Standardna stanja

$$\Delta_r H^\circ$$
$$\Delta_r U^\circ$$

- plinovi: idealni plin, $p^\circ = 10^5$ Pa = 1 bar

- krutine, tekućine: čista tvar, $p^\circ = 10^5$ Pa = 1 bar

- smjese i otopine: nema interakcija, $p^\circ = 10^5$ Pa = 1 bar

---

Kemijski procesi

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l);$ $$\Delta_1 H^\circ = \frac{\Delta H^\circ}{\Delta \xi_1} == -571{,}7\ \text{kJ mol}^{-1}$$

$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l);$ $$\Delta \xi_2 = 2\Delta \xi_1$$

$$\Delta_2 H^\circ = \frac{\Delta H^\circ}{\Delta \xi_2} = \frac{\Delta_1 H^\circ}{2} = -285{,}8\ \text{kJ mol}^{-1}$$

$H_2O(l) \rightarrow H_2(g) + 1/2O_2(g)$ $$\Delta_3 H^\circ = -\Delta_2 H^\circ = -\frac{\Delta_1 H^\circ}{2} = 285{,}8\ \text{kJ mol}^{-1}$$

Fizikalne promjene

$H_2O(l) \rightarrow H_2O(g)$

$$\Delta_{\text{vap}} H^\circ = \Delta_l^g H^\circ = 40{,}66\ \text{kJ mol}^{-1}$$

$H_2O(g) \rightarrow H_2O(l)$

$$\Delta_g^l H^\circ = -\Delta_{\text{vap}} H^\circ = -40{,}66\ \text{kJ mol}^{-1}$$

Odnos reakcijskih entalpija i unutrašnjih energija

$$H = U + pV$$

$$\Delta H = \Delta U + \Delta(pV)$$

$$\Delta_r H = \Delta_r U + \Delta_r(pV)$$

$$\Delta_r H = \Delta_r U + \Delta_r(nRT)$$

$$\Delta_r H = \Delta_r U + \mathrm{RT}\Sigma \nu_i(g)$$

Temperatura

Iskustvo – toplo / hladno

Kako mjeriti temperaturu?

Iskustvena temperatura, temperaturne ljestvice:

Réne Antoine Ferchault de Réamur (1683-1757)

Ole Christensen Römer (1644-1710)

Daniel Gabriel Farenheit (1686-1736)

Anders Celsius (1701-1744)

William Thomson, Lord Kelvin (1824-1907)

William John Macquorn Rankine (1820-1872)

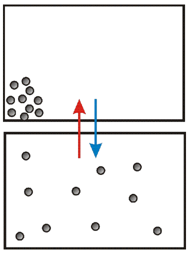
Hessov zakon

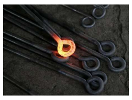
Germain Henri Hess

Entalpije neke reakcije r jednaka
je zbroju entalpija reakcija na koje
reakciju r možemo rastaviti

- Stvaranje $\Delta_r H = \sum_i \nu_i \Delta_f H_i$
- Sagorijevanje $\Delta_r H = -\sum_i \nu_i \Delta_c H_i$
- Atomizacija $\Delta_r H = -\sum_i \nu_i \Delta_{at} H_i$

Spontani procesi





$H_2(g) + O_2(g) \rightarrow H_2O(l)$

$AgNO_3(aq) + KCl(aq) \rightarrow AgCl(s) + KNO_3(aq)$

DRUGI ZAKON TERMODINAMIKE

spontanost neke fizikalne ili kemijske promjene

ENTROPIJA

Entropija svemira raste.

postoji neprekinuta, jednoznačna jedinstvena ekstenzivna funkcija stanja koja se naziva entropija i to takva da vrijedi:

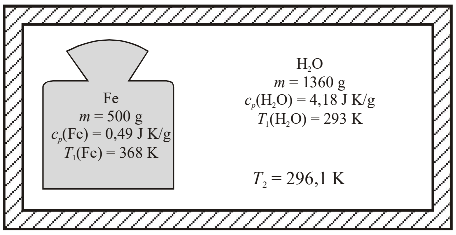
$$dS = \frac{dq_{rev}}{T} \qquad dS \geq \frac{dq}{T}$$

Spontani procesi $\Delta S > 0$

Primjeri:

- Promjena entropije s promjenom volumena
- Promjena entropije s promjenom temperature
- Promjena entropije prilikom fazne transformacije

Spontani procesi u izoliranom sustavu popraćeni su povećanjem ukupne entropije.



Fe
$m = 500$ g
$c_p(Fe) = 0,49$ J K/g
$T_1(Fe) = 368$ K

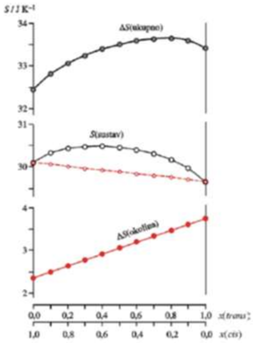
H_2O
$m = 1360$ g
$c_p(H_2O) = 4,18$ J K/g
$T_1(H_2O) = 293$ K

$T_2 = 296,1$ K

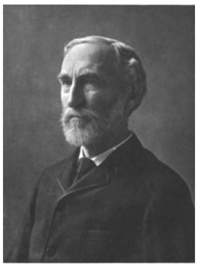
TREĆI ZAKON TERMODINAMIKE

Entropija elemenata i savršenih kristala je nula pri apsolutnoj nuli.

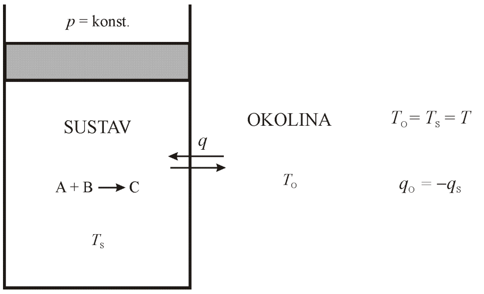
$$S_m(T = 0\ K) = 0$$



Josiah Willard Gibbs



Gibbsova energija, G



p = konst.

SUSTAV

q

$A + B \longrightarrow C$

T_s

OKOLINA

T_o

$T_o = T_s = T$

$q_o = -q_s$

$$G = H - TS$$

Spontani proces: $\Delta S_{uk} > 0 \quad \Rightarrow \quad \Delta G < 0$

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

$\Delta_r G > 0$	Povratna reakcija
$\Delta_r G = 0$	Ravnoteža
$\Delta_r G < 0$	Spontana, napredna reakcija

$$G = H - TS$$

$p = konst.$
$T = konst.$

$$\mathrm{d}G = \mathrm{d}(H - TS) = \mathrm{d}H - \mathrm{d}(TS) = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T$$

$$H = U + pV$$
$$\mathrm{d}H = \mathrm{d}U + \mathrm{d}(pV) = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

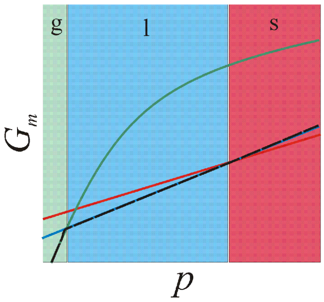
$$\mathrm{d}G = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T$$

$$\mathrm{d}G = \mathrm{d}q - p\mathrm{d}V + p\mathrm{d}V + V\mathrm{d}p - \mathrm{d}q - S\mathrm{d}T$$

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$$

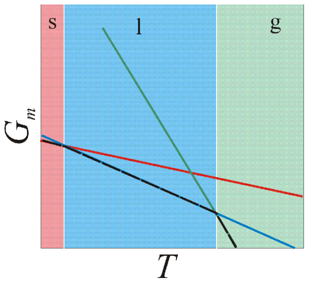
$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$



$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

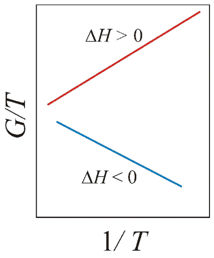


Gibbs-Helmholtzova jednadžba

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\left(\frac{\partial (G/T)}{\partial T}\right)_p = -\frac{H}{T^2}$$

$$\left(\frac{\partial (G/T)}{\partial (1/T)}\right)_p = H$$



Termodinamički potencijali
Kemijski potencijal

PARCIJALNE MOLARNE VELIČINE

$$\left(\frac{\partial X}{\partial n_i}\right)_{p,T,n_{j\neq i}} = \tilde{X}_i$$

Parcijalni molarni volumen

$$\left(\frac{\partial V}{\partial n_i}\right)_{p,T,n_{j\neq i}} = \tilde{V}_i$$

1 mol H_2O u H_2O	1 mol H_2O u C_2H_5OH
$\Delta V = 18\ \mathrm{cm^3}$	$\Delta V = 14\ \mathrm{cm^3}$
$\tilde{V}(\mathrm{H_2O}) = 18\,\mathrm{cm^3\ mol^{-1}}$	$\tilde{V}(\mathrm{H_2O}) = 14\,\mathrm{cm^3\ mol^{-1}}$

$$\left(\frac{\partial S}{\partial n_i}\right)_{p,T,n_{j\neq i}} = \tilde{S}_i$$

$$\left(\frac{\partial H}{\partial n_i}\right)_{p,T,n_{j\neq i}} = \tilde{H}_i$$

$$\left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j\neq i}} = \tilde{G}_i = \mu_i$$

Kemijski potencijal

$$\left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j\neq i}} = \tilde{G}_i = \mu_i$$

1) Čista tvar*

$$\mu_\mathrm{B} * = G_m(B)$$

Čisti plin

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T \qquad T = \text{konst.} \Rightarrow \mathrm{d}G = V\mathrm{d}p$$

$$\int_{G(p_1)}^{G(p_2)} \mathrm{d}G = \int_{p_1}^{p_2} V\mathrm{d}p$$

$$G(p_2) - G(p_1) = nRT\ln\left(p_2 / p_1\right)$$

$$\mu\left(p_2\right) - \mu\left(p_1\right) = RT\ln\frac{p_2}{p_1}$$

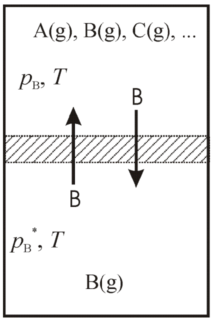
$$p_1 = p^\circ = 10^5 \text{ Pa}$$

$$p_2 = p$$

Kemijski potencijal čistog idealnog plina

$$\mu^* = \mu^\circ + RT\ln\frac{p}{p^\circ}$$

2) Kemijski potencijal plina u idealnoj smjesi



RAVNOTEŽA

$$p_B^* = p_B \qquad \mathrm{d}G = 0 \qquad \mu_B^* = \mu_B$$

Kemijski potencijal čistog idealnog plina:

$$\mu_\mathrm{B} = \mu^\circ + RT\ln\frac{p_\mathrm{B}}{p^\circ}$$

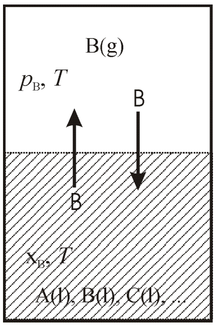
Kemijski potencijal plina u idealnoj smjesi:

$$\mu_\mathrm{B} = \mu^\circ + RT\ln x_\mathrm{B} + RT\ln\frac{p}{p^\circ}$$

Daltonov zakon

$$p_B = x_B p$$

3) Kemijski potencijal tvari u idealnoj smjesi tekućina



$$\mathrm{B(l)} \rightleftarrows \mathrm{B(g)}$$

Ravnoteža

$$\mathrm{d}G = 0$$

$$G_\mathrm{B,g} - G_\mathrm{B,l} = 0$$

$$\mu_\mathrm{B,g} - \mu_\mathrm{B,l} = 0$$

Raoultov zakon: $p_B = x_B p_B^*$

$$\mu_\mathrm{B} = \mu^\circ + RT \ln \frac{p_\mathrm{B}}{p^\circ}$$

$$\mu_\mathrm{B,g} = \mu_\mathrm{g}^\circ + RT \ln x_\mathrm{B} + RT \ln \frac{p_\mathrm{B}^*}{p^\circ}$$

$$\mu_\mathrm{B,g}{}^* = \mu_\mathrm{g}^\circ + RT \ln \frac{p_\mathrm{B}^*}{p^\circ}$$

$$\mu_\mathrm{B,g} = \mu_\mathrm{B,g}^* + RT \ln x_\mathrm{B}$$

Čista tekućina u ravnoteži: $\mu_\mathrm{B,g}{}^* = \mu_\mathrm{B,l}{}^*$

Tekuća smjesa u ravnoteži: $\mu_\mathrm{B,g} = \mu_\mathrm{B,l}$

$$\mu_\mathrm{B,l} = \mu_\mathrm{B,l}^* + RT \ln x_\mathrm{B}$$

$$\mu_\mathrm{B} = \mu_\mathrm{B}^* + RT \ln x_\mathrm{B}$$

Kemijski potencijal sastojka B u kondenziranim smjesama (tekućim i čvrstim) pri standardnom tlaku:

$p = p^\circ$ $\qquad$ $\mu_\mathrm{B} = \mu^\circ + RT \ln x_\mathrm{B}$

Kemijski potencijal sastojka B u kondenziranim smjesama (tekućim i čvrstim) pri tlaku p:

$p \neq p^\circ$ $\qquad$ $\mu_\mathrm{B} = \mu^\circ + RT \ln x_\mathrm{B} + \int_{p^\circ}^{p} \tilde{V}_\mathrm{B} \mathrm{d}p$

$$\mu_\mathrm{B} = \mu^\circ + RT \ln x_\mathrm{B} + \int_{p^\circ}^{p} \tilde{V}_\mathrm{B} \mathrm{d}p$$

$$\mu_\mathrm{B} = \mu^\circ + RT \ln x_\mathrm{B} + \int_{p^\circ}^{p} V_\mathrm{B,m} \mathrm{d}p$$

$$p \neq p^\circ$$

Kemijski potencijal sastojka B u idealnim plinskim smjesama:

$$\mu_\mathrm{B} = \mu^\circ + RT \ln x_\mathrm{B} + RT \ln \frac{p}{p^\circ}$$

Kemijski potencijal sastojka B u idealnim kondenziranim smjesama:

$$\mu_\mathrm{B} = \mu^\circ + RT \ln x_\mathrm{B} + V_\mathrm{B,m} \left(p - p^\circ \right)$$

Kemijski potencijal

$$\left(\frac{\partial G}{\partial n_i} \right)_{p,T,n_{j \neq i}} = \tilde{G}_i = \mu_i$$

Kemijski potencijal čistog idealnog plina $\qquad$ $\mu^* = \mu^\circ + RT \ln \frac{p}{p^\circ}$

Kemijski potencijal plina u idealnoj plinskoj smjesi $\qquad$ $\mu_\mathrm{B} = \mu^\circ + RT \ln x_\mathrm{B} + RT \ln \frac{p}{p^\circ}$

Kemijski potencijal tekućine u idealnoj smjesi tekućina $\qquad$ $\mu_\mathrm{B} = \mu_\mathrm{B}^* + RT \ln x_\mathrm{B}$

Kemijski potencijal sastojka B u kondenziranim smjesama (tekućim i čvrstim) pri standardnom tlaku

$p = p^\circ$ $\qquad$ $\mu_\mathrm{B} = \mu^\circ + RT \ln x_\mathrm{B}$

Kemijski potencijal sastojka B u kondenziranim smjesama (tekućim i čvrstim) pri tlaku p

$p \neq p^\circ$ $\qquad$ $\mu_\mathrm{B} = \mu^\circ + RT \ln x_\mathrm{B} + V_\mathrm{B,m} \left(p - p^\circ \right)$

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otopine

$c_\mathrm{B} = \frac{n_\mathrm{B}}{V}$ $\qquad$ $b_\mathrm{B} = \frac{n_\mathrm{B}}{m_\mathrm{A}}$ $\qquad$ $a_\mathrm{B} = \frac{c_\mathrm{B} \gamma_\mathrm{B}}{c^\circ}$

otopinu otopljene tvari B nazivamo idealnom ukoliko je $\gamma_\mathrm{B} = 1$ i ne mijenja se daljnjim razrijeđivanjem

Kemijski potencijal otopljene tvari B u otopini:

$\mu_\mathrm{B} = \mu^\circ + RT \ln \frac{c_\mathrm{B}}{c^\circ}$ $\qquad$ $\mu_\mathrm{B} = \mu^\circ + RT \ln \frac{b_\mathrm{B}}{b^\circ}$

IDEALNI SUSTAVI

REALNI SUSTAVI

INTERAKCIJA MEĐU
ČESTICAMA

Plinovi
Tekućine
Krutine
Otopine

Kemijski potencijal realnih sustava