Sistema P, V, T, N

Parâmetros externos $\Rightarrow$ $V \equiv$ volume; $N \equiv$ nº de partículas $\Longleftrightarrow$ "Forças generalizadas" $P \equiv$ pressão; $\mu \equiv$ potencial químico.

$V \longleftrightarrow P$

$N \longleftrightarrow \mu$

Lei Zero $\Rightarrow$ Temperatura, T

$\boxed{dW = PdV - \mu dN}$ — μdN: nº partículas cte.

1ª Lei $\Longrightarrow$ $\boxed{dU = dQ - dW}$

Energia interna U

$\boxed{f(P, V, T, N) = 0}$ — Equação de Estado

$\boxed{f(U, V, T, N) = 0}$ — Equação de Energia

$\boxed{U = U(T, V, N)}$ $\rightarrow$ Transf. de Legendre $\rightarrow$ Entalpia $H = H(P, T, N)$

Transf. de Legendre $\Updownarrow$ $\boxed{H := U + PV}$ $\rightarrow$ $\boxed{f(H, T, V, N) = 0}$ — Eq. de Entalpia

1ª lei $\rightarrow$ $\boxed{dH = dQ + VdP}$

$dQ \equiv$ Calor trocado $\rightarrow$ calor específico à volume cte. $C_V := \left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$

Calor específico à pressão cte: $C_P := \left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$

$dH = dQ + VdP$

$dQ = \left(\frac{\partial H}{\partial T}\right)_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP$ $\rightarrow$ $C_P := \left(\frac{dQ}{dT}\right)_P$ $\rightarrow$ $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

$dU = dQ - PdV \leftarrow U(V, T)$

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

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

2ª Lei $\Longrightarrow$ Entropia, S $\Longleftrightarrow$ $\boxed{dQ := TdS}$

1ª lei: $\{dU = TdS - PdV\}$

$T \rightarrow S$

1ª lei: $dH = TdS + VdP$

1ª lei: $dH = dQ + VdP$ $\rightarrow$ $\boxed{dH = TdS + VdP}$

1ª lei: $dU = dQ - PdV$ $\rightarrow$ $\boxed{dU = TdS - PdV}$

$\boxed{U = U(S, V)} \Longrightarrow \left(\frac{\partial U}{\partial S}\right)_V = T$, $\left(\frac{\partial U}{\partial V}\right)_S = -P$

$\left(\frac{\partial H}{\partial S}\right)_P = T$, $\left(\frac{\partial H}{\partial P}\right)_S = V$ $\Leftarrow$ $\boxed{H = H(S, P)}$

Transf. de Legendre $\rightarrow$ $F = F(T, V)$

$\boxed{F := U - TS}$ — Energia livre (ou função) Helmholtz

1ª lei $\Rightarrow$ $\boxed{dF = -SdT - PdV}$

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

Transf. de Legendre $\rightarrow$ $G = G(T, P)$

$\boxed{G := H - TS}$ — Energia livre (ou função) de Gibbs ou Entalpia livre

1ª lei $\Rightarrow$ $\boxed{dG = -SdT + VdP}$

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

caso $dN \neq 0$ $\Rightarrow$ $\boxed{đW = PdV - \mu dN}$

1ª lei $\Rightarrow$ $\boxed{dU = đQ - đW}$ $\Rightarrow$ $\boxed{dU = đQ - PdV + \mu dN}$

2ª lei $\Rightarrow$ $\boxed{đQ = TdS}$ $\Rightarrow$ $\boxed{dU = TdS - PdV + \mu dN}$

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

$\boxed{dH = TdS + VdP + \mu dN}$

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

$\boxed{U = U(T,V,N)}$

Transf. de Legendre $H = H(T,P,N)$

$\boxed{H := U + PV}$

1ª lei 2ª lei

$\boxed{dH = đQ + VdP + \mu dN}$

$$\boxed{\left(\frac{\partial U}{\partial S}\right)_{V,N} = T \; ; \; \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P \; e \; \left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu} \Longrightarrow \boxed{S = S(U,V,N)}$$

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

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

$$\boxed{\left(\frac{\partial H}{\partial S}\right)_{P,N} = T \; ; \; \left(\frac{\partial H}{\partial P}\right)_{S,N} = V \; e \; \left(\frac{\partial H}{\partial N}\right)_{S,P} = \mu} \Rightarrow \boxed{S = S(H,P,N)}$$

$$dS = \frac{1}{T}dH - \frac{V}{T}dP - \frac{\mu}{T}dN$$

$$\boxed{\left(\frac{\partial S}{\partial N}\right)_{H,P} = -\frac{\mu}{T}}$$

Transf. de Legendre

$U(S,V,N) \longrightarrow F(T,V,N) \Longrightarrow \boxed{F := U - TS}$

1ª lei

$$\boxed{dF = -SdT - PdV + \mu dN}$$

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

Transf. de Legendre

$H(S,P,N) \longrightarrow G(T,P,N) \Rightarrow \boxed{G := H - TS} \xrightarrow{1^a \text{ lei}} \boxed{dG = -SdT + VdP + \mu dN}$

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

$U(S,V,N) \longrightarrow J = J(T,V,\mu)$

Transf. de Legendre

$\boxed{J := U - TS - \mu N} \xrightarrow{1^a \text{ lei}} \boxed{dJ = -SdT - PdV - Nd\mu}$

Potencial grande canônico ou macrocanônico. Φ (Salinas)

$$\left(\frac{\partial J}{\partial T}\right)_{V,\mu} = -S \; ; \; \left(\frac{\partial J}{\partial V}\right)_{T,\mu} = -P \; e \; \left(\frac{\partial J}{\partial \mu}\right) = -N$$