

I. věta

$$dU = \delta Q + \delta W$$

$$dU = \delta Q + \delta W^{\text{obj}} + \delta W^{\text{jiná}} = \delta Q - p_{\text{vn}} dV + \delta W^{\text{jiná}}$$

$$[V] \quad \delta Q_V = dU (-\delta W^{\text{jiná}})$$

$$[p] \quad \delta Q_p = dU + p dV (-\delta W^{\text{jiná}}) \\ = d(U + pV) (-\delta W^{\text{jiná}}) = dH (-\delta W^{\text{jiná}})$$

$$[\text{ad}] \quad dU = \delta W^{\text{obj}} (+\delta W^{\text{jiná}})$$



II. věta

$$dS \geq \frac{dQ_{\text{rev}}}{T}$$

$$dU = T dS - p dV \\ (\leq)$$

$$dH = T dS + V dp \\ (\leq)$$

Spojené formulace (rev, $\delta W^{\text{jiná}} = 0$)

III. věta

$$\lim_{T \rightarrow 0} S = 0 \\ (\text{ideální krystal})$$

Kritéria samovolnosti a rovnováhy

Entropie (izolovaná soustava)	$[U, V]$	$dS \geq 0$	
Vnitřní energie	$[S, V]$	$dU \leq T dS - p dV + \delta W^{\text{jiná}} \quad (dQ_{\text{rev}} \leq T dS)$	$[S, V, \delta W^{\text{jiná}} = 0] \quad dU \leq 0$
Entalpie	$[S, p]$	$dH \leq T dS + V dp + \delta W^{\text{jiná}}$	$[S, p, \delta W^{\text{jiná}} = 0] \quad dH \leq 0$
Uzavřené soustavy Helmholtzova energie	$[T, V]$	$\underbrace{dU - T dS}_F + \underbrace{p dV}_0 \leq +\delta W^{\text{jiná}}$ $dF \leq \delta W^{\text{jiná}}$	$[T, V, \delta W^{\text{jiná}} = 0] \quad \boxed{dF \leq 0}$
Gibbsova energie	$[T, p]$	$\underbrace{dH - T dS}_G - \underbrace{V dp}_0 \leq +\delta W^{\text{jiná}}$ $dG \leq \delta W^{\text{jiná}}$	$[T, p, \delta W^{\text{jiná}} = 0] \quad \boxed{dG \leq 0}$

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

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

$$\boxed{H = H(T, p)}$$

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

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

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

$$\boxed{S = S(T, p)}$$

$$dS = \underbrace{\left(\frac{\partial S}{\partial T}\right)_p}_{C_p/T} dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

Závislost na teplotě (tabelle: $[p] C_p = a + b \cdot T + c \cdot T^2 + d \cdot T^2 + \dots$)

$$[V] \quad dU = C_V dT \quad , \quad [p] \quad dH = C_p dT$$

$$\Delta U = \int_{T_1}^{T_2} C_V(T) dT \quad , \quad \Delta H = \int_{T_1}^{T_2} C_p(T) dT$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V = \frac{C_V(T)}{T} \quad , \quad \left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T} \left(\frac{\partial H}{\partial T}\right)_p = \frac{C_p(T)}{T}$$

$$[V] \quad S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT \quad , \quad [p] \quad S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT$$

Reakční tepla $\Delta_r H^\ominus = \Delta_r U^\ominus + \Delta(pV) = \Delta_r U^\ominus + \sum \nu_i^{(g)} RT$

Hess $\Delta_r H^\ominus = \sum_i \nu_i \Delta_{sl} H_i^\ominus$, $\Delta_r H^\ominus = -\sum_i \nu_i \Delta_{spal} H_i^\ominus$
Kirchhoff

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \underbrace{\int_{T_1}^{T_2} \left[\sum_{\text{prod}} \nu_{i,\text{prod}} C_{pm}^\ominus(i, \text{prod}) - \sum_{\text{vých}} \nu_{i,\text{vých}} C_{pm}^\ominus(i, \text{vých}) \right] dT}_{\Delta C_p^\ominus}$$

$$\left(\frac{\partial \Delta_r H^\ominus}{\partial T}\right)_p = \Delta C_p^\ominus$$

Obecná entalpická bilance

$$Q = \sum_{\text{vých}} \int_{T_{\text{vých}}}^{T_{\text{ref}}} n_{i,\text{vých}} C_{pm}(i, \text{vých}) dT + \xi \cdot \Delta_r H^\ominus(T_{\text{ref}}) + \sum_{\text{prod}} \int_{T_{\text{ref}}}^{T_{\text{prod}}} n_{i,\text{prod}} C_{pm}(i, \text{prod}) dT$$

Reakční entropie

$$\Delta_r S^\ominus = \sum_i \nu_i S_{mi}^\ominus$$

Absolutní entropie

$$S_m^\ominus = \int_0^{14} \frac{a T^3}{T} dT + \int_{14}^{T_{\text{zvratu}}} \frac{C_{pm}^{(\alpha)}}{T} dT + \frac{(\Delta_{\text{zvratu}} H_m)}{T_{\text{zvratu}}} + \int_{T_{\text{zvratu}}}^{T_{\text{tání}}} \frac{C_{pm}^{(\beta)}}{T} dT +$$

$$+ \frac{(\Delta_{\text{tání}} H_m)}{T_{\text{tání}}} + \int_{T_{\text{tání}}}^{T_{\text{varu}}} \frac{C_{pm}^{(\ell)}}{T} dT + \frac{(\Delta_{\text{výp}} H_m)}{T_{\text{varu}}} + \int_{T_{\text{varu}}}^T \frac{C_{pm}^{(g)}}{T} dT - \int_{p^{\text{st}}}^p \left(\frac{\partial V}{\partial T}\right)_p dp$$

Závislost na tlaku a objemu

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - p = T \left(\frac{\partial p}{\partial T}\right)_V - p \stackrel{[*]}{=} 0$$

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

$$dH = T dS + V dp$$

$$\left(\frac{\partial H}{\partial p}\right)_T = T \left(\frac{\partial S}{\partial p}\right)_T + V = -T \left(\frac{\partial V}{\partial T}\right)_p + V \stackrel{[*]}{=} 0$$

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

$$dU = T dS - p dV$$

Tepelné kapacity

$$C_V = C_V(T, V) \quad , \quad C_p = C_p(T, p)$$

tabelace: $[p]$ $C_p = a + b \cdot T + c \cdot T^2 + d \cdot T^2 + \dots$

$$C_p - C_V = T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p \stackrel{[*]}{=} nR$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \left(\frac{\partial}{\partial p} \left(\frac{\partial H}{\partial T}\right)_p\right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial p}\right)_T\right)_p = \left(\frac{\partial}{\partial T} \left(-T \left(\frac{\partial V}{\partial T}\right)_p + V\right)\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p \stackrel{[*]}{=} 0$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial T} \left(T \left(\frac{\partial p}{\partial T}\right)_V - p\right)\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V \stackrel{[*]}{=} 0$$