial c_p}{\partial p}\right)_T = \frac{\partial}{\partial T}\left[T\left(\frac{\partial s}{\partial T}\right)_p\right]_T = T\frac{\partial^2 s}{\partial p\,\partial T} = T\frac{\partial^2 s}{\partial T\,\partial p} =$$

$$= T\frac{\partial}{\partial T}\left[\left(\frac{\partial s}{\partial p}\right)_T\right]_p = T\frac{\partial}{\partial T}\left[-\left(\frac{\partial v}{\partial T}\right)_p\right]_p = -T\frac{\partial}{\partial T}(v\alpha)_p =$$

$$= -T\left[\left(\frac{\partial v}{\partial T}\right)_p\alpha + v\left(\frac{\partial \alpha}{\partial T}\right)_p\right] = -T\left[v\alpha^2 + v\left(\frac{\partial \alpha}{\partial T}\right)_p\right] =$$

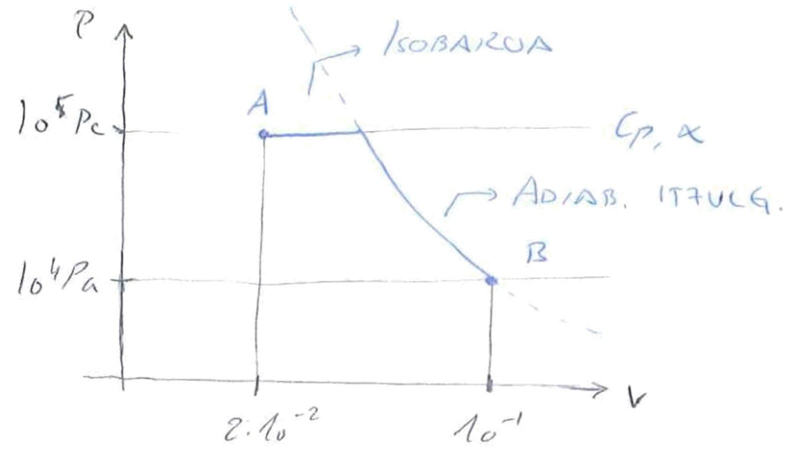
$$= -Tv\left[\alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_p\right]$$

PROPOIAMENA $\Rightarrow$ $\left[\frac{\partial c_v}{\partial v}\right]_T$ Kalkulatu

PROPOIAMENA:

Frogatu $\frac{k_s}{k_T} = \frac{c_v}{c_p}$; $k_s = \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_s$

ARIKETA:



A:
$p_A = 10^5 Pa$
$V_A = 2\cdot 10^{-2} m^3/mol$
$T_A = 350,9 K$

B:
$p_B = 10^4 Pa$
$V_B = 10^{-1} m^3/mol$
$T_B = 150 K$

$pv^2 = K \quad (S = KTE)$

$p = KTE, \; p = p_A \Rightarrow c_p = p v^{2/3}$

$p = KTE, \; p = p_A \Rightarrow \alpha = \frac{3}{T}$

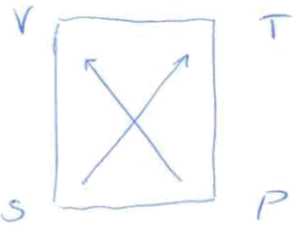
$D = 10^{3/8} J/m^3K$

Zein da atera daitekeen lan maximoa?

$$W^{max} = -\Delta f^{SIST}_{(T=T_0)} = -(\Delta u^{SIST} - T^{RI} \Delta S^{SIST})$$

$u = u(p, V)$

$S = S(p, V)$



$$du = \left(\frac{\partial u}{\partial p}\right)_V dp + \left(\frac{\partial u}{\partial V}\right)_p dV$$

$$\left(\frac{\partial u}{\partial p}\right)_V = [du = TdS - pdV] = T\left(\frac{\partial S}{\partial p}\right)_V - p\cancel{\left(\frac{\partial V}{\partial p}\right)_V}^{0} =$$

$$= T\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial p}\right)_V = c_V\left(\frac{\partial T}{\partial p}\right)_V = c_V \frac{\kappa_T}{\alpha}$$

$$\left(\frac{\partial u}{\partial V}\right)_p = T\left(\frac{\partial S}{\partial V}\right)_p - p\cancel{\left(\frac{\partial V}{\partial V}\right)_p}^{1} = T\left(\frac{\partial S}{\partial V}\right)_p - p =$$

$$= T\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p - p = c_p\left(\frac{\partial T}{\partial V}\right)_p - p = c_p\frac{1}{V\alpha} - p$$

$$du = c_V \frac{\kappa_T}{\alpha} dp + \left[\frac{c_p}{V\alpha} - p\right] dV$$

$$dS = \left(\frac{\partial S}{\partial p}\right)_V dp + \left(\frac{\partial S}{\partial V}\right)_p dV$$

$$\left(\frac{\partial S}{\partial p}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial p}\right)_V = \frac{C_V}{T} \cdot \frac{\kappa_T}{\alpha}$$

$$\left(\frac{\partial S}{\partial V}\right)_p = \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial V}\right)_p = \frac{C_p}{T} \cdot \frac{1}{V\alpha},$$

44, 45, 43, 27,

$$dS = \frac{C_V}{T} \cdot \frac{\kappa_T}{\alpha} dp + \frac{C_p}{T} \cdot \frac{1}{V\alpha} dV$$

1.P: $$\delta Q = \frac{C_V \kappa_T}{\alpha} dp + \frac{C_p}{V\alpha} dV$$

$$dU - \delta W = \frac{C_V \kappa_T}{\alpha} dp + \left[\frac{C_p}{V\alpha} - p\right] dV + p\, dV$$

$$\delta Q = dU - \delta W \quad !!!$$

PROPOIATENA: Amcilu (bi lemocKin)

FASE TRANTSIZIOAK

Orain arte bi gauzak asumitu ditugu

- $N = KTE$
- Sistema homogeneoak: Edozein puntutan neurketak egin ezkero balio berbera lortuko genuke.

Fase trantsizioetan bigarren puntua ez da betetzen.

T eta P konstanteko sistemetan Gibbs-en energia askea da potentzial egokiena: $G = G(T,p,N)$

EGONKORTASUN BALDINTZAK

- LE'CHATELIER-EN PRINTZIPIOA:

  Edozein sistematan agertuko den edozein perturbazioak berau desagertzeko joera duen prozesu zuzena eragingo du.

  PROZESU ZUZENA: Sistemaren lehen mailako erantzuna.

- LE'CHATELIER - BRAUN-EN PRINTZIPIOA:

  Edozein sistematan agertuko den edozein perturbazioak berau desagertzeko joera duten zeharkako prozesuak eragingo ditu.

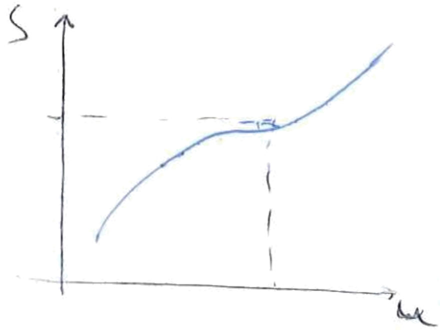
  ZEHARKAKO PROZESUA: Sistemaren goi-mailako erantzuna.

NOTA: Printzipio hauek sistema egonkorrei dagozkie

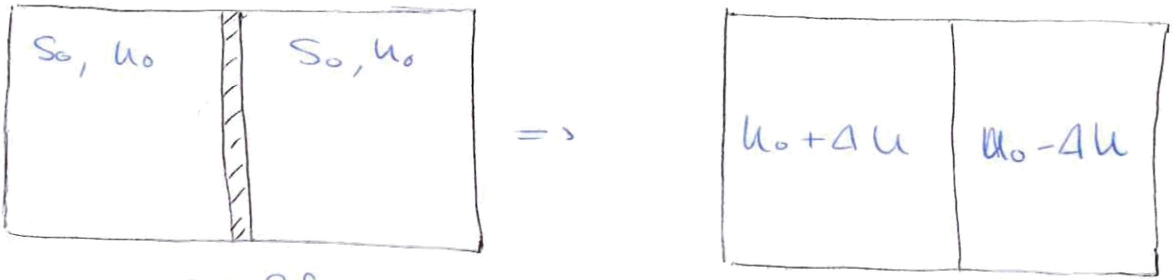
- ONDORIOA: Sistema egonkorrek edozein perturbazioei emango dion erantzunaren helburua orekako egoerara bueltatzea da.

Demagun bi sistema ditugula non:

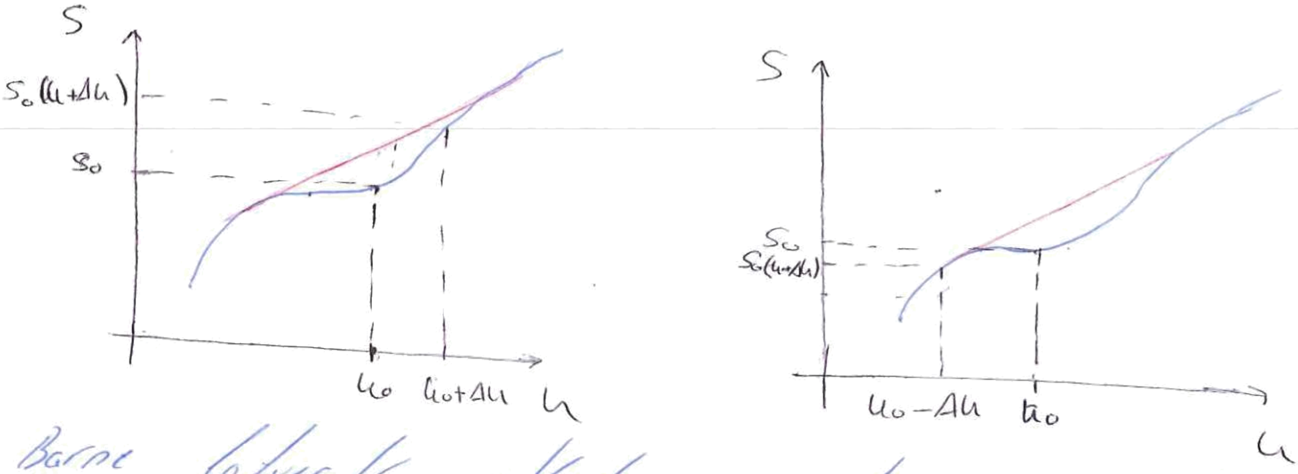
$S = S(U,V,N)$ $\quad$ $S = S(U,V,N)$



Biek bakoitzak ditugu eta energia apur bat batetik bestera eramango dugu



$S = 2S_0 \neq S = S(u_0 + \Delta u) + S(u_0 - \Delta u)$



Barne loturak askatzean sistema "mugitu" egiten da entropiaren maximoa bilatuz. Beraz, gure sisteman bi fase lortzen ditugu.
Zer egin beharko genuke hori ekiditeko? Hau da, nola lortuko genuke sistemak beren energia ez trukatzea?
Entropia maximoan ertean egon beharko litzateke "atxikituta". Bestela pilota bat bezala irristatuko litzateke.

SISTEMA EGONKORREAN:

$$\boxed{\begin{array}{c} C_p \geq C_v \geq 0 \\ k_T \geq k_S \geq 0 \end{array}}$$

EGONKORTASUN BALDINTZAK POTENTZIALETAN

$F_{TT} \leq 0$	$F_{VV} \geq 0$		min
$H_{SS} \geq 0$	$H_{PP} \leq 0$		min
$G_{TT} \leq 0$	$G_{PP} \leq 0$	$G_{TT} G_{PP} - G_{TP}^2 \geq 0$	min
$S_{UU} \leq 0$	$S_{VV} \leq 0$	$S_{UU} S_{VV} - S_{UV}^2 \geq 0$	max
$U_{SS} \geq 0$	$U_{VV} \geq 0$	$U_{SS} U_{VV} - U_{SV}^2 \geq 0$	min

CALLEN (8.3-210)

Addition of heat, either at constant pressure or at constant volume, necessarily increases the temperature of a stable system – the more so at constant volume than at constant pressure. And decreasing the volume, either isothermally or isentropically, necessarily increases the pressure of a stable system – the less so isothermally than isentropically.

$$Q \uparrow \Rightarrow \left(\begin{array}{c} V = KTE \\ edo \\ P = KTE \end{array} \right) \Rightarrow T \uparrow$$

$$V \downarrow \Rightarrow \left(\begin{array}{c} T = KTE \\ edo \\ S = KTE \end{array} \right) \Rightarrow P \uparrow$$

VAN DE WAALS-EN FLUIDOAK

Gas ideal

$$PV = RT \longrightarrow \underbrace{\left(p + \frac{a}{V^2}\right)}_{\text{Elkarrekintza partikulen artean}} \overbrace{(V-b)}^{\text{Bolumena ez dago hutsik (partikulak ez dira puntuak)}} = RT$$

$$G = G(T, p, N)$$

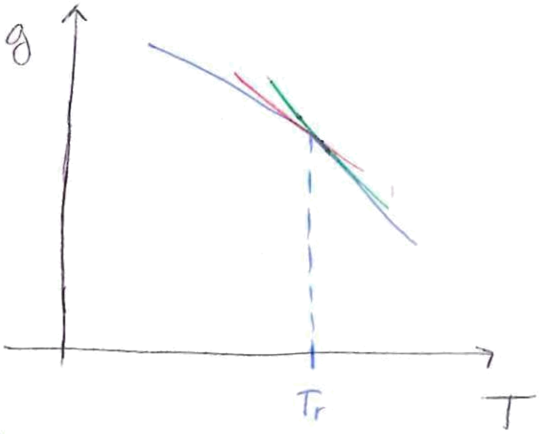
$$\mu = g = g(T, p)$$

$$d\mu = dg = -s\,dT + v\,dp$$

$$\Delta\mu = \Delta g = -\Delta s T + \Delta v p$$

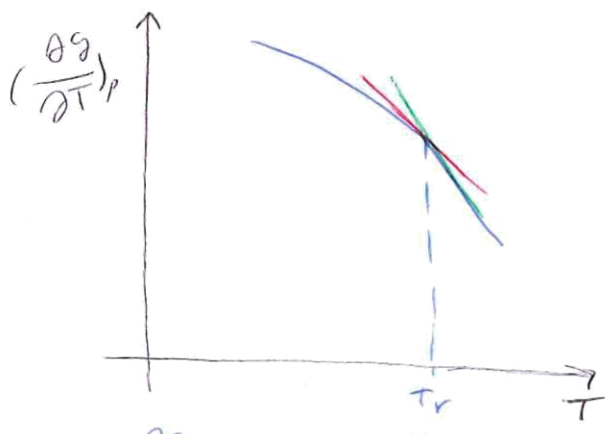
- Lehen ordenako fase trantsizioetan p eta T konstanteak dira: g-ren lehen ordenako deribatuak gauzak dituzte. g ✓ ; g' ✗
- Bigarren ordenako fase trantsizioetan g-ren bigarren ordenako deribatuak gauzak dituzte.

g ✓ ; g' ✓ ; g'' ✗



$$\left(\frac{\partial g}{\partial T}\right)_p = -s$$

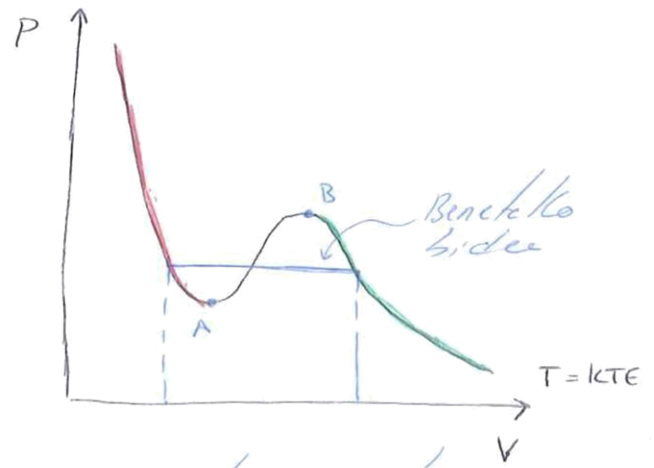
Fase trantsizio ez-jarraituak



$$\left(\frac{\partial s}{\partial T}\right)_p = -\frac{c_p}{T}$$

Fase trantsizio jarraituak

VdW fluidoaren kasuan:



Egonkortasun baldintza

$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \geq 0$$

$$\Rightarrow \left(\frac{\partial V}{\partial P}\right)_T < 0 \Rightarrow$$

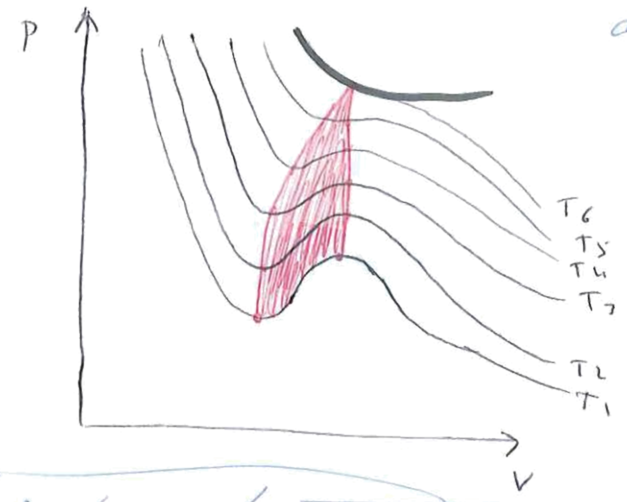
$$\Rightarrow \left(\frac{\partial P}{\partial V}\right)_T < 0$$

A-B tartean sistema ez da egonkorra eta bi fasetan banatuko da entropia maximizatzeko.

- Tartean materia fase ez-kondentsatuan egongo da
- Tartean materia fase kondentsatuan egongo da.

Esperimentalki, bi faseko tartean lehenengo sartzen da eta bertan, bolumena aldatzen den arren, presioa ez da aldatzen baizik eta likido-gas proportzioa. Behin dena likido bihurtzen denean presioa igotzen hasiko da (likidoak ia konprimi-gaitzak direnez, presioa ez da asko igoko —ezin delako—)

"Existentziarik gabeko tartea"

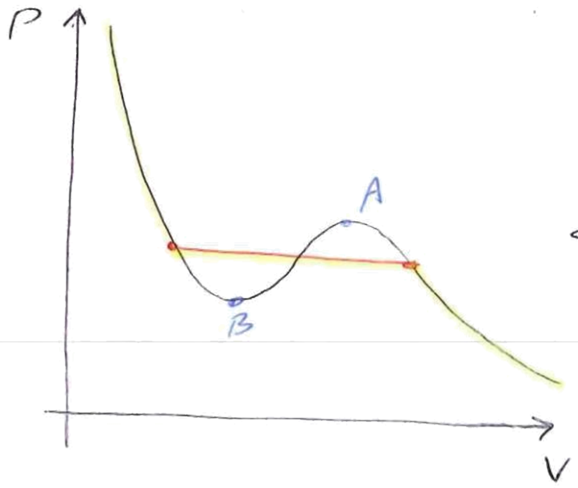


Tenperatura gero eta altuagoa izatean A-B tartea eta bi-fase tartea esperimentala gero eta gehiago estutzen joango da puntu bakar batean konbergitu arte. Tenperatura horri tenperatura kritikoa deritzo eta hortik aurrera bi faseko egoera ez da egongo.

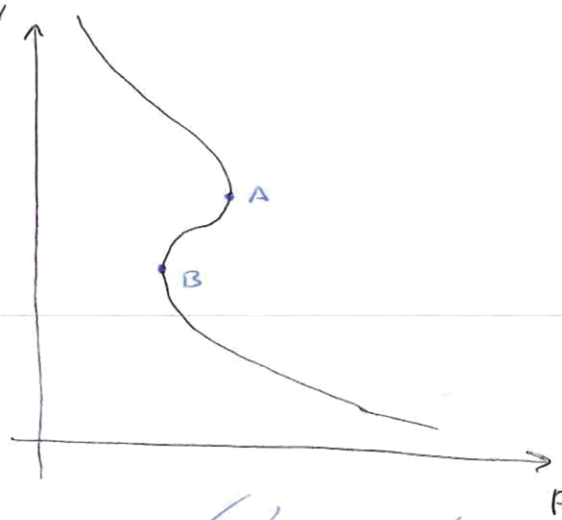
FASE-TRANTSIZIOAREN EZAUGARRIEN AZTERKETA:

$(P,V) \Rightarrow (V,P)(V(P),P) \Rightarrow (\mu,P)$.

POTENTZIAL KIMIKOAREN EZAUGARRIKETA

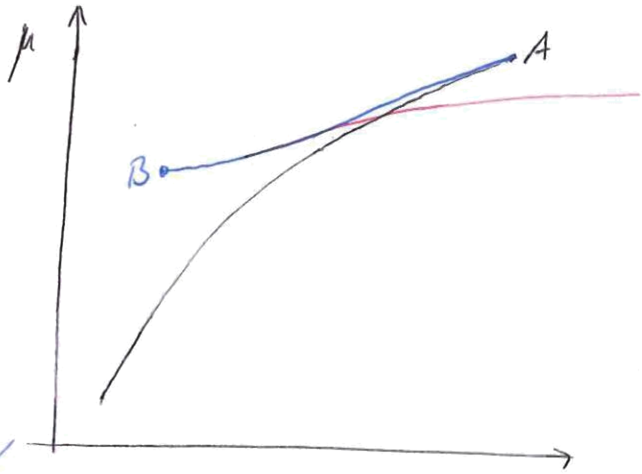


$\Leftrightarrow$

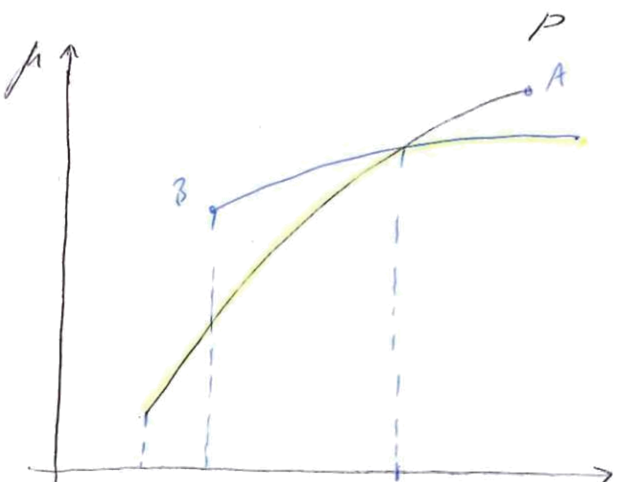


A-B tarteen azpiko azalera negatiboa da ($dp<0$)

$$\mu_B-\mu_A=\int_A^B v(p)\,dp$$



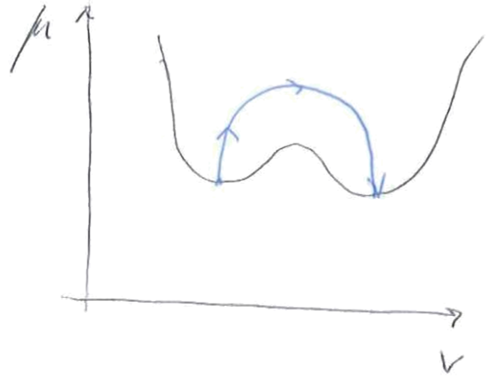
Benetan dena



(I) → Sistemak μ bakarra aukeratzeko du arazorik gabe

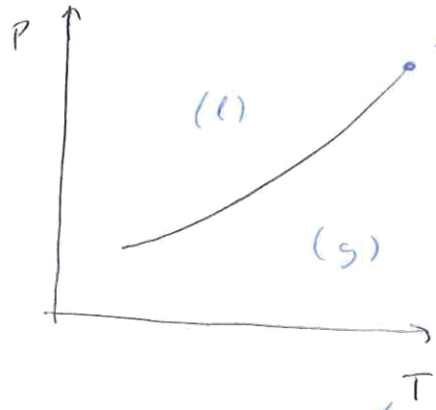
(II) → Bi μ ditu aukeratzeko, baina G minimizatuko duena aukeratuko du "erosoena" dagoelako. (μ txikiena)

(?) → Bi potentzial kimikoek berdin "erakarrillo" dute eta sisteme bietan egongo da puntu horretan fase trantsizioa gertatzen da. Ademaz aldatuko da μ minimoa iristeko.



⇒ Fase bakoitzak bereizko puntuko da, gutxiz beti minimora iguro arte ≡ P

V = KTE mantenduz berdin egin genezake eta P/T diagrama osatu (ikusi apunteak). Honelako grafikoa lortuko genuke.



Zuzena fase trantsizioko puntuak adierazten ditu eta planoa bi fasetan banatzen du.

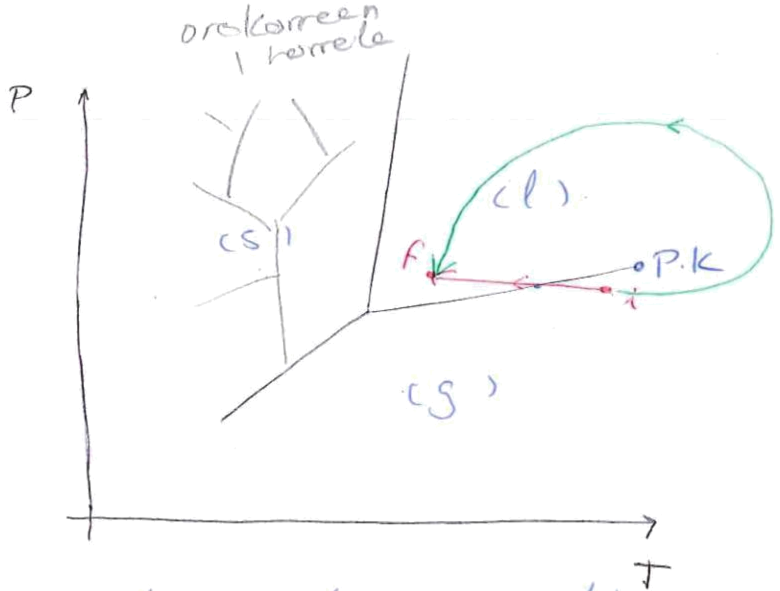
T gora egiten duen einean ΔB tartea gero eta txikiagoa da puntu bat bihurtu arte ⇒ ez dago existentziarik gabeko gunea ⇒ ez dago fase trantsiziorik.

μ ⇒ jarraitua + deribagarria (deribatua bakarra eta jakina) (lehen eta zen deribagarria)

⇒ Puntu kritikoa deritzo puntu honi

$$\boxed{\left(\frac{\partial^k P}{\partial V^k}\right)_T = 0}$$ ⇔ Puntu kritikoa

"Oreko kurbaren muga"



Planoko edozein puntuk sistemaren egoera ekuazioak beteko ditu.
Aurreko gaietan ez zegoen fase-trantsiziorik, baina hemen bai. Hala ere ez da beti behemerkoa fase-trantsizioko lerroa zeharkatzea.

- Lehenengo mailako fase trantsizioa:
Tenperatura aldatuz, sistemak beroa erabiltzen du gasa likido bihurtzeko presioan aregiñik izan gabe.
- Bigarren mailako fase trantsizioan gas-likido aldaketa modu jarraituan gertatzen da.
Eta ameiera "Konturatu gabe" likidoa lortzen da. Tarte honetan dugun substantziari fluido deritzo.

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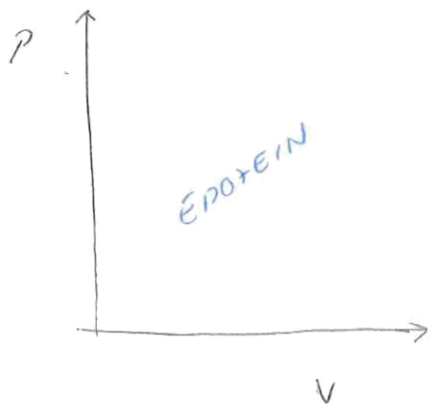
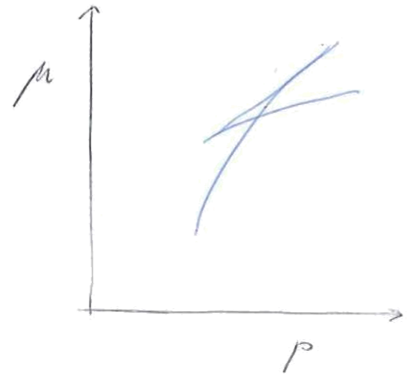
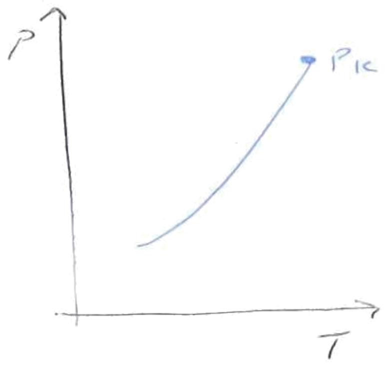
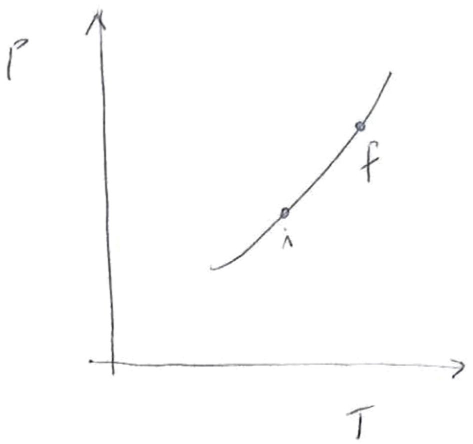
CLAUSIUS – CLAPEYRON EKUAZIOA







Dagiten ari garenean fase trantsizio lerroaren gainean beine fase bateko puntuak hartuz edo besteko puntuak hartuz:



$$\mu = \mu'$$

$$\left.\begin{array}{l} \mu_f = \mu_i + d\mu \\ (\mu_f = \mu_i + d\mu)' \end{array}\right\} \; d\mu = d\mu'$$

$$d\mu = -s\,dT + v\,dp$$

$$\shortparallel$$

$$d\mu' = -s'\,dT + v'\,dp$$

$$-s\,dT + v\,dp = -s'\,dT + v'\,dp$$

$$\boxed{\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{s - s'}{v - v'}}$$

ΔS eta Δv fase trantsizioan dauden gauzak dira eta neurgarriak dira. Horrenbestez ekuazio hau jarraitu lortu dezakegu beti P/T diagramaren malda edozein puntutan; hau da, orekako kurbaren malda

Dena malda

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \cdot \frac{T}{T} = \frac{\varphi_{FT}}{T \Delta V_{FT}} \overset{p=KTE}{=} \boxed{\frac{\Delta h_{FT}}{T \Delta V_{FT}}}$$

$$\left(\frac{dp}{dT} = \frac{\Delta S}{\Delta V}\right)_{FT} \Rightarrow \left(\frac{dp}{dT} = \frac{T\Delta S}{T\Delta V} = \frac{\varphi}{T\Delta V} = \frac{\Delta h}{T\Delta V}\right)_{F=T}$$

Adierazpen orokorra bi kasu konkretu adierazteko erabiltzeko dugu: SOLIDO → GAS eta LIKIDO → GAS

1. $\Delta V = V_g - V_{s,l} \simeq V_g \qquad V_g >> V_s, V_l$

2. Gasa ≅ gas ideala $(p <<)$

$$pV_g = RT \Rightarrow V_g = \frac{RT}{p}$$

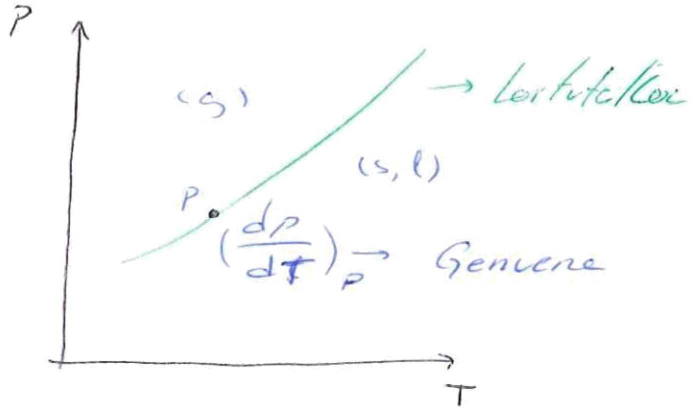
$$\frac{dp}{dT} \simeq \frac{\Delta h}{T\frac{RT}{p}} \simeq p\frac{\Delta h}{RT^2} \Rightarrow \frac{dp}{p} \simeq \frac{\Delta h}{RT^2} dT$$

$\Delta h = \Delta h(T, p)$ balitz genuke integratzeko

3. $\Delta h \simeq$ KTE

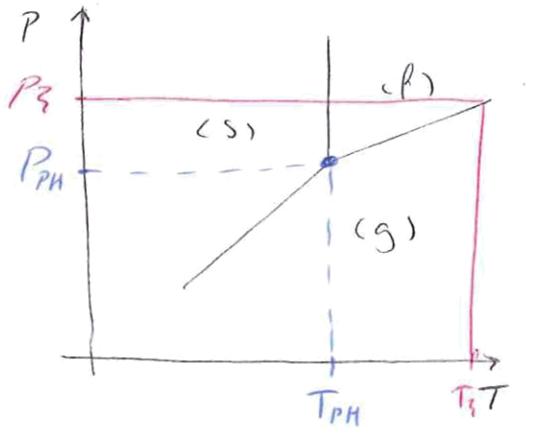
Hau da, fase trantsizioa egiteko beharrezkoa den energia konstantea dela.

$$\ln p = -\frac{\Delta h}{R} \cdot \frac{1}{T} + k$$



K konstantea falta zaigu ekuazio osoa lortzeko. Horretarako fase trantsizioko puntuen bat behar dugu: puntu inkoitza kasu askotan.

HEMENDIK AURRERAKO ARIKETAK:



- Normalean oreka kurbari buruzko informazio partziala izango dugu.
- Galdetuko digute puntuen

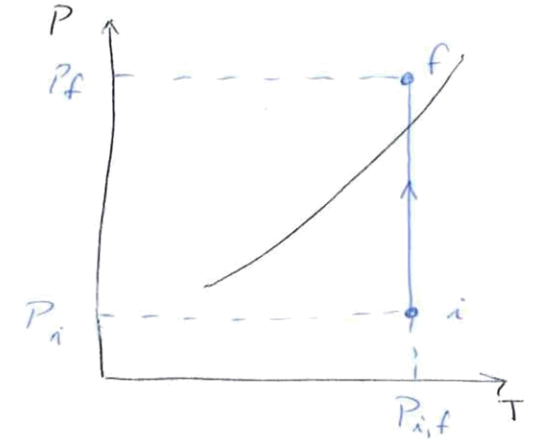
bateen gertatuko denari buruz
"$P = 3$ bada ze tenperaturatan irakingo du?"

- Beiteriik ezaten ez badute $\Delta h = kte$ onartuko dugu
- K lortuko dugu puntu kritikoaren bidez
- Edozein trantsizio punturen informazioa lortu genezake orain.

Demagun $\Delta S = s_0 (T - T_0)$ menpekotasuna duela, orduan egingo genuke $ST \to \varphi \to h$ aldaketa egin, baina prozesua $\frac{dp}{dT}$-tik berdintsua izango litzateke.

BESTE AUKERA BAT

Fase homogeneoak (orain artekoak) eta fase trantsizioak nahastea.



Adb:

$$\Delta S = \left(\frac{\partial S}{\partial P}\right)_{(g)} + \left(\frac{\partial S}{\partial P}\right)_{(l)} + \left(\frac{\partial S}{\partial P}\right)_{FT}$$