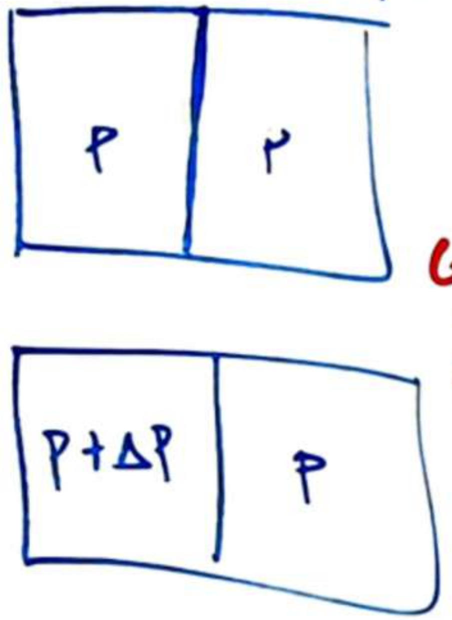
MOTO PERPÉTUO
DE 1ª ESPÉCIE



GERAR TRABALHO DO NADA

ΔT ✓

ΔP ✓

Δm ✓

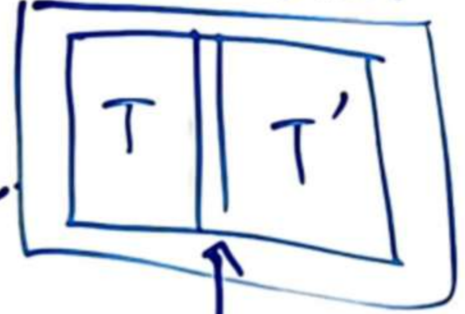
INTRODUÇÃO

- 1ª LEI

CONSERVAÇÃO ENERGIA $U = 0$

(SISTEMAS ISOLADOS) $\Delta U = 0$

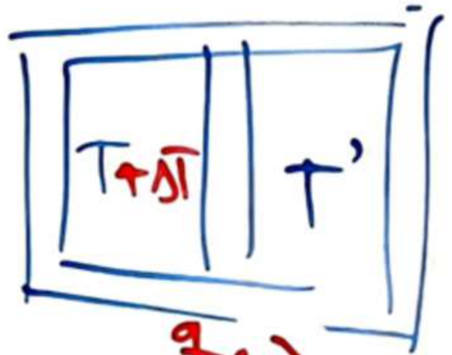
SIS. VIZ.



ADIABÁTICA → ~~q~~

RÍGIDA → ~~w~~

IMPERM. → ~~n~~



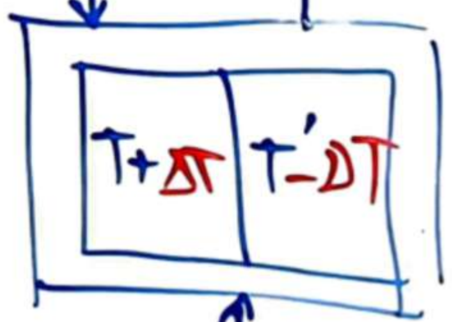
$\Delta U_s \neq 0$

$\Delta U_v = 0$

$\Delta U_s + \Delta U_v \neq 0$

VIOLA 1ª LEI

$q_s > 0$



DIATÉRMICA
RÍGIDA
IMP.

$\Delta U_s \neq 0$

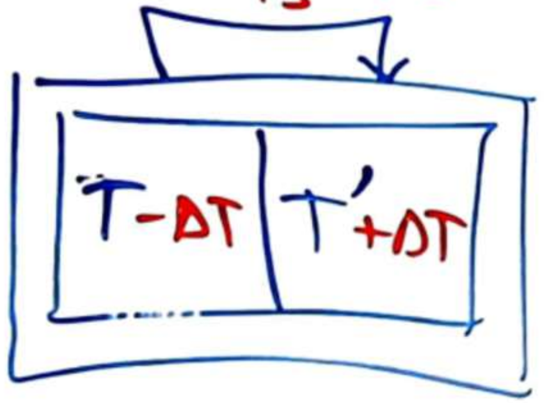
$\Delta U_v \neq 0$

$\Delta U_v = -\Delta U_s$

$\Delta U_v + \Delta U_s = 0$

OK PELA 1ª

$q_s < 0$



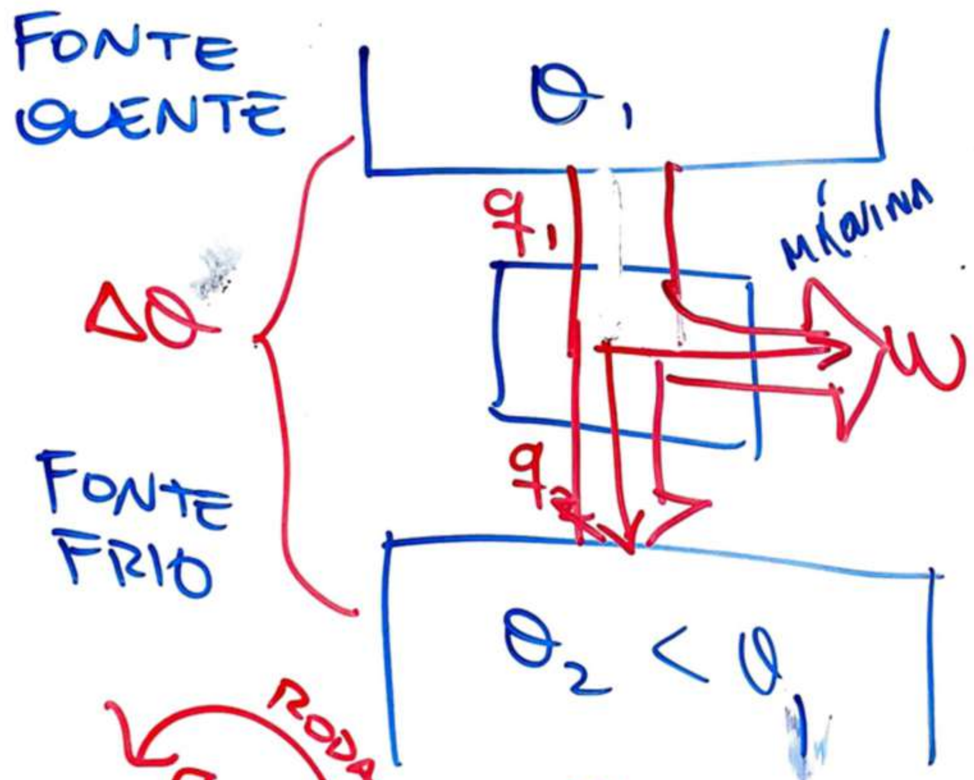
QUENTE $\xrightarrow{q}$ FRIO

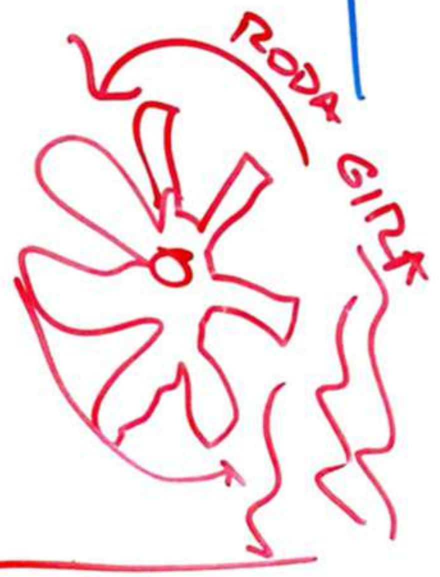
~~q~~

MÁQUINAS TÉRMICAS

$\Downarrow$

GERAM TRABALHO A PARTIR DE ΔT

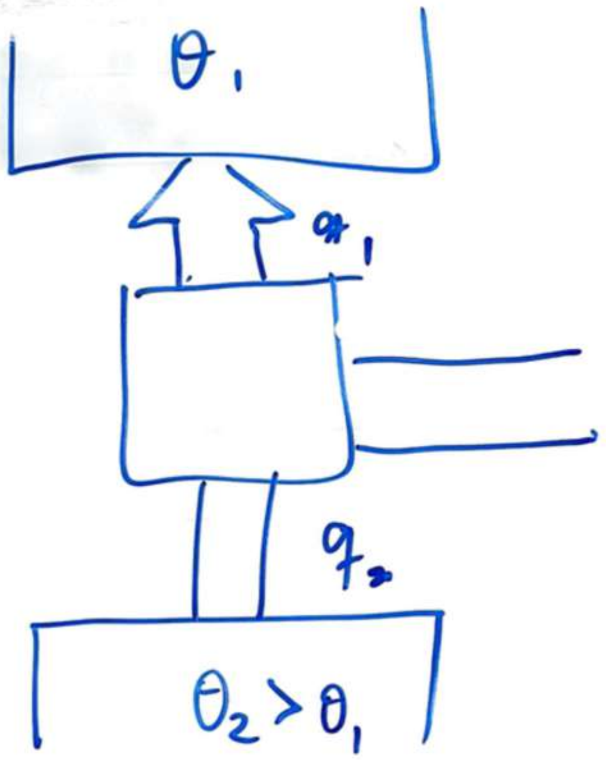




$q_1 = w + q_2$

100% 90% 10%

REFRIGADOR



$q_1 = w + q_2$

(MOTOR)

EFICIÊNCIA: $\eta = \frac{w}{q_1} = \frac{q_1 - q_2}{q_1} = 1 - \frac{q_2}{q_1}$

$\eta' = \frac{q_2}{q_1}$ (REFRIGERA

REFRIGERADOR = − MOTOR

2ª ~~ESPECIE~~

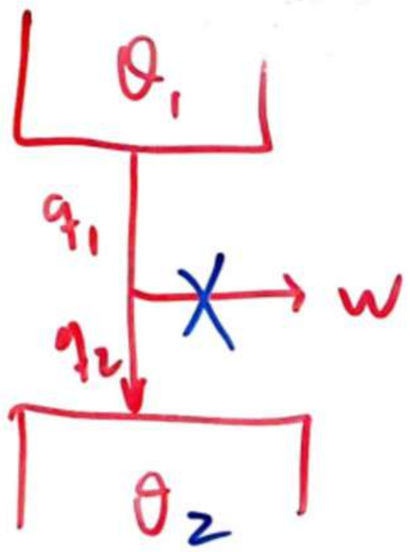
KELVIN (K): MOTOR MIRACULOSO NÃO EXISTE

CLAUSIUS (C): REFRIGERADOR MIRACULOSO NÃO EXISTE

$K \longleftrightarrow C$

NÃO PODE FAZER W DO NADA

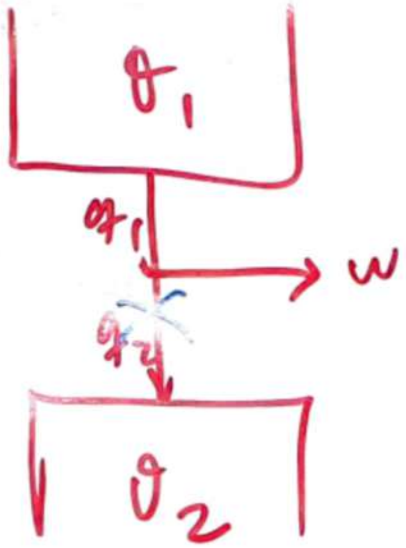
NÃO PODE PASSAR CALOR PARA FRIO



MOTOR PIOR POSSÍVEL

$W = 0$ $\quad q_1 = q_2$

$\eta = \dfrac{0}{q_1} = 0$



~~MOTOR MIRACULOSO~~

$W = q_1$

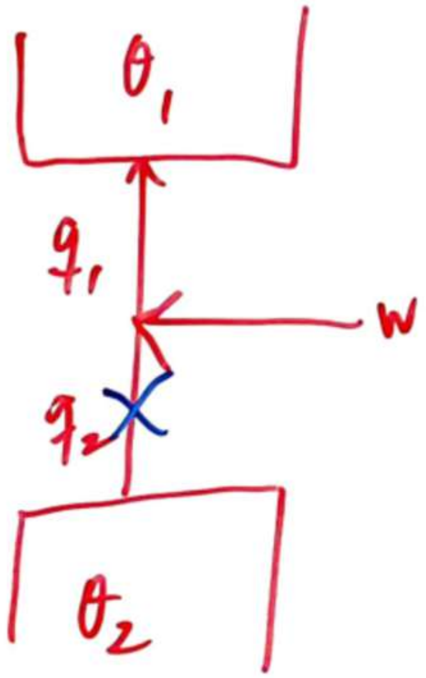
$q_2 = 0$

$\eta = \dfrac{q_1}{q_1} = 1$

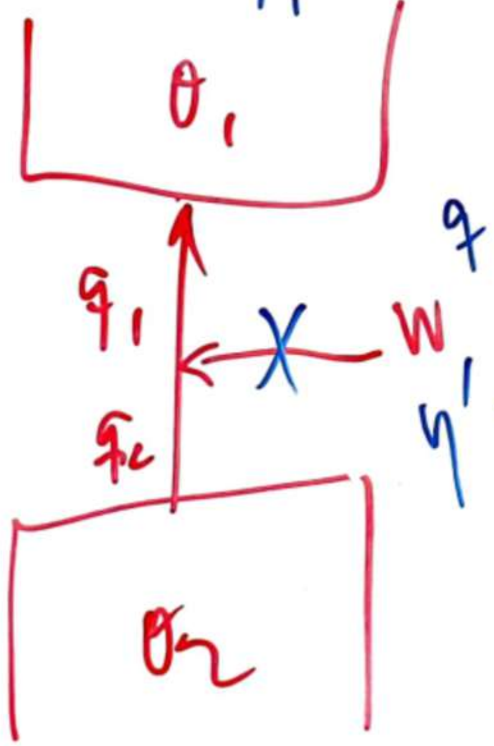
REFRIG. RUIM

$q_2 = 0$

$\eta' = 0$



REFRIG. BOM



$q_1 = q_2$

$\eta' = 1$

$0 \leq \eta \leq 1$ 1ª LEI

$0 \leq \eta < 1$ 1ª LEI, 2ª LEI (K)

$0 \leq \eta \leq \eta_{MÁX}$

$\Delta S > 0$

MÁQUINAS TÉRMICAS

MOTOR → KELVIN $\eta \neq 1$

REFRIG. → CLAUSIUS $\eta' \neq 1$

MAIS EFIC. $\eta_{IRR} \leq \eta_{REV}$

UNIVERSAL $\eta_{REV} = \eta'_{REV}$

TEMPERATURA ABS. $\eta_{REV} = f(\theta_1, \theta_2)$

$$\eta_{REV} = 1 - \frac{q_1}{q_2}$$

$$q_1 = f(\theta_1) = T_1$$

$$q_2 = f(\theta_2) = T_2$$

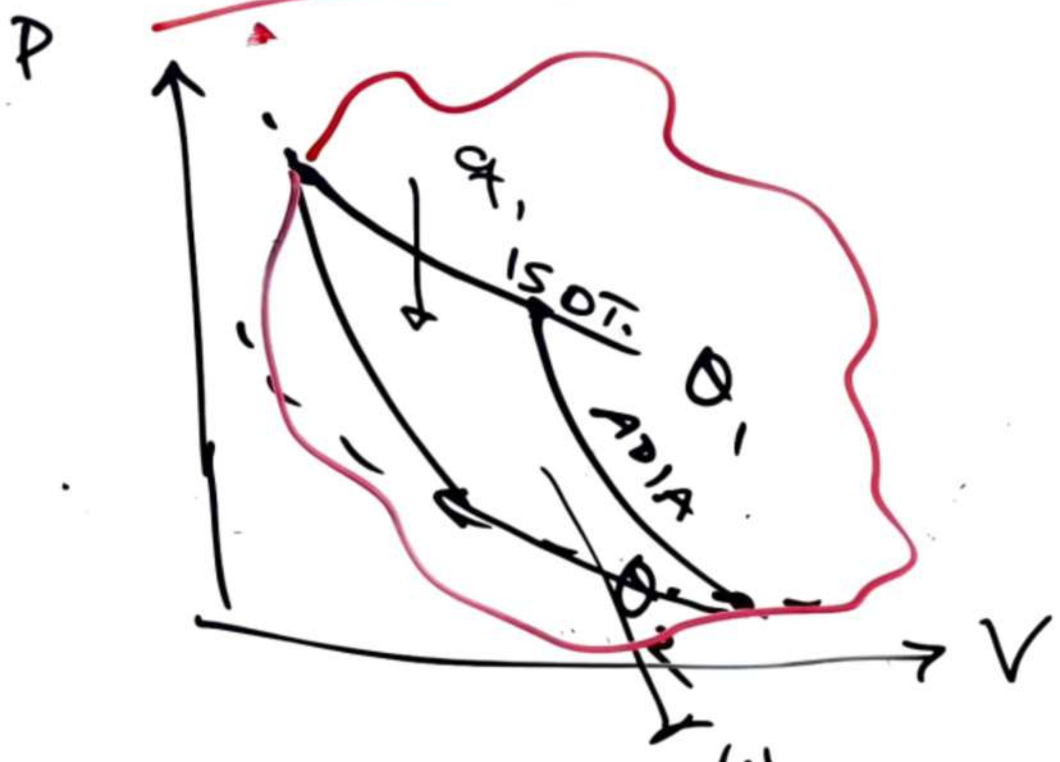
MÁQUINA REVERS.

$\Downarrow$

MÁQUINA DE CARNOT

$$\Delta S \geq \frac{q}{T}$$

$$\oint \frac{\delta q}{T} \geq 0$$



$$\eta_{REV} = 1 - \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

$$\frac{q_2}{q_1} = \frac{T_2}{T_1} \Rightarrow \frac{q_2}{T_2} = \frac{q_1}{T_1} \Rightarrow \frac{q_2}{T_2} - \frac{q_1}{T_1} = 0$$

DIOGO TERMODINÂMICA DE MUDANÇAS DE ESTADO FÍSICOS (MAXWELL, VdW, CLAPEYRON, ΔH, ΔS, ΔG, REGRA DAS FASES)

- LUIZ " DE SOLUÇÕES (LEI DE HENRY, LEI DE RAOULT, POTENCIAL PADRÃO, ATIVIDADE)

HIP. ~~KAWAN~~ " DE PROCESSOS QUÍMICOS (EQUILÍBRIO QUÍMICO, ΔG, K, ATIVIDADE, LE CHATELIER, ΔH, ΔS)

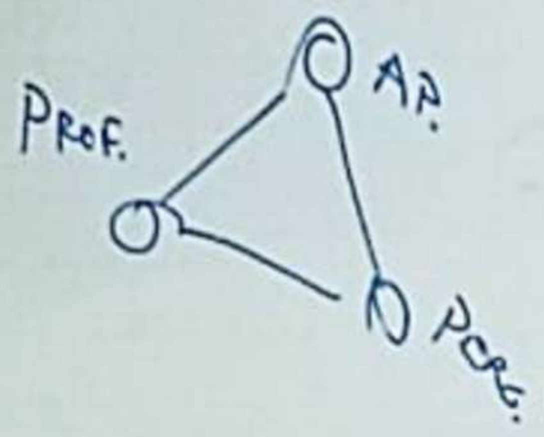
BRUNA " DE PROCESSOS ELETROQUÍMICOS (POTENCIAL ELETROQUÍMICO, POTENCIAL DE CÉLULA, ΔG, EQUAÇÃO DE NERNST, CÉLULAS GALVÂNICA ELETROLÍTICA)

GABRIEL " IRREVERSÍVEL (REGIME LINEAR, APROX. DE EQUILÍBRIO LOCAL, EXTENSÃO DA REAÇÃO, RELAÇÕES DE RECIPROCIDADE DE ONSAGER)

DAVI " APLICADA À ASTROFÍSICA (INFORMAÇÃO, ÁREA DE BURACO NEGRO, ENTROPIA DO UNIVERSO, EQUILÍBRIO TÉRMICO – FIM)

~~" EM SISTEMAS BIOLÓGICOS~~

KAWAN HIP~~ORANGE~~ " EM MEIOS CONTÍNUOS (EQUAÇÕES DE FLUXO E CONSERVAÇÃO DE MASSA, CARGA E MOMENTO EQS FOURIER, FICK, ...)



$$\eta \equiv -\frac{w}{q}$$

PROCESSOS EM GASES IDEAIS

PARA CICLO DE CARNOT

PROCESSO	q	w	ΔU	ΔH	ΔS
ISOTÉRMICO	$nRT \ln\left(\frac{V_f}{V_i}\right)$	$-nRT \ln\left(\frac{V_f}{V_i}\right)$	0	0	$nR \ln(V_f/V_i)$
ISOCÓRICO	$C_V \Delta T$	0	$C_V \Delta T$	$C_V \Delta T + V \Delta p$	$C_V \ln(T_f/T_i)$
ISOBÁRICO	$C_p \Delta T$	$-p \Delta V$	$C_p \Delta T - p \Delta V$	$C_p \Delta T$	$C_p \ln(T_f/T_i)$
ADIABÁTICO	0	$C_V \Delta T$	$C_V \Delta T$	$C_p \Delta T$	0
CÍCLICO	$-w$	$-q$	0	0	0

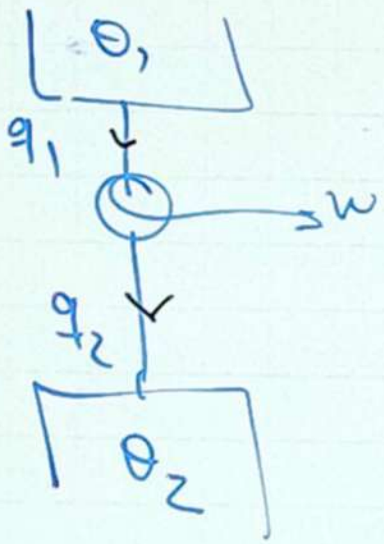
* CICLOS DE CARNOT

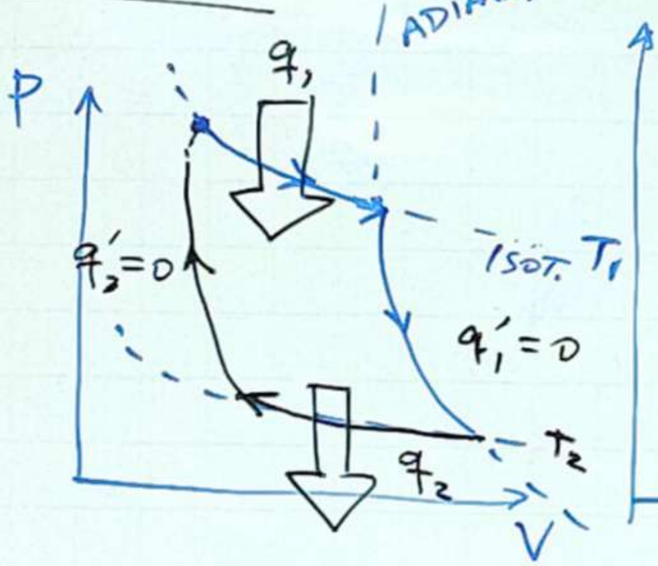
BASSI

CHEMKEYS

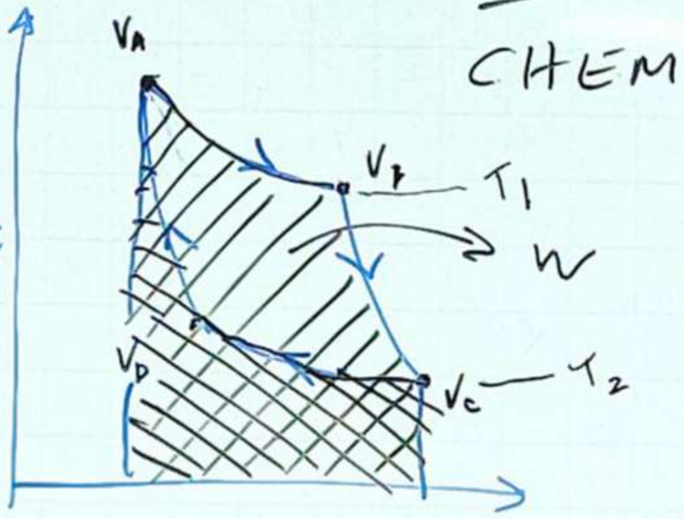
- MÁQUINA REVERSÍVEL (DE CARNOT)

$$\eta_{rev} = 1 - \frac{\tau_2}{\tau_1}$$





CALOR



TRABALHO

$$\eta_{rev} = \frac{-w}{q_1} = \frac{q_1 + q_2}{q_1} = 1 + \frac{q_2}{q_1}$$

$$\oint dU = 0 = \oint \delta q + \oint \delta w$$

$$\oint \delta w = -\oint \delta q$$

$$w = w_1 + w_1' + w_2' + w_2 = -(q_1 + \cancel{q_1'}^{0} + \cancel{q_2'}^{0} + q_2)$$

$$-w = q_1 + q_2 \Rightarrow \ldots$$

PROCESSO ISOT.

$$\Delta U = 0 = q + w$$

$$q = -w$$

$$q_1 = -w_1 = -\left[-nRT_1 \ln\left(\frac{V_B}{V_A}\right)\right]$$

$$q_2 = -w_2 = -\left[-nRT_2 \ln\left(\frac{V_D}{V_C}\right)\right]$$

$$\boxed{\eta_{rev} = 1 - \frac{\tau_2}{\tau_1} = 1 - \frac{T_2}{T_1} \Rightarrow \tau = T}$$

$$\eta_{rev} = 1 + \frac{\cancel{nR}T_2 \ln\left(\frac{V_D}{V_C}\right)}{\cancel{nR}T_1 \ln\left(\frac{V_B}{V_A}\right)} = 1 + \frac{T_2}{T_1}\frac{\ln\left(\frac{V_A}{V_B}\right)}{\ln\left(\frac{V_B}{V_A}\right)} = 1 - \frac{T_2}{T_1}\frac{\cancel{\ln\left(\frac{V_B}{V_A}\right)}}{\cancel{\ln\left(\frac{V_B}{V_A}\right)}} \Rightarrow \eta_{rev} = 1 - \frac{T_2}{T_1}$$

$$-\ln\left(\frac{V_B}{V_A}\right)$$

$$= 1 - T$$

ISOT. $\Rightarrow P_A V_A = P_B V_B \longrightarrow \frac{P_B}{P_A} = \frac{V_A}{V_B}$

$$P_C V_C = P_D V_D \longrightarrow \frac{P_D}{P_C} = \frac{V_C}{V_D}$$

ADIAB. $\Rightarrow P_B V_B^{\gamma} = P_C V_C^{\gamma}$

$$P_D V_D^{\gamma} = P_A V_A^{\gamma} \Rightarrow \frac{P_B V_B^{\gamma}}{P_A V_A^{\gamma}} = \frac{P_C V_C^{\gamma}}{P_D V_D^{\gamma}}$$

$$\frac{V_B^{\gamma}}{V_B} \cdot \frac{V_A}{V_A^{\gamma}} = \frac{V_C^{\gamma}}{V_C} \cdot \frac{V_D}{V_D^{\gamma}}$$

$$\frac{V_B^{\gamma-1}}{V_A^{\gamma-1}} = \frac{V_C^{\gamma-1}}{V_D^{\gamma-1}} \Rightarrow \left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1}$$

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}$$

$$\eta_{rev} = 1 + \frac{q_2^{rev}}{q_1^{rev}} = 1 - \frac{T_2}{T_1} \Rightarrow \frac{q_2^{rev}}{q_1^{rev}} = -\frac{T_2}{T_1} \Rightarrow \frac{q_2^{rev}}{T_2} = -\frac{q_1^{rev}}{T_1}$$

$$\frac{q_1^{rev}}{T_1} + \frac{q_2^{rev}}{T_2} = 0$$

$$\frac{q_1^{rev}}{T_1} + \frac{q_1'^{rev}}{T_1} + \frac{q_2'^{rev}}{T_2} + \frac{q_2^{rev}}{T_2} = 0$$

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

$$\frac{\delta q_{rev}}{T} = \text{FUNÇÃO DE ESTADO}$$

$$\boxed{dS = \frac{\delta q_{rev}}{T}}$$

$$\eta_{REV} = 1 - \frac{T_2}{T_1} = 1 + \frac{q_2^{rev}}{q_1^{rev}} \Longrightarrow dS = \frac{\delta q_{rev}}{T}$$

$[cal\,K^{-1}]$ $[J]$ $[cal]$

$[J\cdot K^{-1}]$ $[K]$ $[K]$

- TEOREMA DE CLAUSIUS

$$\delta w_{irr} > \delta w_{rev} \begin{cases} \xrightarrow{EXP.} \delta w_{irr}^{e} > \delta w_{rev}^{e} \\ + \\ \xrightarrow{COM.} \delta w_{irr}^{c} > \delta w_{rev}^{c} \end{cases}$$

$$\delta w_{irr}^{e} + \delta w_{irr}^{c} > \delta w_{rev}^{e} + \delta w_{rev}^{c}$$

$$\oint dU = 0 \Longrightarrow \oint \delta w = -\oint \delta q$$

$$\oint \delta w_{irr} > \oint \delta w_{rev}$$

$$-\oint \delta q_{irr} > -\oint \delta q_{rev}$$

$$\oint \delta q_{irr} < \oint \delta q_{rev}$$

$$\oint \frac{\delta q_{irr}}{T} < \oint \overset{dS}{\overset{\shortparallel}{\left(\frac{\delta q_{rev}}{T}\right)}}$$

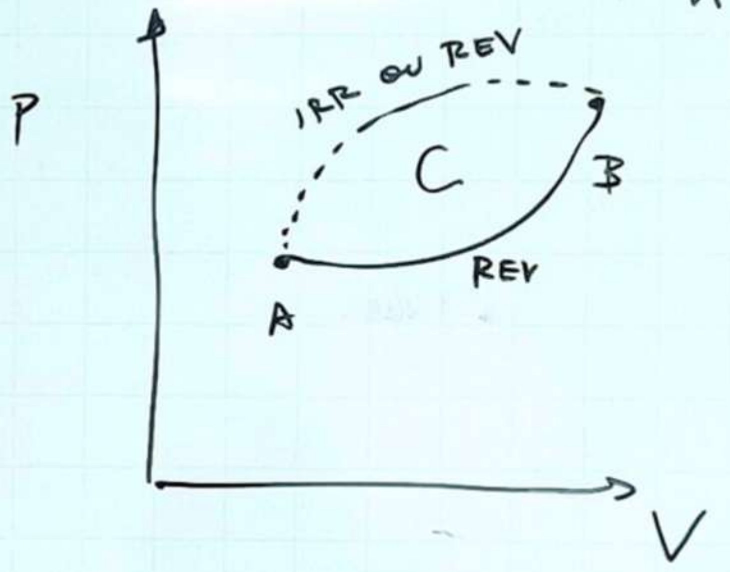
$$\oint \frac{\delta q_{irr}}{T} < 0$$

$$\oint \frac{\delta q}{T} \leq 0$$

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

- INEQUAÇÃO DE CLAUSIUS

$$\oint dS \rightarrow \int_A^B dS$$



$$\oint_C \frac{\delta q}{T} = \int_A^B \frac{\delta q}{T} + \int_B^A \frac{\delta q_{rev}}{T} \leq 0$$

$$\int_A^B \frac{\delta q}{T} + \int_B^A \frac{\delta q_{rev}}{T} \leq 0$$

$$\int_A^B \frac{\delta q}{T} \leq -\int_B^A \frac{\delta q_{rev}}{T}$$

$$\int_A^B \frac{\delta q}{T} \leq \int_A^B \frac{\delta q_{rev}}{T} = \Delta S(A \rightarrow B)$$

$$\Delta S(A \rightarrow B) \geq \int_A^B \frac{\delta q}{T}$$

REVER.

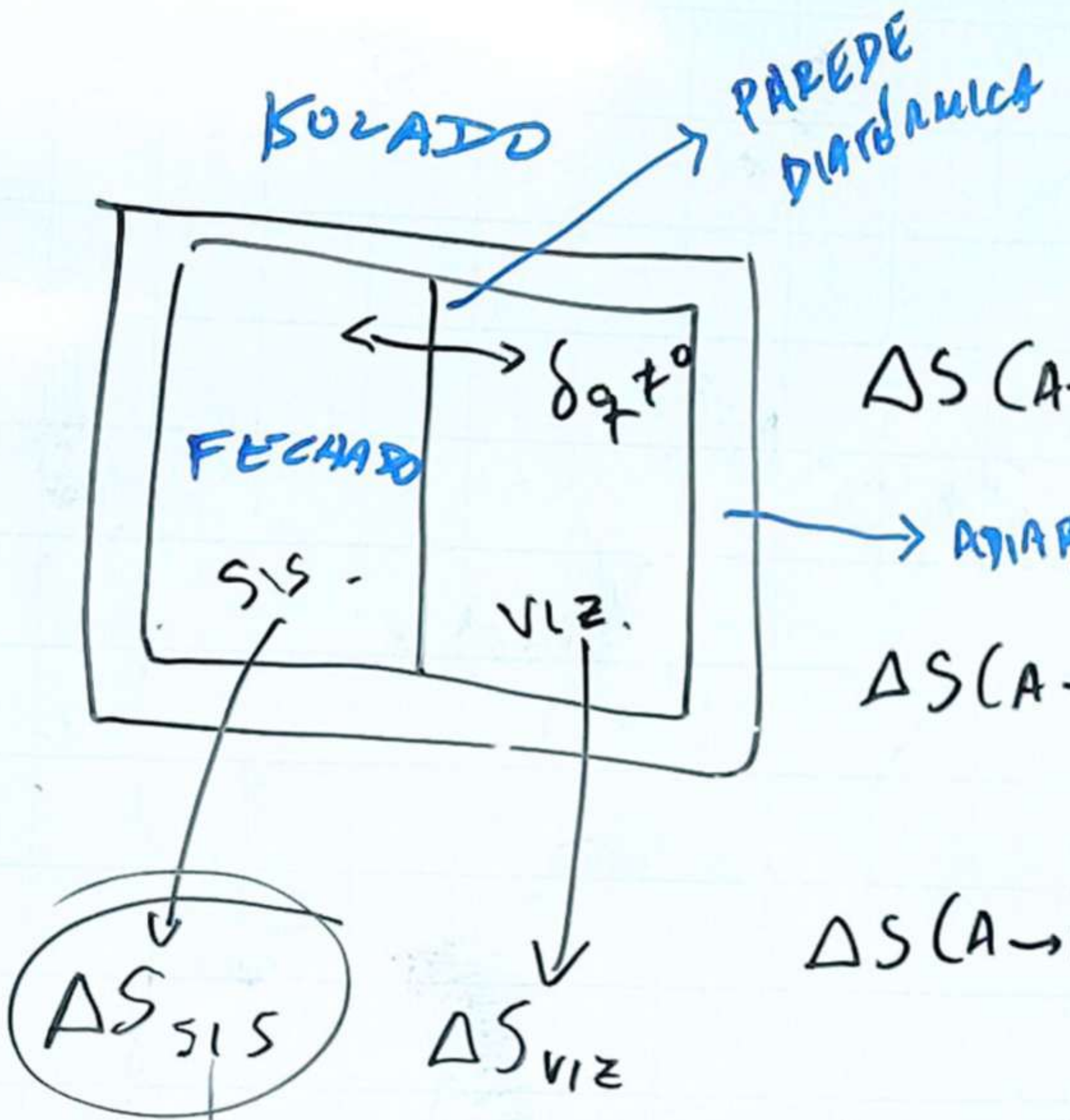
PARA SISTEMAS ISOLADOS: $\delta q = 0$

$$\Delta S(A \to B) \geq 0$$

$$dU = \delta q + \delta w$$
$$= \delta q - p_{ex} dV$$
$$\delta q = dU + p dV$$

$$dS \geq \frac{\overbrace{dU + p dV}^{\delta q}}{T}$$

FECHADOS



$$\Delta S(A \to B) \geq \int_A^B \frac{\delta q}{T}$$

$$\Delta S(A \to B) \geq \frac{q}{T}$$

$$\Delta S(A \to B) = \frac{q_{rev}}{T}$$

$$\Delta S(A \to B) > \frac{q_{irr}}{T}$$

$$\Delta S_T = \Delta S_{SIS} + \Delta S_{VIZ} \geq 0$$

$$\rightarrow \quad dS \geq \frac{\delta q}{T} \quad \begin{cases} \xrightarrow{\text{REV.}} dS = \dfrac{\delta q_{rev}}{T} \\ \xrightarrow{\text{IRR.}} dS > \dfrac{\delta q_{irr}}{T} \end{cases} \rightarrow \text{CALOR TROCADO ENTRE SIS. E VIZ.}$$

$\Downarrow$

SISTEMA FECHADO

↳ ISOLADO: $dS \geq 0$

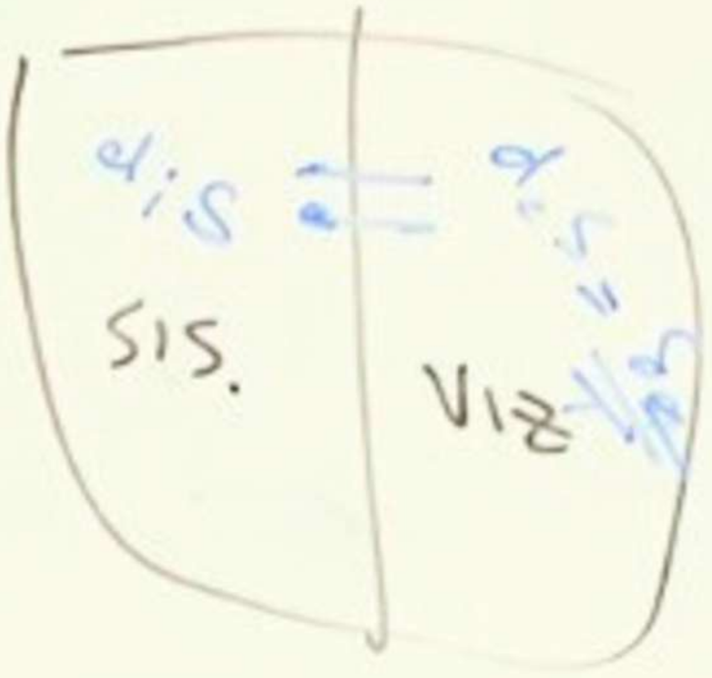
$$d_iS \equiv dS - \underbrace{\frac{\delta q}{T}}_{d_eS} \geq 0 \longrightarrow dS = d_iS + d_eS \geq 0$$

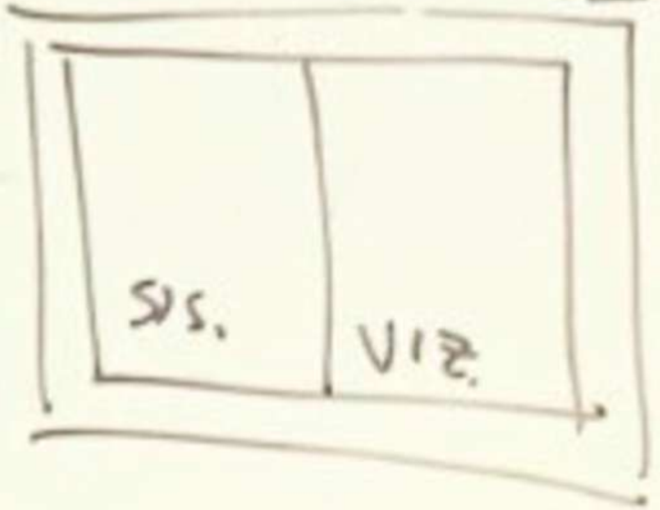
↳ $d_iS \geq 0$

$$d_eS \begin{cases} = 0 \\ > 0 \\ < 0 \end{cases}$$

d_iS ⇓ VARIAÇÃO DE S DEVIDO A PROCESSO IRREVERSÍVEL (INTERNO)

d_eS TROCA DE ENERGIA (EXTERNA





- SISTEMA ISOLADO: $d_eS = 0$, $d_iS \geq 0$, $dS = d_iS + d_eS \geq 0$
$= d_iS > 0$

SISTEMA FECHADO: $d_eS = \frac{\delta q}{T}$, $d_iS \geq 0$ $\quad dS = d_iS + \underset{\Downarrow \atop \frac{\delta q}{T}}{d_eS} \geq 0$

$$dU = \delta q + \delta w \Rightarrow \delta q = dU - \delta w$$
$$= dU + p_{ext}\,dV$$
$$= dU + p\,dV$$

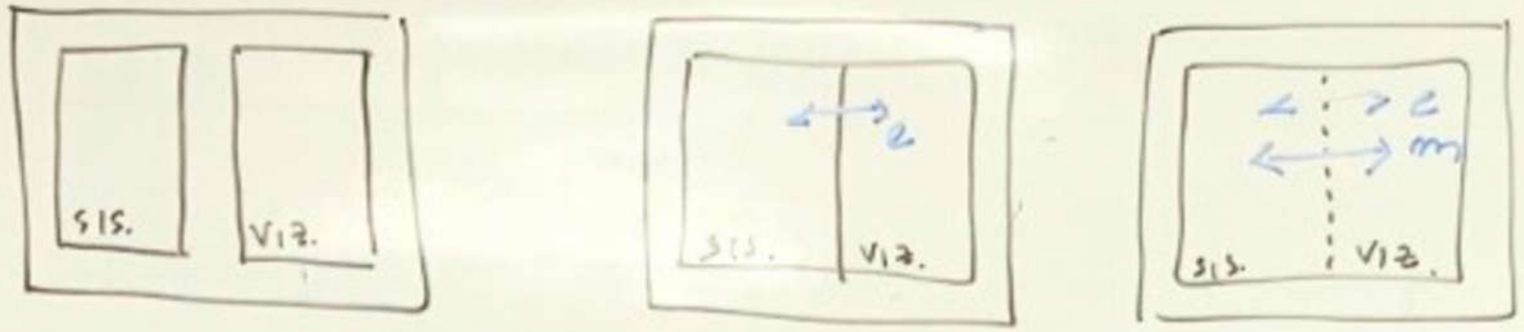
SÓ TRABALHO PV

REVERS.

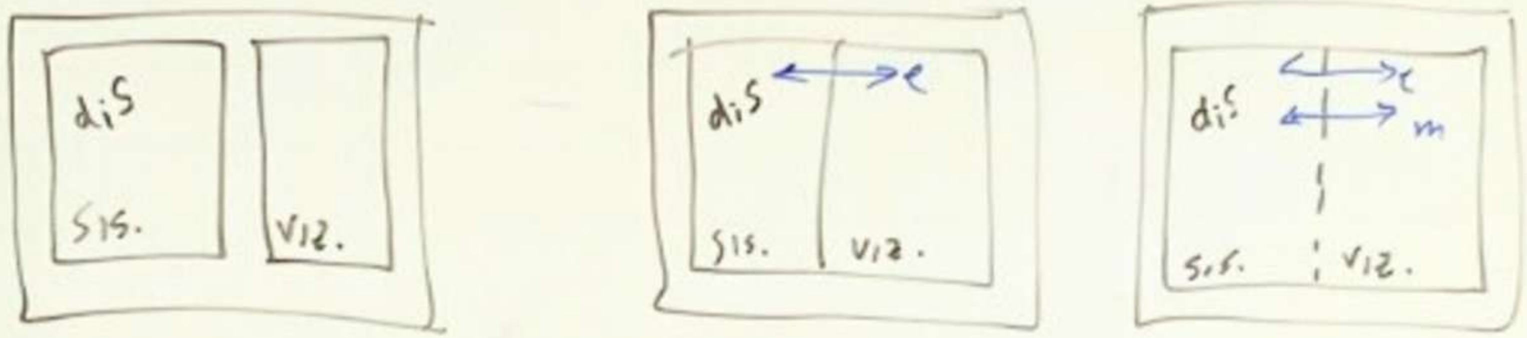
$$d_eS = \frac{\delta q_{rev}}{T} \qquad \delta q_{rev} = dU + p\,dV$$
$$= \frac{dU + p\,dV}{T} \Rightarrow \underline{dU = TdS - p\,dV}$$

1ª lei: $dU = \delta q + \delta w \Rightarrow \delta q = dU - \delta w$

2ª lei: $d_iS = dS - \frac{\delta q}{T} \geq 0$



ISOLADO | FECHADO | ABERTO



Isolado

$$d_iS \geq 0$$
$$d_eS = 0$$
$$dS = d_iS + d_eS$$
$$= d_iS + 0$$
$$= d_iS \geq 0$$

Fechado

$$d_iS \geq 0$$
$$d_eS = \frac{\delta q}{T}$$
$$dS = d_iS + d_eS$$
$$= d_iS + \frac{\delta q}{T} \geq 0$$

Aberto

$$d_iS \geq 0$$
$$d_eS + d_mS = \frac{\delta q}{T} + d_mS$$
$$dS = d_iS + \frac{\delta q}{T} + d_mS$$
$$\geq 0$$

TEMPERATURA E FATOR INTEGRANTE DA ENTROPIA

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

V, T

$V \longleftrightarrow T$

$U = cte$

$dU = 0$

$$\left(\frac{\partial U}{\partial V}\right) dV + \left(\frac{\partial U}{\partial T}\right)_V dT = 0$$

$$M(V,T)\,dV + N(V,T)\,dT = 0$$

$$\Downarrow \qquad \Downarrow$$

$$M(x,y)\,dx + N(x,y)\,dy = 0$$

$$\frac{dy}{dx} = -\frac{M(x,y)}{N(x,y)} = f(x,y) \Longleftarrow$$ EQ. DIF DE PRIMEIRA ORDEM

$M(x)$ $\quad N(y)$ — CASO SEPARÁVEL

$$\frac{dy}{dx} = -\frac{M(x)}{N(y)} \Rightarrow N(y)\,dy = -M(x)\,dx$$

$$\int N(y)\,dy = -\int M(x)\,dx$$

EQUAÇÕES DIF. EXATAS

$$M(x,y)\,dx + N(x,y)\,dy = 0 = df$$

$$\underbrace{\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y}_{\text{CONDIÇÃO DE EULER}} \Rightarrow$$ DIFERENCIAL EXATA

$$\left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = df = 0$$

$$\int_x \left(\frac{\partial f}{\partial x}\right)_y dx = -\int_y \left(\frac{\partial f}{\partial y}\right)_x dy$$

$$f(x) + C(y) = -\left[f(y) + C'(x)\right]$$

$$x \longleftrightarrow y$$

EQUAÇÕES DIFERENCIAIS HOMOGÊNEAS

FUNÇÃO HOMOGÊNEA DE GRAU p : $\quad f(\lambda x, \lambda y) = \lambda^p f(x,y)$

$M(x,y) \Longrightarrow$ FUNÇÃO DE GRAU p

$N(x,y) \Longrightarrow$ FUNÇÃO DE GRAU p

$\Big\} \; w = \frac{y}{x} \Longrightarrow$ SEPARÁVEL

- VARIÁVEIS EXTENSIVAS: $p = 1$ $\qquad U(\lambda N) = \lambda^1 U(N)$
- VARIÁVEIS INTENSIVAS: $p = 0$ $\qquad U(\lambda T) = \lambda^0 U(T)$

$\Rightarrow$ TEOREMA DE EULER (UM DOS):

$$F(x_1, x_2, \ldots x_k)$$

$$F(\lambda x_1, \lambda x_2, \ldots, \lambda x_k) = \lambda^p F(x_1, x_2, \ldots, x_k)$$

$$pF(x_1, x_2, \ldots) = \sum_{j=1}^{k} \left(\frac{\partial F}{\partial x_j}\right) x_j \xrightarrow{p=1} \boxed{F(x_1, x_2, \ldots, x_k) = \sum_{j=1}^{k} \left(\frac{\partial F}{\partial x_j}\right) x_j}$$

$M(x,y)\,dx + N(x,y)\,dy = df = 0$

$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \rightarrow$ EXATA

$\left(\frac{\partial M}{\partial y}\right)_x \neq \left(\frac{\partial N}{\partial x}\right)_y \Rightarrow$ USAR FATOR INTEGRANTE

$\bar{\mu}(x,y)\,M(x,y)\,dx + \bar{\mu}(x,y)\,N(x,y)\,dy = 0$

$$\left[\frac{\partial}{\partial y}\left[\bar{\mu}(x,y)\,M(x,y)\right]_x\right] = \left[\frac{\partial}{\partial x}\left[\bar{\mu}(x,y)\,N(x,y)\right]_y\right]$$

$$M(x,y)\left(\frac{\partial \bar{\mu}(x,y)}{\partial y}\right)_x + \bar{\mu}(x,y)\left(\frac{\partial M(x,y)}{\partial y}\right)_x = N(x,y)\left(\frac{\partial \bar{\mu}(x,y)}{\partial x}\right)_y + \bar{\mu}(x,y)\left(\frac{\partial N(x,y)}{\partial x}\right)_y$$

PARA FACILITAR

$\bar{\mu}(x,y) \rightarrow \bar{\mu}(x)$

$\left(\frac{\partial \bar{\mu}(x,y)}{\partial x}\right)_y \rightarrow \frac{d\bar{\mu}(x)}{dx}$

$$\bar{\mu}(x)\left[\frac{\partial M(x,y)}{\partial y} - \frac{\partial N(x,y)}{\partial x}\right] = N(x,y)\,\frac{d\bar{\mu}(x)}{dx}$$

$$\frac{d\bar{\mu}(x)}{dx} = \frac{\bar{\mu}(x)}{N(x,y)}\left[\frac{\partial M(x,y)}{\partial y} - \frac{\partial N(x,y)}{\partial x}\right]$$

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

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

$\delta q = dU - \delta w$

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

$x = T$

$y = V$

$$= \underbrace{\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]}_{N} dV + \underbrace{C_V(T)}_{M}\,dT$$

$$= C_V(T)\,dT + \left[\underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{\Pi_T} + p\right] dV = 0$$

C_V cte em gás ideal

Π_T gás ideal $\Pi_T = 0$

δq é exato?

$\left(\frac{\partial N}{\partial T}\right)_V = \left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V} \neq 0$

$\left(\frac{\partial M}{\partial V}\right)_T = \left(\frac{\partial C_V(T)}{\partial V}\right)_T = \varnothing$

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

$\frac{\partial}{\partial V}\left[\bar{\mu}(T)M\right] = \frac{\partial}{\partial T}\left[\bar{\mu}(T)p\right]$

$\frac{d\bar{\mu}(T)}{dT} = \frac{\bar{\mu}(T)}{p}\left[0 - \frac{nR}{V}\right] = -\frac{\bar{\mu}(T)}{T}$

$-\frac{nR}{pV} = -\frac{1}{T}$

$pV = nRT$

$\frac{pV}{nR} = T \Rightarrow \left(\frac{pV}{nR}\right)^{-1} = \frac{1}{T}$

$\frac{d\bar{\mu}(T)}{\bar{\mu}(T)} = -\frac{dT}{T}$

$\ln\bar{\mu} + C = -\ln T + C'$

$\ln\bar{\mu} = \ln\left(\frac{1}{T}\right) + C' - C$

$\ln(\bar{\mu}) = \ln\left(\frac{C_0}{T}\right)$ $\quad \ln C_0$

$\bar{\mu} = \frac{C_0}{T}$ $\quad C_0 = 1$ $\quad \bar{\mu}(T) = \frac{1}{T}$

$\frac{\delta q}{T}$

$$\delta q = C_V\, dT + p\, dV$$

$$\frac{\delta q}{T} = \underbrace{\frac{C_V\, dT}{T}}_{M} + \underbrace{\frac{p}{T}}_{N} dV$$

$$\left(\frac{\partial M}{\partial V}\right)_T = \frac{\partial}{\partial V}\left(\frac{C_V}{T}\right)_T = 0$$

$$\left(\frac{\partial N}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{nR}{V}\right)_T = 0$$

$pV = nRT$

$\frac{p}{T} = \frac{nR}{V}$

DA

$\frac{1}{T}$ É FATOR INTEGRANTE DE δq

E $\frac{\delta q}{T}$ É FUNÇÃO DE ESTADO!!!

$\Downarrow$

δq_{rev}

* ENTROPIA DE ALGUNS PROCESSOS

$$dS = \frac{\delta q_{rev}}{T} \qquad dU = \delta q + \delta w$$

- ADIABÁTICO ($\delta q = 0$)

$$dS = \frac{\delta q_{AD}}{T} = \varnothing$$

- ISOTÉRMICO ($T = cte$)

$$dU = \delta q + \delta w = 0 \Rightarrow \delta q = -\underset{-pdV}{\delta w} \Rightarrow \delta q_{rev} = +pdV$$

$$dS = \frac{\delta q_{rev}}{T} = \frac{pdV}{T} = \frac{nR\,dV}{V} \Rightarrow \Delta S = \int \frac{nR\,dV}{V}$$

$pV = nRT$

$\frac{p}{T} = \frac{nR}{V}$

$$\Delta S(i \to f) = nR \ln\left(\frac{V_f}{V_i}\right)$$

$V \uparrow \Rightarrow \Delta S \uparrow$

• ISOCÓRICO (V = cte) $C_x = \left(\frac{\partial X}{\partial y}\right)_x$

$$dS = \frac{\delta q_{rev}}{T} \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\delta q_V}{dT} \equiv C_V$$

$$= \frac{C_V\,dT}{T} \Rightarrow \Delta S(i\to f) = \int_{T_i}^{T_f} \frac{C_V(T)}{T}\,dT = C_V \int_{T_i}^{T_f} \frac{dT}{T} = C_V \ln\left(\frac{T_f}{T_i}\right)$$

GÁS IDEAL   T ↑   ΔS ↑

• ISOBÁRICO (p = cte)

$$dS = \frac{\delta q_{rev}}{T} \qquad C_p \equiv \frac{\delta q_p}{dT}$$

$$= \frac{C_p\,dT}{T} \Rightarrow \Delta S(i\to f) = \int_{T_i}^{T_f} \frac{C_p(T)\,dT}{T} \Rightarrow \Delta S(i\to f) = C_p \ln\left(\frac{T_f}{T_i}\right)$$

GÁS IDEAL

• CÍCLICO:

$$dS = \frac{\delta q_{rev}}{T} \qquad \oint dS = \oint \frac{\delta q_{rev}}{T} = 0$$

$$\oint dS = \oint \frac{\delta q_{irr}}{T} > 0$$

TEOREMA DE CLAUSIUS

• MUDANÇAS DE FASE

$$dS(\alpha\to\beta) = \frac{\delta q_p(\alpha\to\beta)}{T^*}$$

TEMPERATURA DE EQUILÍBRIO

$$dS(\alpha\to\beta) = \frac{dH(\alpha\to\beta)}{T^*}$$

* ENTROPIA DE GASES IDEAIS

• V,T

$$dS = \frac{\delta q}{T} = \frac{dU + p\,dV}{T} = \frac{C_V\,dT + p\,dV}{T}$$

$$\Delta S(i\to f) = S(T_f,V_f) - S(T_i,V_i) = \int_{T_i}^{T_f} \frac{C_V\,dT}{T} + \int_{V_i}^{V_f} \frac{nR}{V}\,dV = C_V \ln\left(\frac{T_f}{T_i}\right) + nR\ln\left(\frac{V_f}{V_i}\right)$$

DE INTEGRAL DEFINIDA

$$S = C_V \ln T + nR \ln V + \text{CONSTANTE}$$
$$= n\bar{C}_V \ln T + nR \ln V + \text{CONSTANTE}$$

DE INTEGRAL INDEFINIDA (i, f INDEFINIDOS)

• p, T

$$p\,dV + V\,dp = nR\,dT \Rightarrow p\,dV = nR\,dT - V\,dp$$

$$dS = \frac{C_V\,dT}{T} + \frac{nR\,dT - V\,dp}{T} = \frac{(n\bar{C}_V + nR)\,dT}{T} - \frac{V\,dp}{T}$$

$= \bar{C}_V n$ C_p nR/p $pV = nRT$ $\frac{V}{T} = \frac{nR}{p}$

$$dS = \frac{C_p\,dT}{T} - \frac{nR\,dp}{p}$$

$$\Delta S(i\to f) = S(T_f,p_f) - S(T_i,p_i) = C_p \ln\left(\frac{T_f}{T_i}\right) - nR\ln\left(\frac{p_f}{p_i}\right)$$

INTEGRAL DEFINIDA

$$S = C_p \ln T + nR \ln p + \text{CONSTANTE}$$

P, V

$$S = C_V \ln T + nR\ln(V) + \text{CONSTANTE}$$

$$pV = nRT \Rightarrow \ln(pV) = \ln(T) + \ln(nR)$$

$$S = C_V \ln(pV) + \text{CONSTANTE} + nR\ln V$$

$$= C_V \ln(p) + C_V \ln(V) + nR\ln V + \text{CONSTANTE}$$

$$= C_V \ln(p) + \underbrace{\left[C_V + nR\right]} \ln V + \text{CONSTANTE}$$

$$= C_V \ln(p) + C_p \ln V + \text{CONSTANTE}$$

$$= C_V \left[\ln p + \frac{C_p}{C_V} \ln V\right] + \text{CONSTANTE}, \quad \frac{C_p}{C_V} = \gamma$$

$$= C_V \left[\ln p + \ln V^{\gamma}\right] + \text{CONSTANTE}$$

$$= C_V \ln(pV^{\gamma}) + \text{CONSTANTE}$$

PROCESSOS ADIABÁTICOS SÃO ISENTRÓPICOS (ENTROPIA CONSTANTE)

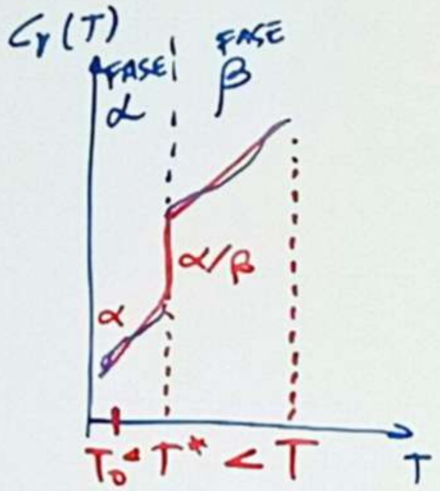
$\Delta S(i \to f) = 0$

* MEDINDO ENTROPIA

⇒ REVISANDO: $U \longleftrightarrow \delta q_V$

$H \longleftrightarrow \delta q_P = H$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad C_P = \left(\frac{\partial U}{\partial T}\right)_P$$



$$\Delta U(T_0 \to T) = U(T) - U(T_0) = \int_{T_0}^{T} C_V(T')\,dT'$$

$$\Delta H(T_0 \to T) = H(T) - H(T_0) = \int_{T_0}^{T} C_P(T')\,dT'$$

N, P ctes

$$U(T) = U(T_0) + \int_{T_0}^{T} \underbrace{C_V(T')}_{F(T)}\,dT'$$

$$H(T) = H(T_0) + \int_{T_0}^{T} C_P(T')\,dT'$$

$$H(T) = H(T_0) + \int_{T_0}^{T^*} C_P^{\alpha}(T')\,dT' + \Delta_{\alpha}^{\beta} H(T^*) + \int_{T^*}^{T} C_P^{\beta}(T')\,dT'$$

SUBST. PURA {N, V CONSTANTES

$$U(T) = U(T_0) + \int_{T_0}^{T^*} C_V^{\alpha}(T')\,dT' + \Delta_{\alpha}^{\beta} U(T^*) + \int_{T^*}^{T} C_V^{\beta}(T')\,dT'$$

* TERCEIRA LEI

$$dS = \frac{\delta q_{rev}}{T} \;\to\; = \frac{C_V\,dT}{T} \quad \text{(ISOCÓRICO)}$$

$$\phantom{dS = \frac{\delta q_{rev}}{T}} \;\to\; = \frac{C_P\,dT}{T} \quad \text{(ISOBÁRICO)}$$

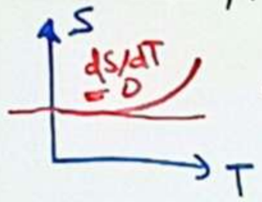
$C_x \to V, P$

$$S(T) = S(T_0) + \int_{T_0}^{T^*} \frac{C_x^{\alpha}(T')\,dT'}{T'} + \Delta_{\alpha}^{\beta} S(T^*) + \int_{T^*}^{T} \frac{C_x^{\beta}(T')\,dT'}{T'}$$

P = cte

$$\Delta_{\alpha}^{\beta} S(T^*) = \frac{\Delta_{\alpha}^{\beta} H(T^*)}{T}$$

$U(T_0), H(T_0) \Rightarrow$ ARBITRÁRIOS



$T \to T_0 = 0\,K \qquad S(T) \to 0\ kJ\,mol^{-1}$

$$\lim_{T\to 0} \frac{dS(T)}{dT} = S_0 \longrightarrow \lim_{T\to 0} S(T) = 0$$

TEOREMA DE CALOR DE NERNST

PLANCK

"A ENTROPIA DE UM CRISTAL PURO PERFEITO NO ZERO ABSOLUTO É NULA" LEWIS

"NÃO EXISTE PROCEDIMENTO QUE PERMITA LEVAR UM SISTEMA AO ZERO ABSOLUTO" INATINGIBILIDADE NERNST

* MISTURANDO 1ª E 2ª LEI

1º) $dU = \delta q + \delta w = \delta q_{rev} + \delta w_{rev}$

2º) $dS = \frac{\delta q_{rev}}{T} \rightarrow TdS - pdV$

$dU = TdS - pdV \rightarrow$ DESLOCAMENTO GENERALIZADO

FORÇA GENERALIZADA

$\delta w = -pdV + 0dP$

$\frac{\partial(-P)}{\partial P} = -1 \neq \frac{\partial 0}{\partial V} = 0$

INEXATA

$\delta q \xrightarrow[\text{FATOR INTEG}]{1/T} dS$

DIFERENCIAL INEXATA — DIFERENCIAL EXATA

$\delta w \xrightarrow{-1/P} dV$

DIFERENCIAL INEXATA — DIFERENCIAL EXATA

$dU = TdS - pdV$

VARIÁVEIS INTENSIVAS = FORÇAS TERM.

VARIÁVEIS EXTENSIVAS = DESLOC. GEN.

$dU = X_i dY_i$

$dU = \sum_i X_i dY_i$

$-\frac{\delta w}{p} = 1dV + 0dp$

EXATA

$X_i = \left(\frac{\partial U}{\partial Y_i}\right)_{Y_{j \neq i}}$

$dU = TdS - pdV$

$= \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$

INTENSIVA $= \frac{\partial \text{ EXTENSIVA}}{\partial \text{ EXTENSIVA}}$ → HOMOGÊNEA GRAU 1 / HOMOGÊNEA DE GRAU 1

HOM. GRAU 0

$f(\lambda x, \lambda y) = \lambda f(x,y)$

$g(\lambda x, \lambda y) = \lambda g(x,y)$

$U(S,V)$

$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \qquad dN = 0$

$P = U_M / V \qquad T = U_T / S \qquad \mu = U_C / N$

POTENCIAL QUÍMICO

$U(S,V,N)$

$dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,N}}_{T} dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{N,S}}_{-P} dV + \underbrace{\left(\frac{\partial U}{\partial N}\right)_{V,S}}_{\mu} dN \Rightarrow \boxed{dU = TdS - pdV + \mu dN}$

EQUAÇÃO FUNDAMENTAL DA TERMODINÂMICA

$dU_{térmica}$ — $dU_{mecânica}$ — $dU_{química}$

$dU = TdS - pdV + \sum_j \mu_j dN_j$ SUBSTÂNCIAS DIFERENTES MISTURA HOMOGÊNEA (1 FASE)

$dU = TdS - pdV + \sum_\alpha \sum_j \mu_{j,\alpha} dN_{j,\alpha}$ SUBSTÂNCIAS DIFERENTES FASES DIFERENTES MISTURA HETEROGÊNEA (MAIS DE 1 FASE)

FASE α | β

SUBS. $i \leftrightarrow i$ $(\mu_{i,\alpha} = \mu_{j,\beta})$ QUÍMICO $\sum_{\alpha,j} \mu_{j,\alpha} dN_{j,\alpha}$

$j \leftrightarrow j$

FÍSICO $(\mu_{i,\alpha} = \mu_{i,\beta})$

* ENTROPIA DE SISTEMAS ABERTOS

$F = \left(\frac{\partial V}{\partial x}\right)$ $\qquad X_i = \left(\frac{\partial U}{\partial Y_i}\right)$

SIST ⟷ VIZ.

TROCAS

$dS = d_iS$ ISOLADO ×

$dS = d_iS + d_eS$ FECHADO ENERGIA — CALOR, TRAB.

$dS = d_iS + \underbrace{d_eS + d_mS}_{d_eS'}$ ABERTO ENERGIA — CALOR, TRAB. MASSA

d_mS ?

$\mu_{J,\alpha} = \left(\frac{\partial U}{\partial N_{J,\alpha}}\right)_{p,T,N_{i\neq J}}$

$dN_{J,\alpha} = d_iN_{J,\alpha} + d_eN_{J,\alpha}$

$\mu \rightarrow J, \alpha$ (J: SUBST., α: FASE)

J,α SIS	J,α VIZ

$dN_{J,\alpha} = d_1N_{J,\alpha} + d_eN_{J,\alpha}$

$dU = TdS - pdV + \sum_\alpha \sum_J \mu_{J,\alpha} dN_{J,\alpha}$

$dU = TdS - pdV + \underbrace{\sum_\alpha \sum_J \mu_{J,\alpha} d_iN_{J,\alpha}}_{SIS.} + \underbrace{\sum_\alpha \sum_J \mu_{J,\alpha} d_eN_{J,\alpha}}_{VIZ.}$

TROCA DE MASSA SIS — VIZ

$dS = \underbrace{\frac{dU + pdV}{T}}_{d_eS} - \underbrace{\frac{1}{T}\sum_\alpha \sum_J \mu_{J,\alpha} d_iN_{J,\alpha}}_{d_iS} - \underbrace{\frac{1}{T}\sum_\alpha \sum_J \mu_{J,\alpha} d_eN_{J,\alpha}}_{d_mS}$

d_eS' (d_eS + d_mS)

* FORMULAÇÃO DA ENTROPIA

$dU = TdS - pdV + \mu dN$ SUBST. PURA, UMA FASE

$= \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,N}}_{T} dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{N,S}}_{-p} dV + \underbrace{\left(\frac{\partial U}{\partial N}\right)_{S,V}}_{\mu} dN$

FORMULAÇÃO DA ENERGIA

$U(S, V, N)$

$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$

$= \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V,N}}_{\frac{1}{T}} dU + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{U,N}}_{+\frac{p}{T}} dV + \underbrace{\left(\frac{\partial S}{\partial N}\right)_{U,V}}_{-\frac{\mu}{T}} dN$

DUAS LEIS

DUAS FORMULAÇÕES

DUAS FUNÇÕES

* EQUAÇÃO DE GIBBS-DUHEM

FUNÇÃO HOMOGÊNEA GRAU P

$$F(\lambda x) = \lambda F(x) \quad \begin{cases} 1 & \text{EXT.} \\ 0 & \text{INT.} \end{cases}$$

$$F(x_1, \dots x_k) = \sum_j \left(\frac{\partial F}{\partial x_j}\right)_{i \neq j} x_j$$

$$\Downarrow$$

$$U \qquad Y_i$$

- CONSIDERE A EQ. FUNDAMENTAL

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

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

$$= \sum_j \left(\frac{\partial U}{\partial Y_j}\right)_{Y_{i \neq j}} dY_j$$

$\Downarrow$ INTEGRADA, FORMA DE EULER

$$\boxed{U = TS - pV + \mu N}$$

EQ. FUND. INTENSIVO . d(EXT.)

EQ. GIBBS-DUHEM EXT. d(INTENSIVO)

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

$$= \cancel{TdS} - \cancel{pdV} + \cancel{\mu dN}$$

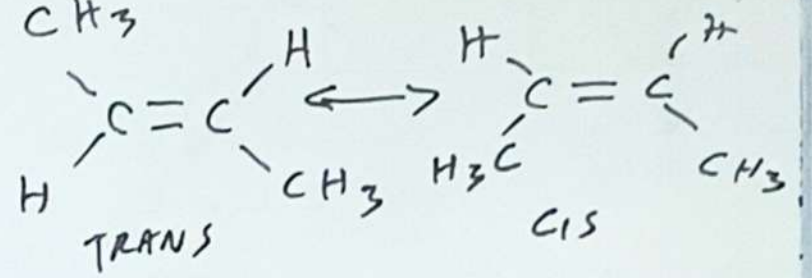
$$\boxed{SdT - Vdp + Nd\mu = 0}$$

EQ. GIBBS-DUHEM. $F(T, \mu, p)$

$$Nd\mu = Vdp - SdT \Rightarrow d\mu = \underbrace{\frac{V}{N}}_{\bar{V}} dp - \underbrace{\frac{S}{N}}_{\bar{S}} dT = \left(\frac{\partial \mu}{\partial p}\right)_T dp + \left(\frac{\partial \mu}{\partial T}\right)_p dT$$

$$\boxed{\left(\frac{\partial \mu}{\partial T}\right)_p = -\bar{S}} \qquad \boxed{\left(\frac{\partial \mu}{\partial p}\right)_T = \bar{V}}$$

$$A \rightleftharpoons B$$



- REGRA DE GIBBS

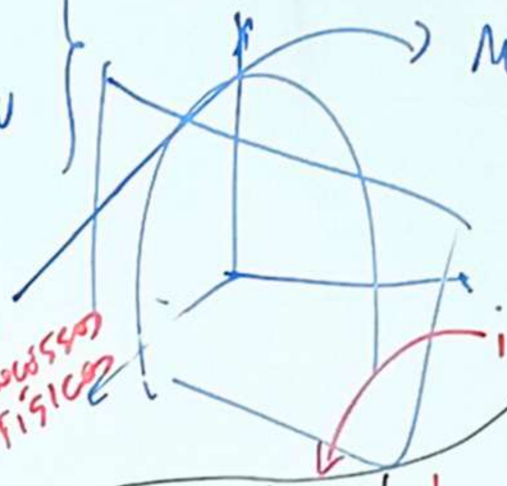
- LEGENDRE $\Rightarrow U \rightarrow H, A, G$
- EQUAÇÕES MAXWELL $f? \quad f? \quad f?$
- MAXIMIZAÇÃO S $\parallel$ MINIMIZAÇÃO DE U
- PRINCÍPIOS DE EXTREMUM

$\mu_{i\alpha} = \mu_{i,\beta}$

EQ. FIS

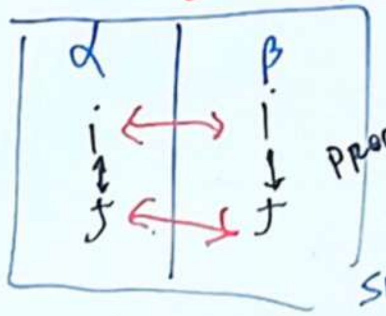
$\mu_{i,\alpha} = \mu_{j,\alpha}$

EQ. QUIM.



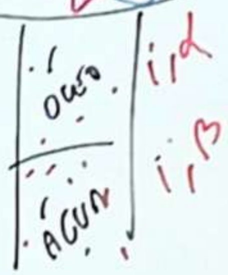
EQUILÍBRIO FASES

PROCESSOS FÍSICOS



PROCESSO QUÍMICO

SIST.



ZOOTOPIA

* POTENCIAIS TERMODINÂMICOS

- $U\,,\,S$ $\left\{ \begin{array}{l} \text{FUNÇÕES DE ESTADO} \\ \text{GENERALIDADE} \\ \text{CARÁTER PREDITIVO} \end{array} \right.$

$\underbrace{U\,,\,S}_{\text{SISTEMAS ISOLADOS}}$

$dU = 0 \qquad dS > 0$

FECHADOS E ABERTOS $\Longrightarrow$ NECESSIDADE PRÁTICA DE OUTRAS FUNÇÕES

- VARIAÇÃO CONTROLADA DE PARÂMETROS

Ex.:
$$\begin{aligned} dU &= \delta q + \delta w \\ &= TdS - pdV \\ &\;\vdots \\ dU &= TdS - pdV + \mu dN \end{aligned}$$

$U\underbrace{(S,V)}_{\text{VARIÁVEIS NATURAIS DE U}}$ ← $dN = 0$

$dN \neq 0 \rightarrow U(S,V,N)$

GIBBS-DUHEM: $SdT + Vdp - Nd\mu = 0$ → MAS VARIA TUDO DE UMA VEZ

- TRANSFORMADAS DE LEG… (…)

$\boxed{\left.\begin{array}{l}\text{FUNÇÃO} \\ \text{BASE}\end{array}\right\} \; XdY} \xrightarrow{\text{T.L.}} \left.\begin{array}{l}\text{FUNÇÃO} \\ \text{DIFERENTE}\end{array}\right\} \; YdX$

POTENCIAL TERMODINÂMICO

$$\left.\begin{array}{ll} TdS \leftrightarrow SdT & \{S,T\} \\ pdV \leftrightarrow Vdp & \{p,V\} \end{array}\right\} \text{PARES CONJUGADOS}$$

$$Z(S,V),\; Z'(T,V),\; Z''(S,p),\; Z'''(T,p)$$

$Z = U(S,V)$

$$d(XY) = XdY + YdX$$

$$\begin{aligned} dZ'(T,V) &= dU(\overset{\to T}{S},V) - d(ST) = dU(S,V) - SdT - TdS \\ &= \cancel{TdS} - pdV - SdT - \cancel{TdS} \end{aligned}$$

$$dZ' = -SdT - pdV$$

$Z'(T,V) \Longrightarrow$ FUNÇÃO DE HELMHOLTZ: $F\,,\,\underline{A}(T,V)$

$$\underline{U(S,V)} \xrightarrow{S\to T} \underline{A(T,V)},\qquad \underline{U(S,V)} \xrightarrow{V\to p} \underline{H(S,p)},\qquad \underline{H(S,p)} \xrightarrow{S\to T} \underline{G(p,T)}$$

$$dZ'' = dU + d(pV) = dU + pdV + Vdp = TdS - \cancel{pdV} + \cancel{pdV} + Vdp$$
$$= TdS + Vdp$$
$$Z''(S,p) = H(S,p)$$

$$dZ''' = dH - d(TS) = dH - SdT - TdS = T\cancel{dS} + Vdp - SdT - T\cancel{dS}$$
$$Z'''(p,T) = -SdT + Vdp \Rightarrow Z''' = G$$
$$\Downarrow$$
ENERGIA DE GIBBS

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

FUNÇÕES	VARIÁVEIS NATURAIS	FORMA INTEGRAL	FORMA DIFERENCIAL ($M\,dx$ $N\,dy$)	RELAÇÕES DE MAXWELL
U	S,V		$dU = TdS - pdV + \mu dN$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
H	S,p	$H = U + pV$	$dH = TdS + Vdp + \mu dN$	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
$\boxed{A}$	T,V	$A = U - TS$	$dA = -SdT - pdV + \mu dN$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$
$\boxed{G}$	T,p	$G = H - TS$	$dG = -SdT + Vdp + \mu dN$	$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$

$\Downarrow$ p, T, V

$$TS = G - H$$
$$A = U + TS = \overbrace{U + G - H}^{-pV} = G - pV$$
$$G = A + pV$$

p, V, T, S

A, H, G

* RELAÇÕES DE MAXWELL

$$U \qquad dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_V}_{T} dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_S}_{-p} dV$$

$$H \qquad dH = \underbrace{\left(\frac{\partial H}{\partial S}\right)_p}_{T} dS + \underbrace{\left(\frac{\partial H}{\partial p}\right)_S}_{V} dp$$

$$A \qquad dA = \underbrace{\left(\frac{\partial A}{\partial T}\right)_V}_{-S} dT + \underbrace{\left(\frac{\partial A}{\partial V}\right)_T}_{-p} dV$$

$$G \qquad dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \underbrace{\left(\frac{\partial G}{\partial p}\right)_T}_{V} dp$$

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p = T \qquad \left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T = V$$

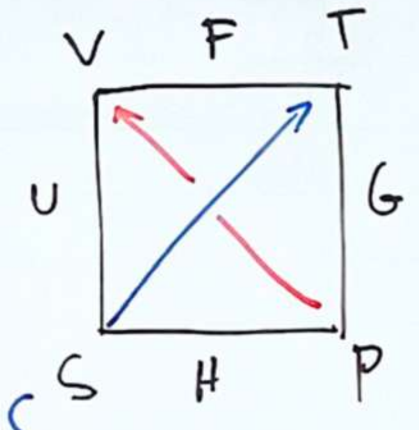
$$\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T = -p \qquad \left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_p = -S$$

CONDIÇÃO DE EULER
(LEI DE SCHWATZ)

$$df = \underbrace{\left(\frac{\partial F}{\partial x}\right)_y}_{M} dx + \underbrace{\left(\frac{\partial F}{\partial y}\right)_x}_{N} dy$$

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

$$\left(\frac{\partial^2 F}{\partial x \partial y}\right) = \left(\frac{\partial^2 F}{\partial y \partial x}\right)$$



MAX BORN

VALID FACTS AND THEORETICAL UNDERSTANDING GENERATE SOLUTIONS TO HARD PROBLEMS

Variáveis naturais são as que surgem da transformada de Legendre de uma função base, mas a nova função pode depender de outras, mantendo a coerência na troca de pares conjugados

U não aparece em tabelas na parte integral porque normalmente ela lista as definições, e energia interna, sendo a função original, não é obtida da mesma forma que as outras (a partir dela)

O sinal nas formas integrais vem do uso de +d(XY) ou -d(XY) na transformada de Legendre. Elas vêm, como mostrado anteriormente, do teorema de Euler de funções homogêneas

APPENDIX A: THERMODYNAMIC MNEMONIC

The sheer feat of memory involved in keeping track of all the thermodynamic definitions, the proper independent variables of each of the energy functions, and so on can become an impediment to the usefulness of thermodynamics. To overcome this problem, there is a well-known mnemonic device for keeping

track of all these things. The device is shown in Fig. 1A.1. You may find it necessary to make up your own mnemonic to remember the mnemonic.

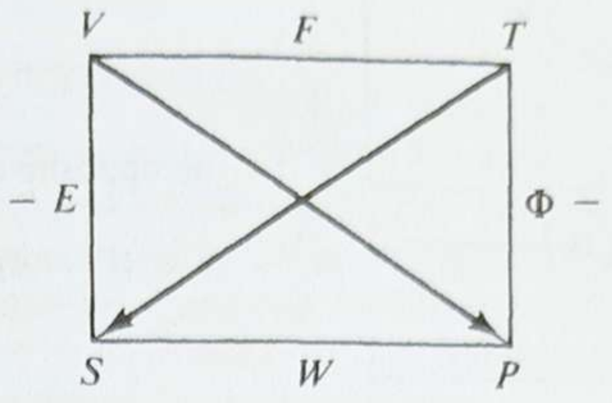


Fig. 1.A.1

We see, first of all, that the four energy functions, each of which occupies an edge of the figure, is each flanked by its proper independent variables at the corners: F by V and T, Φ by T and P, and so on. The energy functions are written in differential form by taking the coefficients from the opposite corners and the differentials from the near corners. If, in going from coefficient to differential the path goes counter to the arrow, the term has a minus sign, as in Fig. 1A.2.

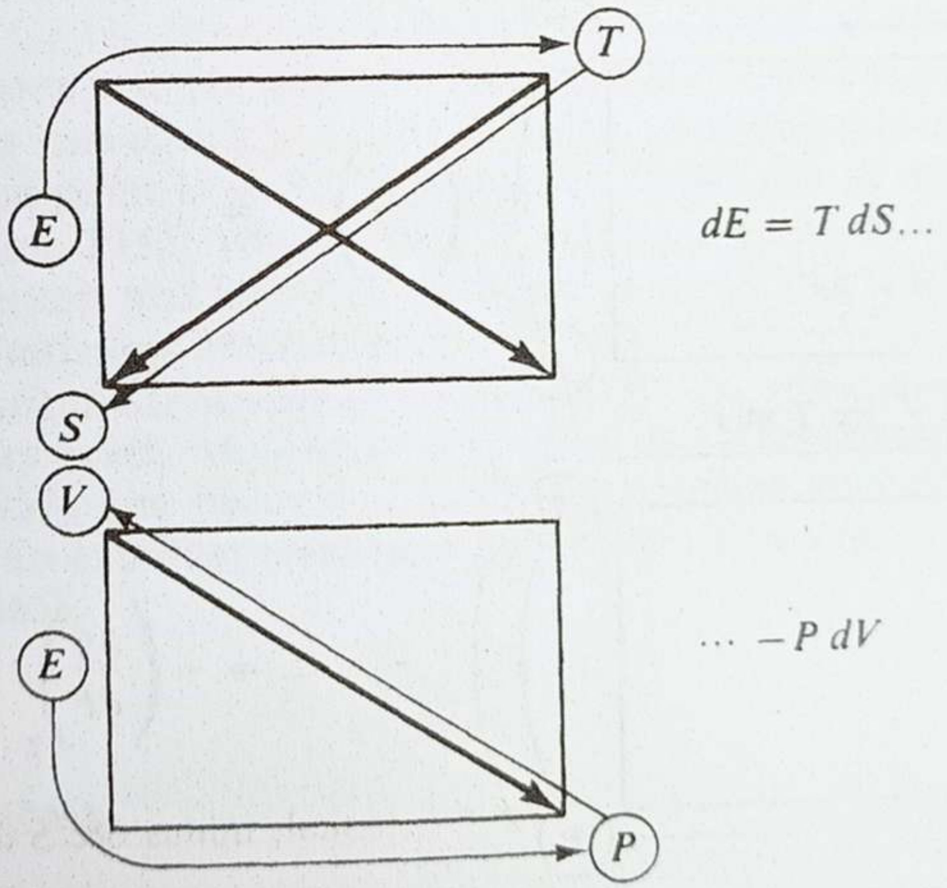
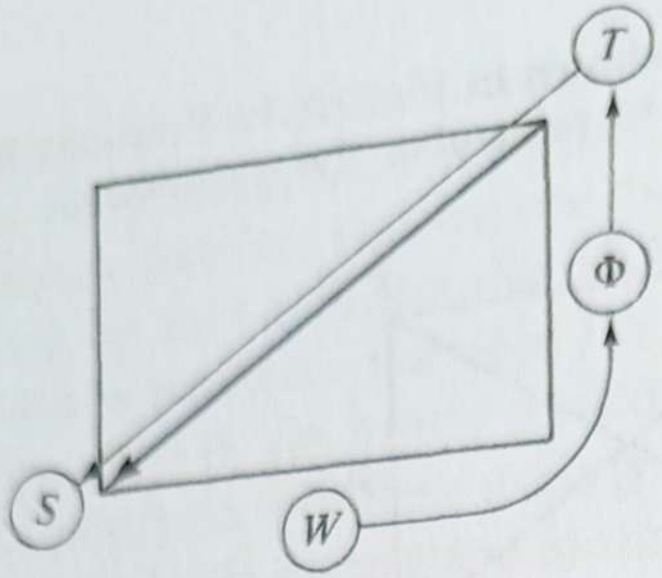


Fig. 1.A.2

Equations of the type $T = (\partial E/\partial S)_V$ follow from these differential forms. In order to get the transformations between the energy functions, start with any one of them. It is equal to the next energy function (in either direction), plus the product of the variable at the next corner times its conjugate across the diagonal, still following the sign convention of the arrows (Fig. 1A.3). The Maxwell relations may also be generated, by going around three corners in order (Fig. 1A.4). In the second step, we go around three corners in the opposite direction, ending on the same side (the paths overlap one side). If there is a minus sign flanking the side where the two paths overlap, there is a minus sign in the result.

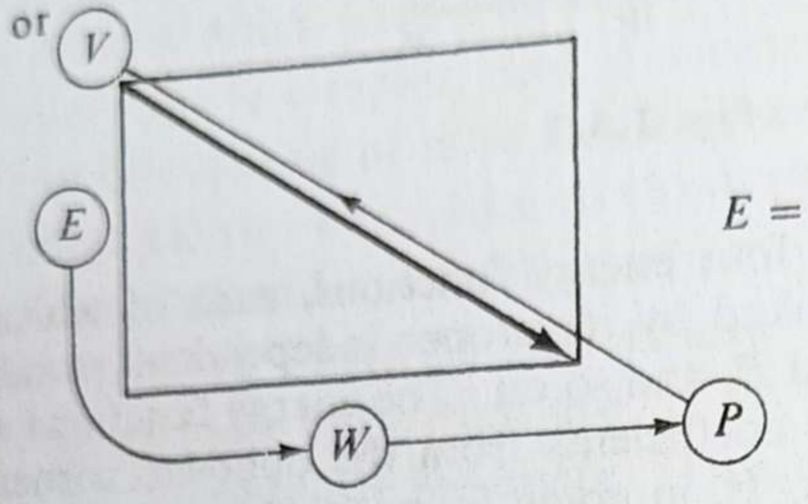


$$W = \Phi + TS$$

or starting with Φ and going in the opposite direction,

$$\Phi = W - ST$$

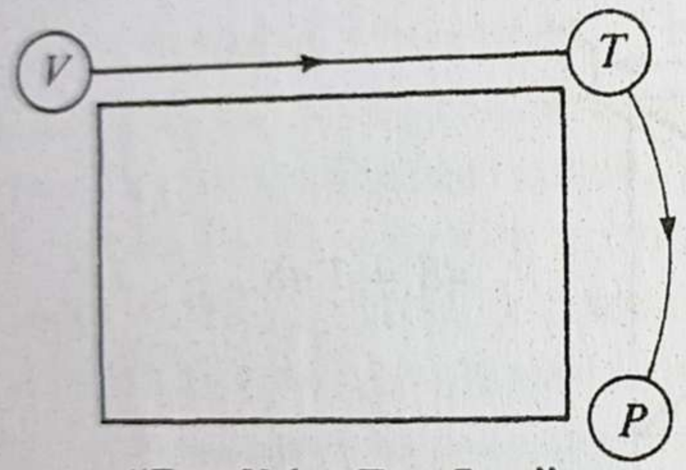
or



$$E = W - PV$$

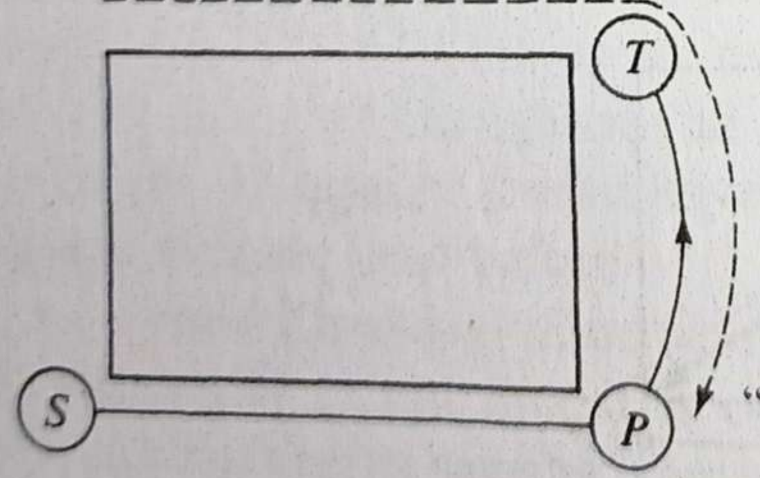
and so on.

Fig. 1.A.3



$$\left(\frac{\partial V}{\partial T}\right)_P = \ldots$$

"Dee V dee T at P ..."



$$- \quad \ldots = -\left(\frac{\partial S}{\partial P}\right)_T$$

"... equals minus dee S dee P at T"

Fig. 1.A.4

All this sounds more complicated than it is; you will find that after a few minutes of practice generating all the relations, use of the mnemonic becomes easy and automatic.

PROCESSOS ADIABÁTICOS REVERSÍVEIS

(1) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$ (1') $\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p = T$

(2) $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$ (2') $\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T = -p$

(3) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \alpha/\beta$ (3') $\left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T = V$

(4) $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p = -V\alpha$ (4') $\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_p = -S$

$\boxed{U = A + TS}$

$H = U + pV$

$A = U - TS \Rightarrow U = A - TS$

$G = H - TS \rightarrow \boxed{H = G + TS}$

- ENERGIA INTERNA

$T \leftrightarrow S$, V $\}$ $dU = TdS - pdV$

$dU = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{\pi_T} dV = C_V dT + \pi_T dV$

$\Downarrow$ EXPRESSÃO MAIS FECHADA

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = \left[\frac{\partial}{\partial V}(A + TS)\right]_T = \underbrace{\left(\frac{\partial A}{\partial V}\right)_T}_{-p\ (2')} + T\underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\left(\frac{\partial p}{\partial T}\right)_V}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \pi_T = -p + T\underbrace{\left(\frac{\partial p}{\partial T}\right)_V}_{=\frac{\alpha}{\beta}} = -p + \frac{T\alpha}{\beta}$$

$$dU = C_V dT + \left[\frac{T\alpha}{\beta} - p\right] dV$$

$$dU = C_V dT + \left[\frac{T\alpha - \beta p}{\beta}\right] dV$$

$p = f(T, V, N)$ EQUAÇÃO DE ESTADO

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

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

EQ. DE ESTADO TERMODINÂMICA P/ PRESSÃO

- ENTALPIA

$$\left.\begin{array}{l} p \\ T \leftrightarrow S \end{array}\right\} dH = \underline{T\,dS + V\,dp}$$

$$dH = \underbrace{\left(\frac{\partial H}{\partial T}\right)_p}\,dT + \left(\frac{\partial H}{\partial p}\right)_T dp = C_p\,dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

$$C_p \equiv \frac{\delta q_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_p$$

(3') (4)

$$\left(\frac{\partial H}{\partial p}\right)_T = \left[\frac{\partial (G+TS)}{\partial p}\right]_T = \underbrace{\left(\frac{\partial G}{\partial p}\right)_T}_{V} + T\left(\frac{\partial S}{\partial p}\right)_T = \underline{V} - T\left(\frac{\partial V}{\partial T}\right)_p$$

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

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

$$dH = C_p\,dT + V(1-\alpha T)\,dp$$

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

EQ. DE ESTADO TERMO. P/ VOLUME

- ENTROPIA

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$dS = \frac{\delta q_{rev}}{T} \xrightarrow{V} dS = \frac{C_V\,dT}{T} \Rightarrow \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$dS = \frac{\delta q_{rev}}{T} \xrightarrow{p} dS = \frac{C_p}{T}dT \Rightarrow \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

$$\begin{cases} dS = C_V\dfrac{dT}{T} + \underbrace{\left(\dfrac{\partial S}{\partial V}\right)_T}_{=\,\alpha/\beta} dV = \dfrac{C_V\,dT}{T} + \dfrac{\alpha}{\beta}\,dV \\[2ex] dS = C_p\dfrac{dT}{T} + \underbrace{\left(\dfrac{\partial S}{\partial p}\right)_T}_{=\,-V\alpha} dp = \dfrac{C_p\,dT}{T} - V\alpha\,dV \end{cases}$$

Table 9.1 Maxwell's relations.

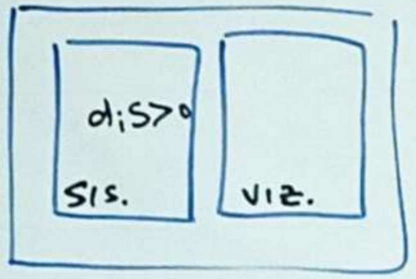
Fundamental Function	Variables to Relate	Maxwell's Relation
$U(S,V,N)$	S,V	$(\partial T/\partial V)_{S,N} = -(\partial p/\partial S)_{V,N}$
$dU = T\,dS - p\,dV + \mu\,dN$	S,N	$(\partial T/\partial N)_{S,V} = (\partial \mu/\partial S)_{V,N}$
	V,N	$-(\partial p/\partial N)_{S,V} = (\partial \mu/\partial V)_{S,N}$
$F(T,V,N)$	T,V	$(\partial S/\partial V)_{T,N} = (\partial p/\partial T)_{V,N}$
$dF = -S\,dT - p\,dV + \mu\,dN$	T,N	$-(\partial S/\partial N)_{T,V} = (\partial \mu/\partial T)_{V,N}$
	V,N	$-(\partial p/\partial N)_{T,V} = (\partial \mu/\partial V)_{T,N}$
$H(S,p,N)$	S,p	$(\partial T/\partial p)_{S,N} = (\partial V/\partial S)_{p,N}$
$dH = T\,dS + V\,dp + \mu\,dN$	S,N	$(\partial T/\partial N)_{S,p} = (\partial \mu/\partial S)_{p,N}$
	p,N	$(\partial V/\partial N)_{S,p} = (\partial \mu/\partial p)_{S,N}$
(S,V,μ)	S,V	$(\partial T/\partial V)_{S,\mu} = -(\partial p/\partial S)_{V,\mu}$
$T\,dS - p\,dV - N\,d\mu$	S,μ	$(\partial T/\partial \mu)_{S,V} = -(\partial N/\partial S)_{V,\mu}$
	V,μ	$(\partial p/\partial \mu)_{S,V} = (\partial N/\partial V)_{S,\mu}$
$G(T,p,N)$	T,p	$-(\partial S/\partial p)_{T,N} = (\partial V/\partial T)_{p,N}$
$dG = -S\,dT + V\,dp + \mu\,dN$	T,N	$-(\partial S/\partial N)_{T,p} = (\partial \mu/\partial T)_{p,N}$
	p,N	$(\partial V/\partial N)_{T,p} = (\partial \mu/\partial p)_{T,N}$
(T,V,μ)	T,V	$(\partial S/\partial V)_{T,\mu} = (\partial p/\partial T)_{V,\mu}$
$-S\,dT - p\,dV - N\,d\mu$	T,μ	$(\partial S/\partial \mu)_{T,V} = (\partial N/\partial T)_{V,\mu}$
	V,μ	$(\partial p/\partial \mu)_{T,V} = (\partial N/\partial V)_{T,\mu}$
(S,p,μ)	S,p	$(\partial T/\partial p)_{S,\mu} = (\partial V/\partial S)_{p,\mu}$
$T\,dS + V\,dp - N\,d\mu$	S,μ	$(\partial T/\partial \mu)_{S,p} = -(\partial N/\partial S)_{p,\mu}$
	p,μ	$(\partial V/\partial \mu)_{S,p} = -(\partial N/\partial p)_{S,\mu}$
(T,p,μ)	S,p	$-(\partial S/\partial p)_{T,\mu} = (\partial V/\partial T)_{p,\mu}$
$-S\,dT + V\,dp - N\,d\mu$	T,μ	$(\partial S/\partial \mu)_{T,p} = (\partial N/\partial T)_{p,\mu}$
	p,μ	$(\partial V/\partial \mu)_{T,p} = -(\partial N/\partial p)_{T,\mu}$

Source: HB Callen, *Thermodynamics and an Introduction to Thermostatistics*, 2nd edition. Wiley, New York, 1985.

- EXTREMIZAÇÃO DE POTENCIAIS TERMOD.

- ENTROPIA MÁXIMA: SISTEMA ISOLADO

$dU = 0 \Leftarrow U = cte$



$dS = d_i S \geq 0$ → PROCESSO

2ª LEI

EQUILÍBRIO

$\left[dS\right]_{U,V} \geq 0$

$U = U(S,V)$

$\boxed{S = S(U,V)} \Longrightarrow dS = \frac{1}{T}dU + \frac{P}{T}dV$

- ENERGIA INTERNA MÍNIMA: SISTEMAS FECHADOS

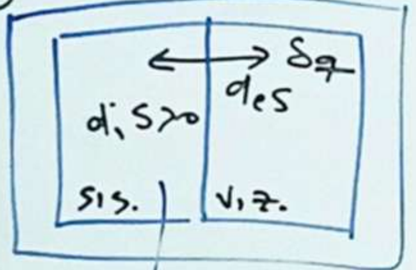
VOLUME CONSTANTE, ENTROPIA CONSTANTE

$dU = -T d_i S \quad [S, V \text{ ctes}]$

$d_i S \geq 0$

$\left[dU\right]_{S,V} \leq 0$

$\boxed{U = U(S,V)}$



$d_i S > 0$

$d_e S = \frac{\delta q}{T}$

$dS = d_i S + d_e S$

$d_e S = dS - d_i S$

S CONSTANTE

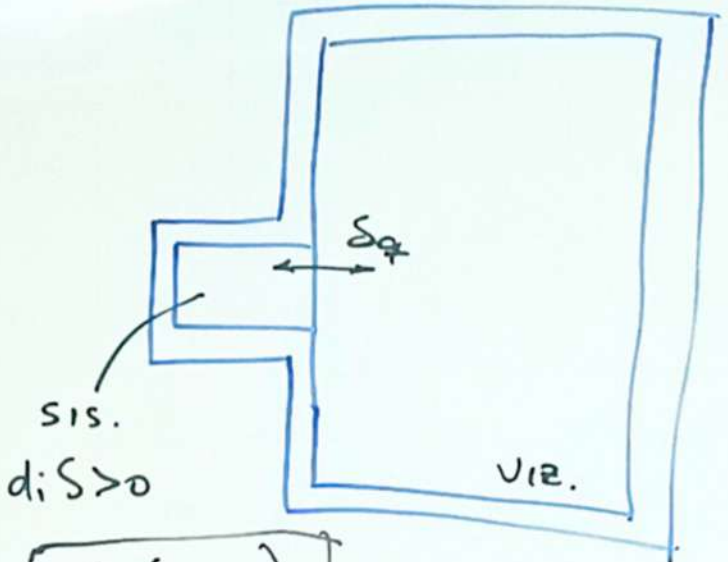
$\underset{\text{SISTEMA}}{dU} = TdS - pdV = TdS - T d_i S - pdV$

0 0

$d_e S = \delta q / T$

- ENERGIA DE HELMHOLTZ MINIMIZADA: SISTEMAS FECHADOS

VOLUME CONSTANTE, TEMPERATURA CONSTANTE



$\boxed{A(T,V)}$

$A = U - TS$

$dA = dU - TdS - SdT$

$= \delta q - pdV - TdS - SdT$

$= \delta q - pdV - T d_i S - \cancel{T d_e S} - SdT$

$= -pdV - T d_i S - SdT$ ($T d_e S = \delta q$, SIST. FECHADO)

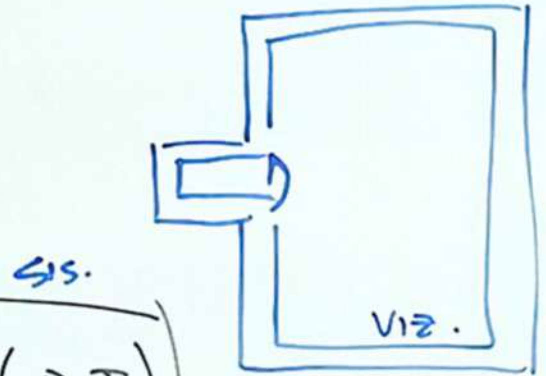
⇓ T, V ctes

$dA = -T d_i S \qquad d_i S \geq 0$

$\left[dA\right]_{T,V} \leq 0$

- ENERGIA DE GIBBS MINIMIZADA:

SISTEMAS FECHADOS, T e P ctes



$\boxed{G(p,T)}$

$G = H - TS = U + pV - TS$

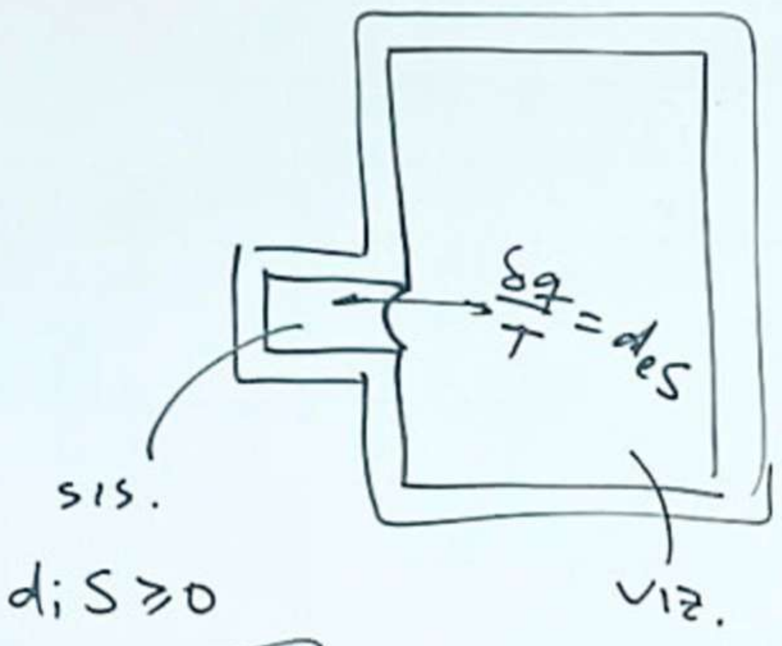
$dG = dU + pdV + Vdp - TdS - SdT$

$= \cancel{\delta q} - \cancel{pdV} + \cancel{pdV} + Vdp - T d_i S - \cancel{T d_e S} - SdT$

$dG = Vdp - T d_i S - SdT \rightarrow dG = -T d_i S$

$p, T \text{ ctes} \quad \left[dG\right]_{p,T} \leq 0$

- ENTALPIA MINIMIZADA: SISTEMAS FECHADOS, ENTROPIA E PRESSÃO CONSTANTES



$d_i S \geq 0$

$$\boxed{H(S,p)}$$

$$H = U + pV$$

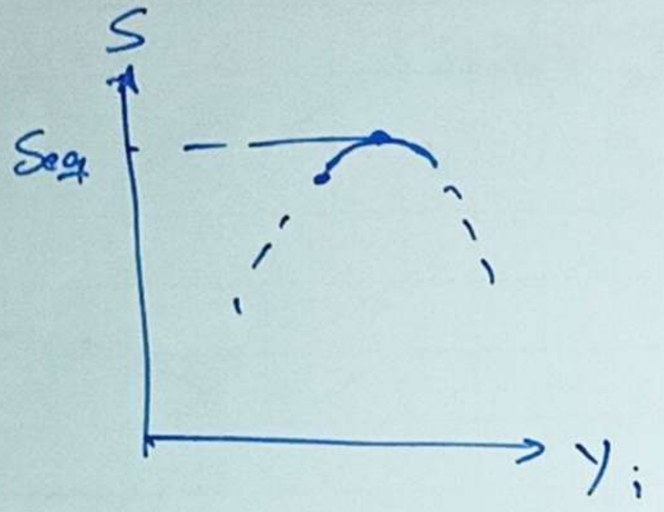
$$dH = \underline{dU} + p\,dV + V\,dp$$
$$= \delta q - p\,dV + V\,dp$$
$$= T\,d_e S + V\,dp$$
$$= T\left(dS - d_i S\right) + V\,dp$$
$$= T\,dS - T\,d_i S + V\,dp$$
$$\Downarrow \quad S, V \text{ ctes}$$

$$dH = -T\,d_i S \qquad d_i S \geq 0$$
$$\Downarrow$$
$$\boxed{[dH]_{S,p} \leq 0}$$

EXT.

	$[dS] \geq 0$
$S(U,V)$	$[dU] \leq 0$
$U(S,V)$	$[dA] \leq 0$
$A(T,V)$	$[dG] \leq 0$
$G(T,p)$	
$H(S,p)$	$[dH] \leq 0$

• ESTABILIDADE



$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

FORÇA X_i

DESLOCAMENTO dY_i

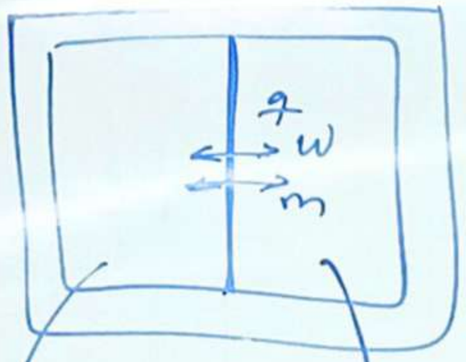
$U_i - U_{eq}$

$$\Delta S_{eq} = S - S_{eq} \cong \left(\frac{\partial S}{\partial U}\right)_{eq}\Delta U_{eq} + \left(\frac{\partial S}{\partial Y}\right)_{eq}\Delta V_{eq} + \left(\frac{\partial S}{\partial N}\right)_{eq}\Delta N_{eq}$$

$S(U,V,N)$ $\quad$ $S(U_{eq},V_{eq},N_{eq})$

$$+\frac{1}{2}\left[\left(\frac{\partial^2 S}{\partial U^2}\right)_{eq}\Delta U_{eq}^2 + \left(\frac{\partial^2 S}{\partial Y^2}\right)_{eq}\Delta V_{eq}^2 + \left(\frac{\partial^2 S}{\partial N^2}\right)_{eq}\Delta N_{eq}^2\right]$$

$$+ \ldots$$



SIST. (A) $\quad$ VIZ. (B)

$$dS = dS_A + dS_B$$

$$dS = \frac{dU_A}{T_A} + \frac{dU_B}{T_B} + \frac{P_A dV_A}{T_A} + \frac{P_B dV_B}{T_B} - \frac{\mu_A dN_A}{T_A} - \frac{\mu_B dN_B}{T_B}$$

$$U_{TOT} = U_A + U_B$$

$$dU_{TOT} = 0$$

$$dU_A = -dU_B = dU$$

$$dV_A = -dV_B = dV$$

$$dN_A = -dN_B = dN$$

$$dS = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)dU + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)dV - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right)dN$$

→ $dS = 0$ eq

CONDIÇÕES

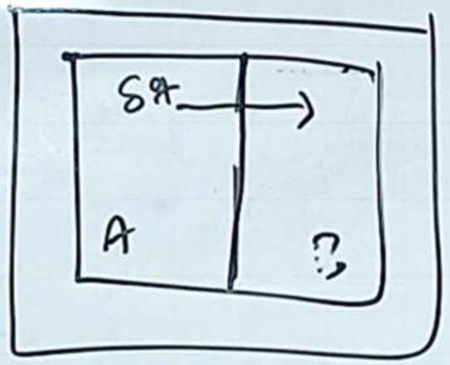
$\frac{1}{T_A} = \frac{1}{T_B} \Rightarrow T_A = T_B$ EQ. TÉRMICO

$\frac{P_A}{T_A} = \frac{P_B}{T_B} \Rightarrow P_A = P_B$ EQ. MECÂNICO

$\frac{\mu_A}{T_A} = \frac{\mu_B}{T_B} \Rightarrow \mu_A = \mu_B$ EQ. COMPOSICIONAL

→ $dS > 0$

PROCESSOS ESPONTÂNEOS



$dU = dU_A = dU_B$

$dU_V = \delta q_V$

$\delta q < 0$

SAINDO DE A.
PARA B

$T_A > T_B$

CALOR FLUI DO QUENTE PRO FRIO

V, N ctes

$$dS = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU$$

$dS > 0$

$\underline{\delta q} < 0$

$$\frac{1}{T_A} - \frac{1}{T_B} < 0 \qquad \frac{1}{T_A} < \frac{1}{T_B}$$

$$\underline{\underline{T_B < T_A}}$$