Relações de Maxwell

P G T
H F
S E V

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T} \Rightarrow \left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V$$

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P} \Rightarrow \left.\frac{\partial S}{\partial P}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_P$$

Capacidades caloríficas:

Dado que um sistema receba $\bar{d}Q$ quasi-estaticamente

$$C_y = \left.\frac{\bar{d}Q}{dT}\right|_y = T\left.\frac{dS}{dT}\right|_y = T\left.\frac{\partial S}{\partial T}\right|_y.$$

Os casos mais comuns são:

$$C_V = \left.\frac{\bar{d}Q}{dT}\right|_V = T\left.\frac{\partial S}{\partial T}\right|_V = \left.\frac{\partial E}{\partial T}\right|_V \quad \text{pois } \bar{d}Q = dE - PdV$$

$$C_P = \left.\frac{\bar{d}Q}{dT}\right|_P = T\left.\frac{\partial S}{\partial T}\right|_P = \left.\frac{\partial H}{\partial T}\right|_P \quad \text{pois } \bar{d}Q = d(E+PV) - VdP$$

Coeficiente de expansão a pressão constante.

$$\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P$$

Coeficiente de compressibilidade isotérmica

$$k_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T$$

Coeficiente de compressibilidade adiabática

$$k_S = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_S$$

Relações importantes entre derivadas parciais

Consideremos as variáveis x, y, z tais que

$f(x,y,z) = \text{const.} \Rightarrow z = z(x,y)$ ou $y = y(x,z)$

ou $x = x(y,z)$

$$\left.\frac{\partial x}{\partial y}\right|_f \left.\frac{\partial y}{\partial z}\right|_f = \left.\frac{\partial x}{\partial z}\right|_f \quad ; \quad \left.\frac{\partial x}{\partial y}\right|_z = \frac{1}{\left.\frac{\partial y}{\partial x}\right|_z}$$

$$\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x \left.\frac{\partial z}{\partial x}\right|_y = -1$$

$$\Rightarrow \left.\frac{\partial T}{\partial P}\right|_V \left.\frac{\partial P}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P = -1$$

Escrevendo $S = S(T,P)$ temos

$$T\,dS = T\left.\frac{\partial S}{\partial T}\right|_P dT + T\left.\frac{\partial S}{\partial P}\right|_T dP$$

$$\Rightarrow T\,dS = C_P\,dT - T\left.\frac{\partial V}{\partial T}\right|_P dP \qquad (1)$$

Se $S = S(T,V)$

$$\Rightarrow T\,dS = T\left.\frac{\partial S}{\partial T}\right|_V dT + T\left.\frac{\partial S}{\partial V}\right|_T dV$$

$$\Rightarrow T\,dS = C_V\,dT + T\left.\frac{\partial P}{\partial T}\right|_V dV \qquad (2)$$

$$\Rightarrow C_P\,dT - T\left.\frac{\partial V}{\partial T}\right|_P dP = C_V\,dT + T\left.\frac{\partial P}{\partial T}\right|_V dV$$

$$(C_P - C_V)\,dT = T\left.\frac{\partial P}{\partial T}\right|_V dV + T\left.\frac{\partial V}{\partial T}\right|_P dP$$

$$dT = \left.\frac{\partial T}{\partial V}\right|_P dV + \left.\frac{\partial T}{\partial P}\right|_V dP$$

$$\Rightarrow \left[(C_P - C_V)\left.\frac{\partial T}{\partial V}\right|_P - T\left.\frac{\partial P}{\partial T}\right|_V\right] dV + \left[(C_P - C_V)\left.\frac{\partial T}{\partial P}\right|_V + T\left.\frac{\partial V}{\partial T}\right|_P\right] dP = 0$$

$$(C_p - C_v)\left.\frac{\partial T}{\partial V}\right|_p = T\left.\frac{\partial P}{\partial T}\right|_V$$

$$\Rightarrow C_p - C_v = TV\frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_p \left.\frac{\partial P}{\partial T}\right|_V = TV\alpha\left.\frac{\partial P}{\partial T}\right|_V$$

$$\left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial T}{\partial V}\right|_P \left.\frac{\partial V}{\partial P}\right|_T = -1 \Rightarrow \left.\frac{\partial P}{\partial T}\right|_V = \left(-\left.\frac{\partial V}{\partial P}\right|_T\right)^{-1} \cdot \left.\frac{\partial V}{\partial T}\right|_P$$

$$= \frac{\alpha}{\kappa_T} \Rightarrow \boxed{C_p - C_v = TV\frac{\alpha^2}{\kappa_T}}$$

$$dS = 0 \Rightarrow \text{por (1)} \rightarrow C_p\, dT = T\left.\frac{\partial V}{\partial T}\right|_p dP$$

$$\text{por (2)} \rightarrow C_v\, dT = -T\left.\frac{\partial P}{\partial T}\right|_V dV$$

$$\Rightarrow C_p = T\left.\frac{\partial V}{\partial T}\right|_p \left.\frac{\partial P}{\partial T}\right|_S = TV\alpha\left.\frac{\partial P}{\partial T}\right|_S$$

$$C_v = -T\left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial V}{\partial T}\right|_S = -T\frac{\alpha}{\kappa_T}\left.\frac{\partial V}{\partial T}\right|_S$$

$$\Rightarrow \frac{C_p}{C_v} = -V\kappa_T\left(\frac{\partial P}{\partial T}\right)_S\left(\frac{\partial T}{\partial V}\right)_S = -V\kappa_T\left.\frac{\partial P}{\partial V}\right|_S = \frac{\kappa_T}{\kappa_S}.$$

$$\boxed{\frac{C_p}{C_v} = \frac{\kappa_T}{\kappa_S}}$$

<u>Relação de Gibbs-Duhem</u>:

Extensividade: $E \to \lambda E$, $V \to \lambda V$ e $N \to \lambda N$

$$\Rightarrow \lambda S = S(\lambda E, \lambda V, \lambda N)$$

$$\Rightarrow S = \frac{\partial S}{\partial(\lambda E)}E + \frac{\partial S}{\partial(\lambda V)}V + \frac{\partial S}{\partial(\lambda N)}N \Rightarrow \lambda = 1$$

$$S = \frac{\partial S}{\partial E}E + \frac{\partial S}{\partial V}V + \frac{\partial S}{\partial N}N$$

(12)

$$\Rightarrow S = \frac{E}{T} + \frac{PV}{T} - \frac{\mu N}{T}$$

$$F = E - TS \qquad G = E - TS + PV \qquad \Omega = E - TS - \mu N$$

$$\Rightarrow TS = E + PV - \mu N \Rightarrow \boxed{F = \mu N - PV}$$

$$\boxed{G = \mu N} \qquad \boxed{\Omega = -PV}$$

$$dG = -S\,dT + V\,dP + \mu\,dN = \mu\,dN + N\,d\mu$$

$$\Rightarrow \boxed{N\,d\mu + S\,dT - V\,dP = 0} \quad \text{Gibbs-Duhem.}$$

Processo isotérmico: $dT = 0$

$$\Rightarrow N\,d\mu = V\,dP \Rightarrow \boxed{\left.\frac{\partial P}{\partial \mu}\right|_T = n = \frac{N}{V}}$$

Grandeza importante: $\left.\frac{\partial \mu}{\partial n}\right|_T = ?$

$$k_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T \Rightarrow \frac{1}{k_T} = -v\left.\frac{\partial P}{\partial v}\right|_T = \frac{-1}{n}\left.\frac{\partial P}{\partial n}\right|_T \left.\frac{\partial n}{\partial v}\right|_T$$

$$n = \frac{1}{v} \Rightarrow \frac{\partial n}{\partial v} = -\frac{1}{v^2} \Rightarrow \frac{1}{k_T} = -\frac{1}{n}\left.\frac{\partial P}{\partial n}\right|_T (-)\frac{1}{v^2}$$

$$\Rightarrow \frac{1}{k_T} = n\left.\frac{\partial P}{\partial n}\right|_T = n\left.\frac{\partial P}{\partial \mu}\right|_T \left.\frac{\partial \mu}{\partial n}\right|_T = n^2\left.\frac{\partial \mu}{\partial n}\right|_T$$

$$\Rightarrow \boxed{\left.\frac{\partial \mu}{\partial n}\right|_T = \frac{1}{n^2 k_T}}$$

Condições de estabilidade.

Concavidade da entropia: generalização p/ N variáveis

$$S(E+\Delta E, V+\Delta V) + S(E-\Delta E, V-\Delta V) \leq 2S(E,V)$$

$$\Rightarrow (\Delta S)_{(E,V)} \leq 0$$

Interpretação:

$$\Rightarrow S(E \pm \Delta E, V \pm \Delta V) \simeq S(E,V) \pm \Delta E \frac{\partial S}{\partial E} \pm \Delta V \frac{\partial S}{\partial V}$$

$$+ \frac{1}{2}(\Delta V)^2 \frac{\partial^2 S}{\partial V^2} + \frac{1}{2}(\Delta E)^2 \frac{\partial^2 S}{\partial E^2} + \Delta E \Delta V \frac{\partial^2 S}{\partial E \partial V}$$

que levado em $(\Delta S)_{(E,V)} \leq 0 \Rightarrow$

$$(\Delta E)^2 \frac{\partial^2 S}{\partial E^2} + (\Delta V)^2 \frac{\partial^2 S}{\partial V^2} + 2\Delta E \Delta V \frac{\partial^2 S}{\partial E \partial V} \leq 0$$

Seja $E = E_1 + E_2$ e $V = V_1 + V_2$

vínculo: $E_1 \to E_1 + \Delta E$ e $E_2 \to E_2 - \Delta E$

$V_1 \to V_1 + \Delta V$ e $V_2 \to V_2 - \Delta V$

$$\Rightarrow S(E_1 + \Delta E, V_1 + \Delta V) + S(E_2 - \Delta E, V_2 - \Delta V) \leq S(E,V)$$

mas S é uma função crescente de $E \Rightarrow \exists\ \tilde{E}$ tal que

$$S(E_1 + \Delta E, V_1 + \Delta V) + S(E_2 - \Delta E, V_2 - \Delta V) = S(\tilde{E}, V)$$

$\Rightarrow$ a entropia constante vínculos impõem

$E_1 + E_2 = E \geq \tilde{E}$ ou $(\Delta E)_{(S,V)} \geq 0$

concavidade de $S \iff$ convexidade de E

$$\Rightarrow (\Delta S)^2 \frac{\partial^2 E}{\partial S^2} + (\Delta V)^2 \frac{\partial^2 E}{\partial V^2} + 2\Delta V \Delta S \frac{\partial^2 E}{\partial S \partial V} \geq 0$$

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ou, em termos de $\mathcal{E}$

$$\mathcal{E} = \begin{pmatrix} \partial^2 E/\partial S^2 & \partial^2 E/\partial S \partial V \\ \partial^2 E/\partial V \partial S & \partial^2 E/\partial V^2 \end{pmatrix} = \begin{pmatrix} E''_{SS} & E''_{SV} \\ E''_{VS} & E''_{VV} \end{pmatrix}$$

Temos $x^T \mathcal{E} x \geq 0$ onde $x^T = (\Delta S, \Delta V)$

Em geral $x^T A x = \sum_{ij=1}^{N} x_i A_{ij} x_j \geq 0$ (matriz positiva)

$x_i = \sum R_{ij} y_j \Rightarrow$ se $R^{-1} A R = \Lambda$ $\quad x^T A x = y^T \Lambda y$

$= \sum_i \lambda_i y_i^2 \geq 0 \Rightarrow \lambda_i \geq 0$

$$\begin{pmatrix} a & b \\ b & c \end{pmatrix} \to \begin{pmatrix} a-\lambda & b \\ b & c-\lambda \end{pmatrix} = (a-\lambda)(c-\lambda) - b^2 = 0$$

$\Rightarrow \lambda^2 - a\lambda - c\lambda + ac - b^2 = 0 \Rightarrow \lambda = \frac{a+c}{2} \pm \frac{1}{2}\sqrt{(a+c)^2 - 4ac + 4b^2}$

$\lambda^2 - (a+c)\lambda + ac - b^2$

$$\lambda = \frac{a+c}{2} \pm \frac{1}{2}\sqrt{(a-c)^2 + b^2} = \frac{a+c}{2} \pm \sqrt{\left(\frac{a-c}{2}\right)^2 + b^2}$$

$$\frac{a+c}{2} \pm \sqrt{\left(\frac{a-c}{2}\right)^2 + b^2} \geq 0 \Rightarrow \frac{a+c}{2} \geq \mp \sqrt{\left(\frac{a-c}{2}\right)^2 + b^2}$$

$$\frac{(a+c)^2}{4} \geq \frac{(a-c)^2}{4} + b^2 \Rightarrow \left(\frac{a+c}{2} + \frac{a-c}{2}\right)\left(\frac{a+c}{2} - \frac{a-c}{2}\right) \geq b^2$$

$ac \geq b^2 \Rightarrow a + c \geq 0$ e $ac \geq b^2 \Rightarrow a \geq 0$ e $c \geq 0$

se a matriz é negativa $a \leq 0$ e $c \leq 0$

$\Rightarrow$ energia é convexa em S e V

o que acontece com os potenciais termodinâmicos?

Seja $f(x)$ convexa $\Rightarrow f''(x) \geq 0$

Queremos estudar $f'(x) = u \Rightarrow$ solução: $x = x(u)$

$\Rightarrow df = f'(x)\,dx = u\,dx = u\,dx + x\,du - x\,du$

$\Rightarrow df = d(xu) - x\,du \Rightarrow d(f - xu) = -x\,du$

$g(u) \equiv f(x(u)) - x(u)u$ e $dg = -x(u)\,du$

Assim $\frac{dg}{du} = -x(u)$ e $\frac{d^2g}{du^2} = -\frac{dx}{du} = -\frac{1}{du/dx}$

$= -\frac{1}{f''(x)} \leq 0 \Rightarrow$ convexidade em $\underline{x} \rightarrow$

concavidade em $\underline{u} \rightarrow$ generalização p/ mais variáveis

Assim: H convexa em S e côncava em P ← sela

F côncava em T e convexa em V ← sela

G côncava em T e côncava em P ← máx.

Estabilidade: G''_{TT}, G''_{TP}, G''_{PP}

$$G''_{TT} = -\left.\frac{\partial S}{\partial T}\right|_P = -\frac{C_P}{T} \leq 0 \Rightarrow C_P \geq 0$$

$$G''_{PP} = \left.\frac{\partial V}{\partial P}\right|_T = -V\kappa_T \leq 0 \Rightarrow \kappa_T \geq 0$$

$$G''_{TT}G''_{PP} - (G''_{TP})^2 \geq 0$$

Usando que $G''_{PT} = \left.\frac{\partial V}{\partial T}\right|_P = \alpha V$ Temos

$$\frac{V}{T}C_P\kappa_T - \alpha^2V^2 \geq 0 \Rightarrow C_P - \frac{\alpha^2TV}{\kappa_T} \geq 0$$

mas $C_P - C_V = \frac{\alpha^2TV}{\kappa_T} \Rightarrow C_V \geq 0$

$\Rightarrow \boxed{C_V \geq 0}$ e $\boxed{\kappa_T \geq 0}$ $\left\} \begin{array}{l} C_P \geq C_V \geq 0 \\ \kappa_T \geq \kappa_S \geq 0 \end{array}\right.$

3ª Lei

$$\lim_{T\to 0} \lim_{V\to\infty} \frac{1}{V} S(V) = 0$$

Comportamento das capacidades caloríficas a $T \to 0$.

$$S(T,P,V) = S_0 + \int_0^T dT' \frac{C_{P,V}(T')}{T'}$$ ao longo de

caminhos com P ou V constantes.

Integral deve convergir p/ $T' \to 0$

$\Rightarrow$ $T \to 0$ $\Rightarrow$ $C_P, C_V \to 0$

Além do mais $\alpha = \frac{1}{V} \left.\frac{\partial V}{\partial T}\right|_P \to 0$ e $\left.\frac{\partial P}{\partial T}\right|_V \to 0$

quando $T \to 0$.

Dem:

rel. Maxwell $\frac{\partial^2 V}{\partial T^2} = -\frac{\partial}{\partial T}\left[\left.\frac{\partial S}{\partial P}\right|_T\right]_P = -\frac{\partial}{\partial P}\left[\frac{C_P}{T}\right]_T$

Por outro lado $\left.\frac{\partial V}{\partial T}\right|_P = -\left.\frac{\partial S}{\partial P}\right|_T = -\frac{\partial}{\partial P}\left[S_0 + \int_0^T dT' \frac{C_P(T')}{T'}\right]_T$

$$\Rightarrow \left.\frac{\partial V}{\partial T}\right|_P = -\int_0^T \frac{dT'}{T'} \left.\frac{\partial C_P}{\partial P}\right|_T = \int_0^T dT' \left.\frac{\partial^2 V}{\partial T'^2}\right|_P = \left.\frac{\partial V}{\partial T}\right|_P - \left.\frac{\partial V}{\partial T}\right|_P^{T=0}$$

$$\Rightarrow \left.\frac{\partial V}{\partial T}\right|_P^{T=0} = 0 \Rightarrow \alpha = 0.$$

Demonstração análoga p/ $\partial P/\partial T|_V$ usando a outra rel. de Maxwell.

Le Bellac: $T \to 0$ $\frac{C_P - C_V}{C_P} \sim \alpha T$