Termodinamička ravnoteža

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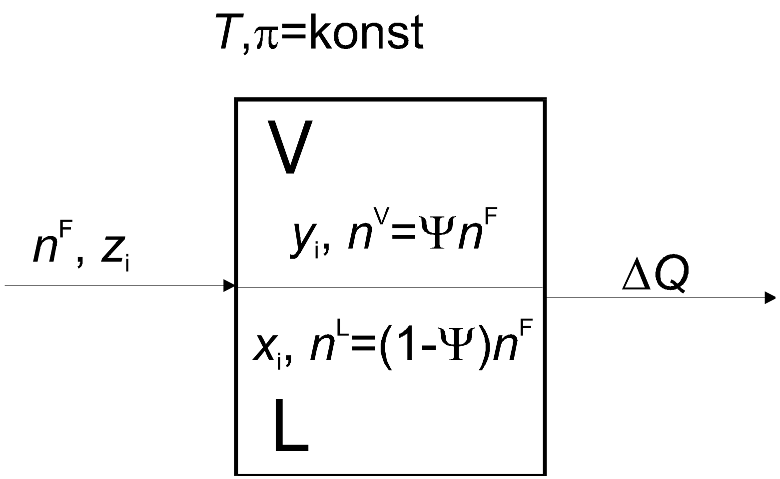
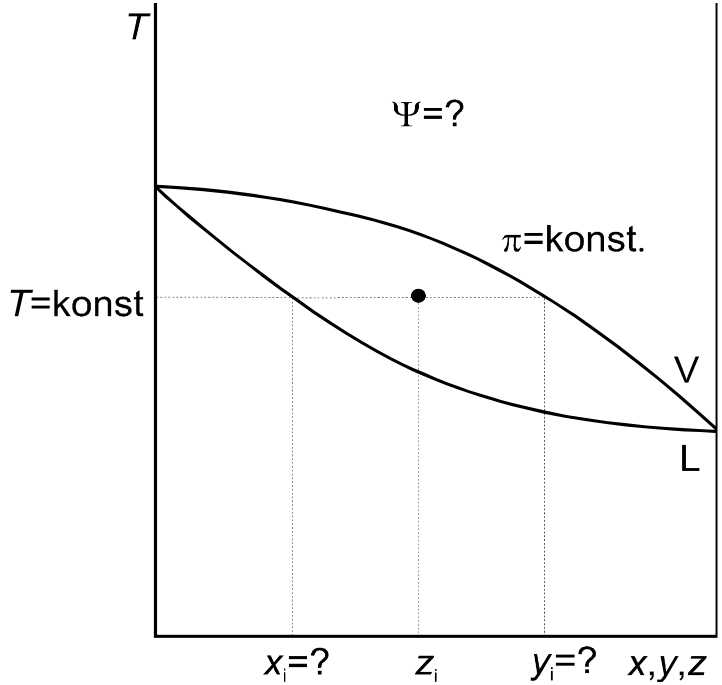
U okviru kemijskog inženjerstva

- Fazna ravnoteža
- Kemijska ravnoteža
- Elektrokemijska ravnoteža





$$\dot{n}_i = KA\left(c_i - c_i^*\right)$$

$$\dot{n}_i = KA\left(p_i - p_i^*\right) \quad \dot{n}_i = KA\left(x_i - x_i^*\right)$$

Termodinamička ravnoteža

Uvjeti ravnoteže

I. ZAKON TERMODINAMIKE

- bilanca tvari
- bilanca energije (ekvivalencija mase i energije)
- bilanca naboja (subatomske čestice)

II. ZAKON TERMODINAMIKE

Fazna ravnoteža

$$\mu_i^{\mathrm{I}} = \mu_i^{\mathrm{II}} = \cdots \mu_i^{\mathrm{F}}$$

Kemijska ravnoteža

$$\sum_{i=1}^{nk} \nu_i \mu_i = 0$$

$$\Delta_{\mathrm{r}} G = -RT \ln K_{\mathrm{r}}$$

Elektrokemijska ravnoteža

$$\Delta_{\mathrm{er}} G = -zFE$$

Uvjeti fazne ravnoteže

Klasični pristup

Bilanca energije $$dU = \delta Q - pdV$$

Neravnotežni uvjeti $$\frac{dU}{dt} = \frac{\delta Q}{dt} - p\frac{dV}{dt}$$

Izolirani sustav $$\frac{\delta Q}{dt} = 0 \qquad \frac{\delta V}{dt} = 0 \qquad \frac{dU}{dt} = 0$$

Izolirani sustav ne izmjenjuje tvar niti energiju s okolinom

Uvjeti fazne ravnoteže

Klasični pristup — Promjene se mogu događati unutar izoliranoga sustava!

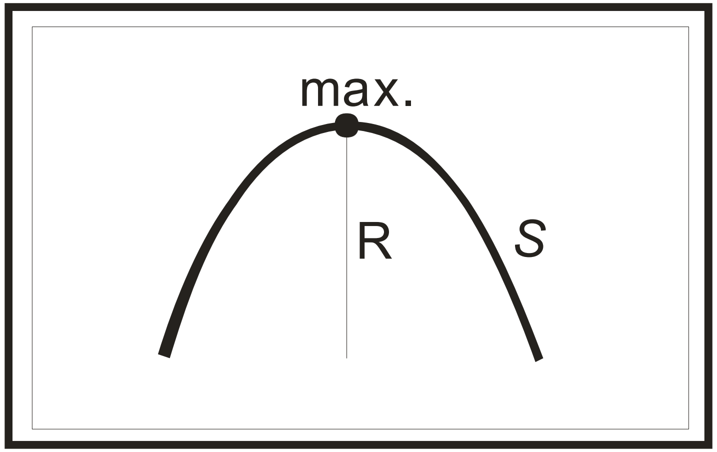
Bilanca entropije
$$dS = \left(\frac{\delta Q}{T}\right)^{\mathrm{rev}} + (dS)^{\mathrm{irev}} \qquad (dS)^{\mathrm{irev}} \geq 0$$

Neravnotežni uvjeti
$$\frac{dS}{dt} = \left(\frac{1}{T}\frac{\delta Q}{dt}\right)^{\mathrm{rev}} + \left(\frac{dS}{dt}\right)^{\mathrm{irev}}$$

Izolirani sustav
$$\frac{\delta Q^{\mathrm{rev}}}{dt} = 0$$

$$\frac{dS}{dt} = \left(\frac{dS}{dt}\right)^{\mathrm{irev}} \geq 0$$

$$S^{\mathrm{eq}} = \max$$

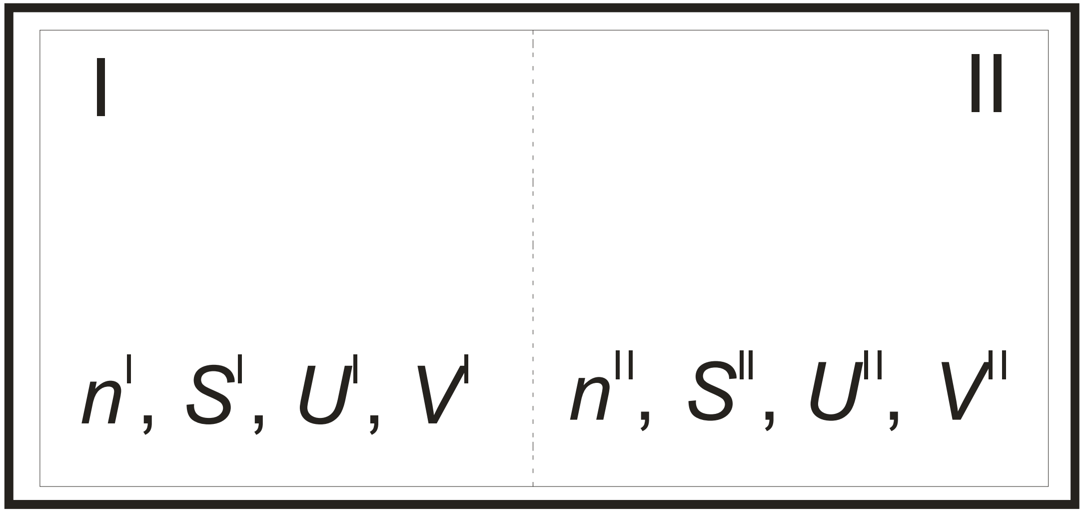


izolirani sustav

Uvjeti fazne ravnoteže

Klasični pristup

Razlaganje uvjeta



izolirani sustav

Podsustavi:

$$n = n^{\mathrm{I}} + n^{\mathrm{II}} \qquad dn = dn^{\mathrm{I}} + dn^{\mathrm{II}} = 0 \qquad dn^{\mathrm{II}} = -dn^{\mathrm{I}}$$

$$S = S^{\mathrm{I}} + S^{\mathrm{II}}$$

$$U = U^{\mathrm{I}} + U^{\mathrm{II}} \qquad dU = dU^{\mathrm{I}} + dU^{\mathrm{II}} = 0 \qquad dU^{\mathrm{II}} = -dU^{\mathrm{I}}$$

$$V = V^{\mathrm{I}} + V^{\mathrm{II}} \qquad dV = dV^{\mathrm{I}} + dV^{\mathrm{II}} = 0 \qquad dV^{\mathrm{II}} = -dV^{\mathrm{I}}$$

Uvjeti fazne ravnoteže

Totalni diferencijal

$$dS^{\mathrm{I}} = \left(\frac{\partial S^{\mathrm{I}}}{\partial U^{\mathrm{I}}}\right)_{n^{\mathrm{I}},V^{\mathrm{I}}} dU^{\mathrm{I}} + \left(\frac{\partial S^{\mathrm{I}}}{\partial V^{\mathrm{I}}}\right)_{n^{\mathrm{I}},U^{\mathrm{I}}} dV^{\mathrm{I}} + \left(\frac{\partial S^{\mathrm{I}}}{\partial n^{\mathrm{I}}}\right)_{U^{\mathrm{I}},V^{\mathrm{I}}} dn^{\mathrm{I}}$$

$$dS^{\mathrm{II}} = \left(\frac{\partial S^{\mathrm{II}}}{\partial U^{\mathrm{II}}}\right)_{n^{\mathrm{II}},V^{\mathrm{II}}} dU^{\mathrm{II}} + \left(\frac{\partial S^{\mathrm{II}}}{\partial V^{\mathrm{II}}}\right)_{n^{\mathrm{II}},U^{\mathrm{II}}} dV^{\mathrm{II}} + \left(\frac{\partial S^{\mathrm{II}}}{\partial n^{\mathrm{II}}}\right)_{U^{\mathrm{II}},V^{\mathrm{II}}} dn^{\mathrm{II}}$$

Iz opće termodinamike

$$\left(\frac{\partial S}{\partial U}\right)_{n^{\mathrm{I}},V^{\mathrm{I}}} = \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_{n^{\mathrm{I}},U^{\mathrm{I}}} = \frac{p}{T}$$

$$\left(\frac{\partial S}{\partial n}\right)_{U^{\mathrm{I}},V^{\mathrm{I}}} = \frac{g}{T}$$

$$dS^{\mathrm{I}} = \frac{1}{T^{\mathrm{I}}} dU^{\mathrm{I}} + \frac{p^{\mathrm{I}}}{T^{\mathrm{I}}} dV^{\mathrm{I}} - \frac{g^{\mathrm{I}}}{T^{\mathrm{I}}} dn^{\mathrm{I}}$$

$$dS^{\mathrm{II}} = \frac{1}{T^{\mathrm{II}}} dU^{\mathrm{II}} + \frac{p^{\mathrm{II}}}{T^{\mathrm{II}}} dV^{\mathrm{II}} - \frac{g^{\mathrm{II}}}{T^{\mathrm{II}}} dn^{\mathrm{II}}$$

Uvjeti fazne ravnoteže

Zbroj entropija podsustava

$$dS = dS^{\mathrm{I}} + dS^{\mathrm{II}}$$

$$dS = \left(\frac{1}{T^{\mathrm{I}}} - \frac{1}{T^{\mathrm{II}}}\right) dU^{\mathrm{I}} + \left(\frac{p^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{p^{\mathrm{II}}}{T^{\mathrm{II}}}\right) dV^{\mathrm{I}} - \left(\frac{g^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{g^{\mathrm{II}}}{T^{\mathrm{II}}}\right) dn^{\mathrm{I}}$$

Uvjet ravnoteže $dS = 0$

Koeficijenti uz članove jednaki su 0

$$\left(\frac{1}{T^{\mathrm{I}}} - \frac{1}{T^{\mathrm{II}}}\right) = 0 \qquad \left(\frac{p^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{p^{\mathrm{II}}}{T^{\mathrm{II}}}\right) = 0 \qquad \left(\frac{g^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{g^{\mathrm{II}}}{T^{\mathrm{II}}}\right) = 0$$

$$T^{\mathrm{I}} = T^{\mathrm{II}} \qquad p^{\mathrm{I}} = p^{\mathrm{II}} \qquad g^{\mathrm{I}} = g^{\mathrm{II}}$$

Uvjeti fazne ravnoteže

Višefazni, višekomponentni sustavi

$$T^{\mathrm{I}} = T^{\mathrm{II}} = \cdots T^{\mathrm{F}}$$

$$p^{\mathrm{I}} = p^{\mathrm{II}} = \cdots p^{\mathrm{F}}$$

$$\mu_{\mathrm{i}}^{\mathrm{I}} = \mu_{\mathrm{i}}^{\mathrm{II}} = \cdots \mu_{\mathrm{i}}^{\mathrm{F}}$$

Zatvoreni sustavi

Sustavi stalne temperature i tlaka

$$T = \text{konst.} \quad p = \text{konst.}$$

$$dT = 0 \qquad dp = 0$$

Promjena Gibbsove energije

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

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

$$dT = 0 \qquad dp = 0$$

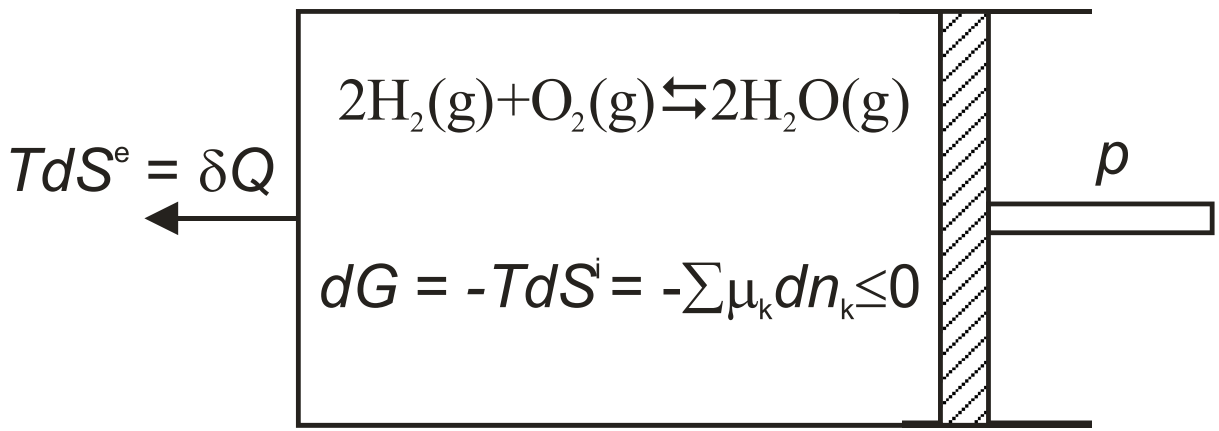
$$dG = dU + pdV - TdS$$

$$dU = \delta Q - pdV$$

$$dG = \delta Q - TdS$$

$$dG = TdS^{\mathrm{e}} - TdS$$

$$dG = -TdS^{\mathrm{i}} \le 0$$



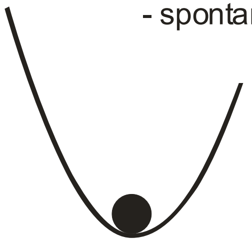
Tražiti minimum *G* sustava isto je što i tražiti maksimum *S* sustava i okoline zajedno

Uvjeti termodinamičke ravnoteže

Vrsta sustava	Ograničenja	Uvjet termodinamičke ravnoteže	
Izolirani		$dS = 0$	$S^{eq} = \max$
Zatvoreni	$S = \text{konst.}$ $V = \text{konst.}$	$dU = 0$	$U^{eq} = \min$
Zatvoreni	$T = \text{konst.}$ $V = \text{konst.}$	$dA = 0$	$A^{eq} = \min$
Zatvoreni	$S = \text{konst.}$ $p = \text{konst.}$	$dH = 0$	$H^{eq} = \min$
Zatvoreni	$T = \text{konst.}$ $p = \text{konst.}$	$dG = 0$	$G^{eq} = \min$

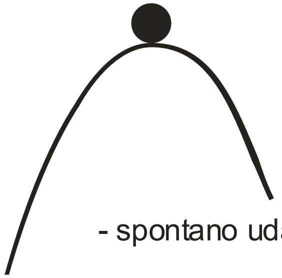
Stabilnost termodinamičkih sustava

STABILNA RAVNOTEŽA



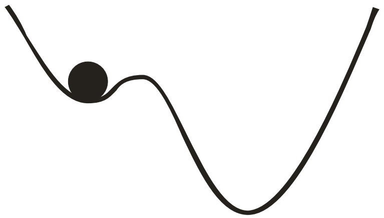
- spontani povratak

NESTABILNA RAVNOTEŽA



- spontano udaljavanje

METASTABILNA RAVNOTEŽA



NEODREĐENA RAVNOTEŽA

Stabilnost termodinamičkih sustava

$$dS = 0 \quad \left(d^2S\right)_{U,V} = \left(\frac{\partial^2 S}{\partial p^2}\right)_{U,V} (dp)^2 + 2\left(\frac{\partial^2 S}{\partial p \partial T}\right)_{U,V} dpdT + \left(\frac{\partial^2 S}{\partial T^2}\right)_{U,V} (dT)^2 < 0$$

$$dG = 0 \quad \left(d^2G\right)_{p,T} > 0$$

$$\left(d^2U\right)_{V,S} = \left(\frac{\partial^2 U}{\partial p^2}\right)_{V,S} (dp)^2 + 2\left(\frac{\partial^2 U}{\partial p \partial T}\right)_{V,S} dpdT + \left(\frac{\partial^2 U}{\partial T^2}\right)_{V,S} (dT)^2 > 0$$

$$\left(d^2H\right)_{p,S} = \left(\frac{\partial^2 H}{\partial V^2}\right)_{p,S} (dV)^2 + 2\left(\frac{\partial^2 H}{\partial V \partial T}\right)_{p,S} dVdT + \left(\frac{\partial^2 H}{\partial T^2}\right)_{p,S} (dT)^2 > 0$$

$$\left(d^2A\right)_{V,T} = \left(\frac{\partial^2 A}{\partial p^2}\right)_{V,T} (dp)^2 + 2\left(\frac{\partial^2 A}{\partial p \partial S}\right)_{V,T} dpdS + \left(\frac{\partial^2 A}{\partial S^2}\right)_{V,T} (dS)^2 > 0$$

$$\left(d^2G\right)_{p,T} = \left(\frac{\partial^2 G}{\partial V^2}\right)_{p,T} (dV)^2 + 2\left(\frac{\partial^2 G}{\partial V \partial S}\right)_{p,T} dVdS + \left(\frac{\partial^2 G}{\partial S^2}\right)_{p,T} (dS)^2 > 0$$

Stabilnost reakcijskog sustava

Gibbsova energija kao funkcija tlaka, temperature i sastava

$$dG=\left(\frac{\partial G}{\partial p}\right)_{T,n} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n} dT + \sum_{i=1}^{nk}\left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j\neq i}} dn_i$$

$$\left(\frac{\partial G}{\partial p}\right)_{T,n} = V \quad \left(\frac{\partial G}{\partial T}\right)_{p,n} = -S \quad \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j\neq i}} = \mu_i$$

$$dG = Vdp - SdT + \sum_{\mathrm{i}=1}^{\mathrm{nk}} \mu_{\mathrm{i}} dn_{\mathrm{i}}$$

Doseg kemijske reakcije

$$d\xi = \frac{dn_i}{\nu_i}$$

$$dG = Vdp + SdT + \left(\sum_{i=1}^{nk} \mu_i \nu_i\right) d\xi$$

Stabilnost reakcijskog sustava

U uvjetima stalne temperature i tlaka

$$T = \text{konst.} \quad p = \text{konst.}$$

$$dT = 0 \qquad dp = 0$$

$$dG = \left(\sum_{\text{i}=1}^{\text{nk}} \mu_\text{i} \nu_\text{i} \right) d\xi \qquad \left(\frac{\partial G}{\partial \xi} \right)_{p,T} = \sum_{\text{i}=1}^{\text{nk}} \mu_\text{i} \nu_\text{i}$$

Reakcijska koordinata

$$dG = Vdp + SdT + \left(\sum_{i=1}^{nk} \mu_i \nu_i \right) d\xi$$

$$dG = Vdp + SdT + \left(\frac{\partial G}{\partial \xi} \right)_{p,T} d\xi$$

Stabilnost reakcijskog sustava

Diferenciranje prethodne jednadžbe po dosegu

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \left(\frac{\partial V}{\partial \xi}\right)_{p,T} dp - \left(\frac{\partial S}{\partial \xi}\right)_{p,T} dT + \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T} d\xi$$

U stanju ravnoteže

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = 0$$

$$\left(\frac{\partial V}{\partial \xi}\right)_{p,T} dp - \left(\frac{\partial S}{\partial \xi}\right)_{p,T} dT + \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T} d\xi = 0$$

Stabilnost reakcijskog sustava

U stanju ravnoteže, pri stalnoj temperaturi

$$\left(\frac{\partial V}{\partial \xi}\right)_{p,T} dp - \left(\frac{\partial S}{\partial \xi}\right)_{p,T} dT + \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T} d\xi = 0$$

$$\left(\frac{\partial V}{\partial \xi}\right)_{p,T} dp + \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T} d\xi = 0$$

$$\left(\frac{\partial \xi}{\partial p}\right)_{T} = -\frac{\left(\partial V/\partial \xi\right)_{p,T}}{\left(\partial^2 G/\partial \xi^2\right)_{p,T}}$$

Stabilna ravnoteža

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T} > 0 \quad \left(\partial V/\partial \xi\right)_{p,T} = ?$$

Primjer (školski)

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

$$\frac{\partial V}{\partial \xi} < 0$$

$$\left(\frac{\partial \xi}{\partial p}\right)_{T} = -\frac{\left(\partial V/\partial \xi\right)_{p,T}}{\left(\partial^2 G/\partial \xi^2\right)_{p,T}} > 0$$

Le Chatelierovo načelo
Termodinamička
interpretacija

Stabilnost reakcijskog sustava

U stanju ravnoteže, pri stalnom tlaku

$$\left(\frac{\partial V}{\partial \xi}\right)_{p,T} dp - \left(\frac{\partial S}{\partial \xi}\right)_{p,T} dT + \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T} d\xi = 0$$

$$-\left(\frac{\partial S}{\partial \xi}\right)_{p,T} dT + \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T} d\xi = 0$$

$$\left(\frac{\partial \xi}{\partial T}\right)_{p} = \frac{\left(\partial S/\partial \xi\right)_{p,T}}{\left(\partial^2 G/\partial \xi^2\right)_{p,T}} = \frac{1}{T}\frac{\left(\partial H/\partial \xi\right)_{p,T}}{\left(\partial^2 G/\partial \xi^2\right)_{p,T}}$$

Stabilna ravnoteža

$$\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T} > 0 \qquad \left(\partial H/\partial \xi\right)_{p,T} = ?$$

Primjer (školski)

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

$\Delta_r H$ = 2·(-45,94) kJ mol^{-1} pri standardnim uvjetima od 1 atm i 25 °C.

$$\frac{\partial H}{\partial \xi} < 0$$

$$\left(\frac{\partial \xi}{\partial T}\right)_{p} = \frac{1}{T}\frac{\left(\partial H/\partial \xi\right)_{p,T}}{\left(\partial^2 G/\partial \xi^2\right)_{p,T}} < 0$$

Le Chatelierovo načelo
Termodinamička interpretacija