Revisão de Termodinâmica – 1

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As representações alternativas da termodinâmica

- Nas representações de **entropia** e **energia**,

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

as variáveis extensivas são independentes, enquanto as intensivas são dependentes (obtidas via derivação),

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \qquad\qquad \left(\frac{\partial U}{\partial S}\right)_{V,N} = T$$

- Será que é possível achar uma **representação** onde as **intensivas são as variáveis independentes**?

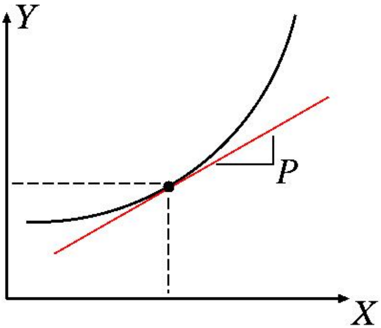
Sim, através das chamadas **transformações de Legendre**

Tipos de transformações de Legendre

→ Funções de Massieu (Massieu, 1869): transformações de Legendre da entropia

→ Potenciais termodinâmicos (Gibbs, 1875): transformações de Legendre da energia interna

Transformações de Legendre



Dado

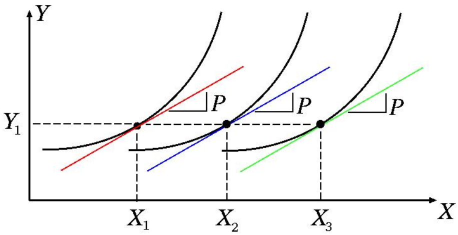
$$Y = Y(X)$$

tal que sua derivada P se escreve como

$$P = \frac{\partial Y}{\partial X} \; .$$

É possível encontrar uma representação onde P é a variável independente?

Adrien-Marie Legendre (1752-1833): uma transformada de Legendre converte uma função Y, definida para um conjunto de variáveis X, para uma outra função, expressa em termos de variáveis P, conjugadas às variáveis originais X da função transformada.



Tomar simplesmente

$$Y = Y(P)$$

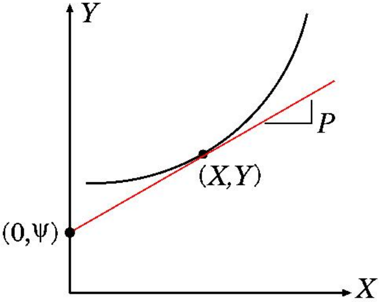
Impossível, pois o conhecimento de Y em função de sua derivada,

$$dY/dX = P$$

não permite a reconstrução da função original

$$Y = Y(X)$$

Transformações de Legendre - 2ª tentativa



Tomar a inclinação P e a intersecção ψ com o eixo Y,

$$P = \frac{Y - \psi}{X - 0}$$

Transformada de Legendre de Y

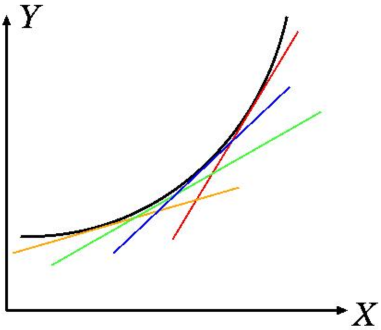
$$\psi = Y - PX$$

$$d\psi = dY - PdX - XdP$$

Mas $P = dY/dX$, ou seja,

$$d\psi = -XdP \quad \rightarrow \quad -X = \frac{d\psi}{dP}$$

Transformações de Legendre - 2ª tentativa



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Roteiro para uma transformação de Legendre

$Y = Y(X)$	$\psi = \psi(P)$
$P = \dfrac{dY}{dX}$	$-X = \dfrac{d\psi}{dP}$
$\psi = -PX + Y$	$Y = XP + \psi$
eliminando X e Y temos: $\psi = \psi(P)$	eliminando P e ψ produzimos: $Y = Y(X)$

De forma geral, para uma função Y qualquer, com n variáveis independentes, existem 2^n possíveis transformações de Legendre ψ.

A função de Massieu $J \equiv S[1/T]$

Transformada de Legendre na formulação de entropia: $S = S(U, V, N)$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N_1,...} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N_1,...} dV + \left(\frac{\partial S}{\partial N_1}\right)_{U,V,N_2,...} dN_1 + \left(\frac{\partial S}{\partial N_2}\right)_{U,V,N_1,...} dN_2 + \dots$$

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu_1}{T}dN_1 - \frac{\mu_2}{T}dN_2 + \dots$$

$$dS = d\left(\frac{U}{T}\right) - Ud\left(\frac{1}{T}\right) + \frac{p}{T}dV - \frac{\mu_1}{T}dN_1 - \frac{\mu_2}{T}dN_2 + \dots$$

$$d\left(S - \frac{U}{T}\right) \equiv dJ = -Ud\left(\frac{1}{T}\right) + \frac{p}{T}dV - \frac{\mu_1}{T}dN_1 - \frac{\mu_2}{T}dN_2 + \dots$$

Função de Massieu

$$J \equiv S - \frac{U}{T}$$

$$J = J\left(\frac{1}{T}, V, N_1, N_2, \dots\right)$$

A função de Massieu $J \equiv S[1/T]$

Como $J = J\left(\frac{1}{T}, V, N\right)$

$$dJ = \left(\frac{\partial J}{\partial(1/T)}\right)_{V,N} d\left(\frac{1}{T}\right) + \left(\frac{\partial J}{\partial V}\right)_{1/T,N} dV + \left(\frac{\partial J}{\partial N}\right)_{1/T,V} dN$$

mas

$$dJ = -Ud\left(\frac{1}{T}\right) + \frac{p}{T}dV - \frac{\mu}{T}dN$$

ou seja,

$$\left(\frac{\partial J}{\partial(1/T)}\right)_{V,N} = -U\,, \quad \text{e} \quad \left(\frac{\partial J}{\partial V}\right)_{1/T,N} = \frac{p}{T}\,, \quad \text{e} \quad \left(\frac{\partial J}{\partial N}\right)_{1/T,V} = -\frac{\mu}{T}$$

$S = S(U, V, N)$	$J = J(1/T, V, N)$
$1/T = (\partial S/\partial U)_V$	$-U = (\partial J/\partial(1/T))_V$
$J = S - U/T$	$S = U/T + J$
eliminando S e U temos: $J = J(1/T, V, N)$	eliminando $1/T$ e J produzimos: $S = S(U, V, N)$

Potencial de Helmholtz $F \equiv U[T]$

Transformada de Legendre na formulação de energia: $U = U(S, V, N)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N_1,\dots} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N_1,\dots} dV + \left(\frac{\partial U}{\partial N_1}\right)_{S,V,N_2,\dots} dN_1 + \left(\frac{\partial U}{\partial N_2}\right)_{S,V,N_1,\dots} dN_2 + \dots$$

$$dU = TdS - pdV + \mu_1 dN_1 + \mu_2 dN_2 + \dots$$

$$\begin{aligned} dU &= d(TS) - SdT - pdV + \mu_1 dN_1 + \mu_2 dN_2 + \dots \\ d(U - TS) &\equiv dF = -SdT - pdV + \mu_1 dN_1 + \mu_2 dN_2 + \dots \end{aligned}$$

Potencial de Helmholtz

$$F \equiv U - TS$$

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

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

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN$$

Mas

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

ou seja,

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

$U = U(S, V, N)$	$F = F(T, V, N)$
$T = (\partial U/\partial S)_V$	$-S = (\partial F/\partial T)_V$
$F = -TS + U$	$U = TS + F$
eliminando S e U temos: $F = F(T, V, N)$	eliminando T e F produzimos: $U = U(S, V, N)$

Entalpia $H \equiv U[p]$

Transformada de Legendre na formulação de energia: $U = U(S, V, N)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N_1,\ldots} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N_1,\ldots} dV + \left(\frac{\partial U}{\partial N_1}\right)_{S,V,N_2,\ldots} dN_1 + \left(\frac{\partial U}{\partial N_2}\right)_{S,V,N_1,\ldots} dN_2 + \ldots$$

$$\begin{aligned} dU &= TdS - pdV + \mu_1 dN_1 + \mu_2 dN_2 + \ldots \\ &= TdS - d(pV) + Vdp + \mu_1 dN_1 + \mu_2 dN_2 + \ldots \\ d(U + pV) &\equiv dH = TdS + Vdp + \mu_1 dN_1 + \mu_2 dN_2 + \ldots \end{aligned}$$

Entalpia

$$H = U + pV$$

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

Entalpia $H \equiv U[p]$

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

$$dF = \left(\frac{\partial H}{\partial S}\right)_{p,N} dS + \left(\frac{\partial H}{\partial p}\right)_{S,N} dp + \left(\frac{\partial H}{\partial N}\right)_{S,p} dN$$

Mas

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

ou seja,

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

$U = U(S, V, N)$	$H = H(S, p, N)$
$-p = (\partial U/\partial V)_S$	$V = (\partial H/\partial p)_S$
$H = pV + U$	$U = -pV + H$
eliminando V e U temos: $H = H(S, p, N)$	eliminando p e H produzimos: $U = U(S, V, N)$

Potencial de Gibbs $G \equiv U[T, p]$

Transformada de Legendre **na formulação de energia:** $U = U(S, V, N)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N_1,\ldots} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N_1,\ldots} dV + \left(\frac{\partial U}{\partial N_1}\right)_{S,V,N_2,\ldots} dN_1 + \left(\frac{\partial U}{\partial N_2}\right)_{S,V,N_1,\ldots} dN_2 + \ldots$$

$$\begin{aligned} dU &= TdS - pdV + \mu_1 dN_1 + \mu_2 dN_2 + \ldots \\ &= d(TS) - SdT - d(pV) + Vdp + \mu_1 dN_1 + \mu_2 dN_2 + \ldots \\ d(U - TS + pV) &\equiv dG = -SdT + Vdp + \mu_1 dN_1 + \mu_2 dN_2 + \ldots \end{aligned}$$

Potencial de Gibbs

$$G = U - TS + pV$$

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

Potencial de Gibbs $G \equiv U[T, p]$

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

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,N} dT + \left(\frac{\partial G}{\partial p}\right)_{T,N} dp + \left(\frac{\partial G}{\partial N}\right)_{T,p} dN$$

Mas

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

ou seja,

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

$U = U(S, V, N)$	$G = G(T, p, N)$
$T = (\partial U/\partial S)_V$	$-S = (\partial G/\partial T)_V$
$p = -(\partial U/\partial V)_S$	$V = (\partial G/\partial p)_T$
$G = U - TS + pV$	$U = TS - pV + G$
eliminando S, V e U temos: $G = G(T, p, N)$	eliminando T, p e G produzimos: $U = U(S, V, N)$

Grande potencial $U[T, \mu]$

Transformada de Legendre na formulação de energia: $U = U(S, V, N)$

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

$$\begin{aligned} dU &= TdS - pdV + \mu dN \\ &= d(TS) - SdT - pdV + d(\mu N) - Nd\mu \\ d(U - TS - \mu N) &\equiv dU[T, \mu] = -SdT - pdV - Nd\mu \end{aligned}$$

Grande potencial

$$U[T, \mu] = U - TS - \mu N$$

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

Grande potencial $U[T, \mu]$

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

$$dU[T, \mu] = \left(\frac{\partial U[T, \mu]}{\partial T}\right)_{V,\mu} dT + \left(\frac{\partial U[T, \mu]}{\partial V}\right)_{T,\mu} dV + \left(\frac{\partial U[T, \mu]}{\partial \mu}\right)_{T,V} d\mu$$

Mas $\quad dU[T, \mu] = -SdT - pdV - Nd\mu$

ou seja,

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

$U = U(S, V, N)$	$U[T, \mu] = U[T, \mu](T, V, \mu)$
$T = (\partial U/\partial S)_{V,N}$	$-S = (\partial U[T, \mu]/\partial T)_{V,\mu}$
$\mu = (\partial U/\partial N)_{S,V}$	$-N = (\partial U[T, \mu]/\partial \mu)_{T,V}$
$U[T, \mu] = U - TS - \mu N$	$U = TS + \mu N + U[T, \mu]$
eliminando S, N e U temos: $U[T, \mu] = U[T, \mu](T, V, \mu)$	eliminando T, μ e $U[T, \mu]$ produzimos: $U = U(S, V, N)$

Origem:

Série de relações entre derivadas do tipo

$$(\partial X/\partial Y)_{Z,W,\ldots}$$

originadas da igualdade entre as derivadas parciais mistas (teorema de Schwarz) das equações fundamentais, nas diferentes representações da termodinâmica.

Relações de Maxwell

Objetivo: Encontrar relações entre as muitas derivadas do tipo $(\partial X/\partial Y)_{Z,W,\ldots}$

$$U = U(S,V,N) \qquad \rightarrow \qquad dU = TdS - pdV + \mu dN$$

$$\left(\frac{\partial^2 U}{\partial S \partial V}\right)_N = \left(\frac{\partial^2 U}{\partial V \partial S}\right)_N$$

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

Mas

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

ou

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

$$\left(\frac{\partial^2 U}{\partial S \partial N}\right)_V = \left(\frac{\partial^2 U}{\partial N \partial S}\right)_V$$

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

Mas

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

ou

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

Relações de Maxwell

Objetivo: Encontrar relações entre as muitas derivadas do tipo $(\partial X/\partial Y)_{Z,W,\dots}$

$$U = U(S,V,N) \qquad \rightarrow \qquad dU = TdS - pdV + \mu dN$$

$$\left(\frac{\partial^2 U}{\partial S \partial V}\right)_N = \left(\frac{\partial^2 U}{\partial V \partial S}\right)_N$$

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

Mas

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

ou

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

$$\left(\frac{\partial^2 U}{\partial V \partial N}\right)_S = \left(\frac{\partial^2 U}{\partial N \partial V}\right)_S$$

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

Mas

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

ou

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

Relações de Maxwell

Objetivo: Encontrar relações entre as muitas derivadas do tipo $(\partial X/\partial Y)_{Z,W,...}$

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

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

$$\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

Mas

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

ou

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

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

$$\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial N}\right)_{T,V} = \frac{\partial}{\partial N}\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

Mas

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

ou

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Relações de Maxwell

Objetivo: Encontrar relações entre as muitas derivadas do tipo $(\partial X/\partial Y)_{Z,W,\ldots}$

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$$\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

Mas

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

ou

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

$$\left(\frac{\partial^2 F}{\partial V \partial N}\right)_T = \left(\frac{\partial^2 F}{\partial N \partial V}\right)_T$$

$$\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial N}\right)_{T,V} = \frac{\partial}{\partial N}\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

Mas

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

ou

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

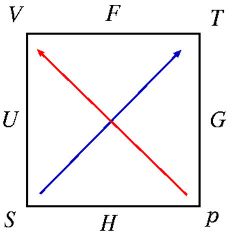
Relações de Maxwell :

De maneira geral, dado um potencial termodinâmico qualquer, expresso em termos de suas $(t+1)$ *variáveis naturais, existem* $t(t+1)/2$ *pares separados de* 2^{as} *derivadas mistas, tal que cada potencial produzirá* $t(t+1)/2$ *relações de Maxwell*

O quadrado termodinâmico

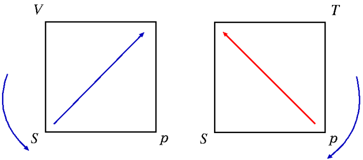
Diagrama mnemônico de Max Born (1929)

F. O. Koenig, J. Chem. Phys. **3**, 29 (1935); **56**, 4556 (1972)
L. T. Klauder, Am. Journ. Phys. **36**, 556 (1968)

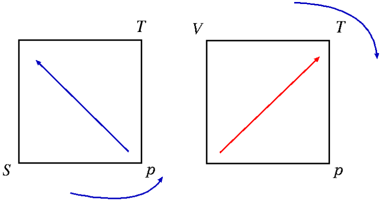


"Valid Facts and Theoretical Understanding Generate Solutions to Hard problems"

O quadrado termodinâmico



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



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

Uma regra mais simples ainda

Como saber de onde saiu a derivada $\left(\frac{\partial p}{\partial T}\right)_{VN}$?

- Encontre o potencial que possui como variáveis independentes T, V, N

$$\left(\frac{\partial p}{\partial T}\right)_{VN} \qquad \rightarrow \qquad F = F(T, V, N)$$

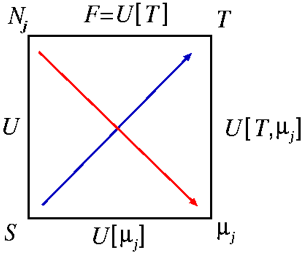
- Encontre a relação de Maxwell correspondente a segunda variação deste potencial

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

Como $\left(\frac{\partial F}{\partial V}\right)_{T,N} = -p$ e $\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S$ segue que

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

Outros tipos de diagramas de Max Born



$$\left(\frac{\partial T}{\partial N_j}\right)_{SV} = \left(\frac{\partial \mu_j}{\partial S}\right)_{N_j V}$$

$$-\left(\frac{\partial S}{\partial N_j}\right)_{TV} = \left(\frac{\partial \mu_j}{\partial T}\right)_{N_j V}$$

$$\left(\frac{\partial T}{\partial \mu_j}\right)_{SV} = -\left(\frac{\partial N_j}{\partial S}\right)_{\mu_j V}$$

$$\left(\frac{\partial S}{\partial \mu_j}\right)_{TV} = \left(\frac{\partial N_j}{\partial T}\right)_{\mu_j V}$$