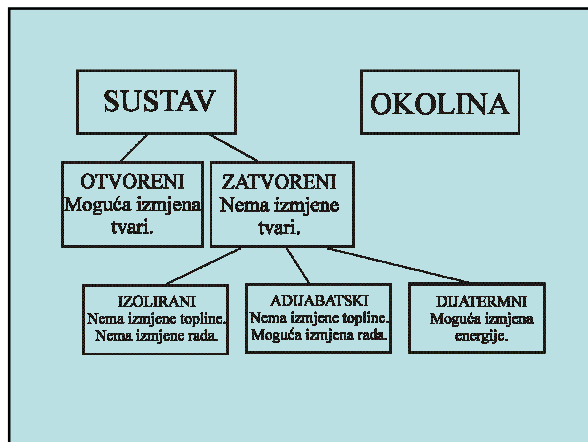


kemijska termodinamika

termodinamika –
proučavanje izmjena energije kao što su rad
i toplina

kemijska termodinamika –
proučavanje izmjene energije koje se
zbivaju pri kemijskim reakcijama,
spontanost kemijskih reakcija i kemijske
ravnoteže



kemijska termodinamika

Stanje sustava opisuju fizikalne veličine:

- množina molekula, masa sustava
- volumen
- temperatura
- tlak

Fizikalne veličine mogu biti *ekstenzivne* (ovise o broju jedinki u sustavu, npr. masa, volumen) i *intenzivne* (ne ovise o broju jedinki u sustavu, npr. temperatura, gustoća).

Proces predstavlja promjenu stanja sustava.
Promjena neke fizikalne veličine, X , jednaka je:

$$\Delta X = X_{\text{konačno}} - X_{\text{početno}} = X_2 - X_1$$

kemijska termodinamika

Agregacijsko (agregatno) stanje tvari

- g - plinovito stanje
- l - tekuće stanje
- s - čvrsto stanje
- cr - kristalno stanje
- sln - otopina
- aq - vodena otopina
- aq,∞ - vodena otopina pri beskonačnom razrijeđenju
- cd - kondenzirano stanje



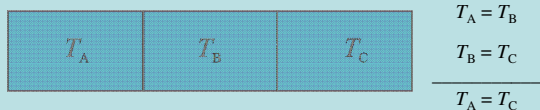
Anders Celsius (1701 – 1744)

Celsius		
Originalna skala	$t_f(\text{H}_2\text{O}) = 0 \text{ } ^\circ\text{C}$	$t_b(\text{H}_2\text{O}) = 100 \text{ } ^\circ\text{C}$
Od 1948.	Apsolutna nula	Trojna točka vode $t_f(\text{H}_2\text{O}) = 0,01 \text{ } ^\circ\text{C}$ $T_f(\text{H}_2\text{O}) = 273,16 \text{ K}$

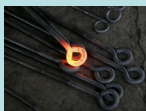
Definicija termodinamičke temperature

$$T = \lim_{p \rightarrow 0} (pV / nR)$$

Nulti stavak termodinamike



TOPLINA je energija prenesena s jednog sustava na drugi kada promatrani sustavi nisu u toplinskoj ravnoteži.



Dogovor: sustav se zagrijava $q > 0$
sustav se hladi $q < 0$

$$dq = C dT \quad C - \text{toplinski kapacitet}$$

Funkcija stanja – veličina koja je određena isključivo stanjem sustava, a ne i putem kojim se u to stanje došlo.

Toplina nije funkcija stanja.

RAD

Dogovor: - sustav vrši rad $w < 0$
- nad sustavom se vrši rad $w > 0$

Volumni rad

$$w = - \int_{V_1}^{V_2} p dV = -p \Delta V \quad p = \text{konst.}$$

$$\begin{aligned} w &= - \int_{V_1}^{V_2} p dV \\ &= -p \int_{V_1}^{V_2} dV \\ &= -p(V_2 - V_1) \\ &= -p \Delta V. \end{aligned}$$

Rad nije funkcija stanja.

Prvi glavni stavak termodinamike

UNUTARNJA ENERGIJA, U

-svojstvo (funkcija) stanja

-unutarnja energija izoliranog sustava je stalna

$$\Delta U = U_2 - U_1 = q + w$$

- u slučaju kada nema drugog rada osim volumnog, toplina prenesena pri stalnom volumenu ($w = 0$) jednaka je promjeni unutarnje energije

$$\Delta U = q_V (V = \text{konst})$$

Entalpija, H

$$H = U + pV$$

- svojstvo (funkcija) stanja

$$dH = dq_p = C_p dT$$

$$dU = dq_V = C_V dT$$

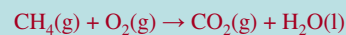
Kemijske reakcije



Stehiometrijski koeficijent

$$v_i = \frac{\Delta N_i}{\Delta N_r} = \frac{\Delta n_i}{\Delta n_r}$$

Primjer:



Zad.: Izračunajte doseg reakcije ako je u reakciji izgorilo 2 g metana.

Doseg (napredak) reakcije

$$\xi = n_r = \frac{N_r}{L} \quad \begin{array}{l} \text{brojnost pretvorbi } r \\ \text{Avogadrova konstanta } (L \approx 6,022 \cdot 10^{23} \text{ mol}^{-1}) \end{array}$$

Reakcijske veličine

Reakcijska veličina $\Delta_r X$ je parcijalna derivacija veličine X po dosegu reakcije

$$\Delta_r X = \frac{\partial X}{\partial \xi}$$

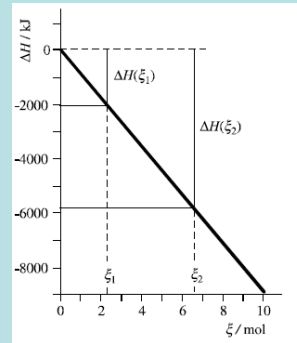
$$\Delta_r H = \frac{\partial H}{\partial \xi}$$

Kako se reakcijska entalpija obično ne mijenja tijekom reakcije vrijedi:

$$\Delta_r H = \frac{\Delta H}{\Delta \xi}$$

$$\Delta_r U = \frac{\partial U}{\partial \xi}$$

$$\Delta_r U = \frac{\Delta U}{\Delta \xi}$$



$$\Delta_r H = \frac{\Delta H}{\Delta \xi}$$

Standardna stanja

$$\Delta_r H^\circ$$

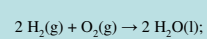
$$\Delta_r U^\circ$$

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

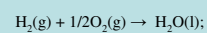
- krutine, tekućine: čista tvar, $p^\circ = 10^5 \text{ Pa} = 1 \text{ bar}$

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

Kemijski procesi

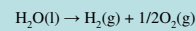


$$\Delta_r H^\circ = \frac{\Delta H^\circ}{\Delta \xi_1} = -571,7 \text{ kJ mol}^{-1}$$



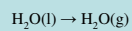
$$\Delta \xi_2 = 2 \Delta \xi_1$$

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

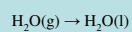


$$\Delta_r H^\circ = -\Delta_r H^\circ = -\frac{\Delta_r H^\circ}{2} = 285,8 \text{ kJ mol}^{-1}$$

Fizikalne promjene



$$\Delta_{\text{vap}} H^\circ = \Delta_1^\text{g} H^\circ = 40,66 \text{ kJ mol}^{-1}$$



$$\Delta_1^\text{l} H^\circ = -\Delta_{\text{vap}} H^\circ = -40,66 \text{ kJ mol}^{-1}$$

Naziv	engleski	Proces	Simboli za gradijent	
fazni prijelaz iz faze α u β	<i>transition</i>	$X(\alpha) \rightarrow X(\beta)$	Δ_α^β	Δ_{tr}
isparavanje	<i>vaporization</i>	$X(\text{l}) \rightarrow X(\text{g})$	Δ_1^g	Δ_{vap}
kondenzacija	<i>condensation</i>	$X(\text{g}) \rightarrow X(\text{l})$	Δ_1^l	
sublimacija	<i>sublimation</i>	$X(\text{s}) \rightarrow X(\text{g})$	Δ_1^g	Δ_{sub}
taljenje	<i>fusion</i>	$X(\text{s}) \rightarrow X(\text{l})$	Δ_1^l	Δ_{fus}
očvršćivanje	<i>freezing</i>	$X(\text{l}) \rightarrow X(\text{s})$	Δ_1^s	

Odnos reakcijskih entalpija i unutrašnjih energija

$$H = U + pV$$

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

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

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

$$\Delta_r H = \Delta_r U + RT \sum \nu_i(g)$$

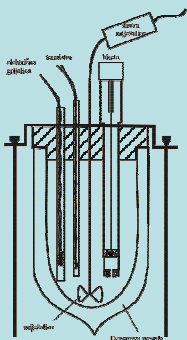
Kalorimetrija

- mjerenje topline izmijenjene u nekom fizikalnom ili kemijskom procesu

$$\Delta H = q_p = -C_p \Delta T$$

$$\Delta U = q_v = -C_v \Delta T$$

Reakcijski kalorimetar

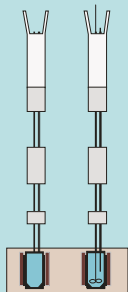


$$\Delta H = q_p = -C \Delta T$$

$p, T = konst.$



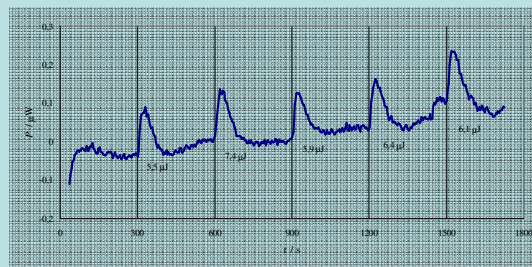
Reakcijska ćelija



- Dvije ćelije: mjerna i referentna
- Ćelije između dva držača
- Umetnuto u zajednički izotermalni blok
- Poluvodički termočlanci nalaze se između držača i izotermalnog bloka
- Izotermalni blok obložen pasivnim slojem
- Stabilna vodena kupelj ($\pm 0,0005 \text{ } ^\circ\text{C}$)


Pokus: Re - voda u Re - vodu

Broj dodataka: 5
 Volumen svakog dodatka: 10 μl
 Razmak između dodataka: 300 s

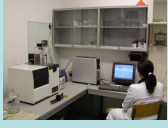


Uzorak:

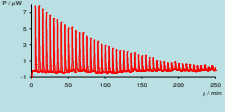
Metoda:
Izotermalna titracijska mikrokolorimetrija



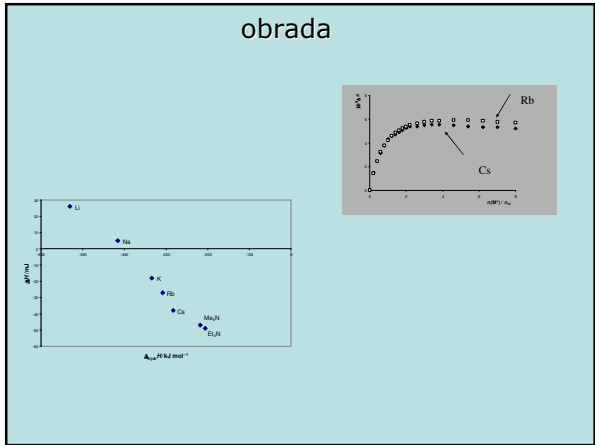
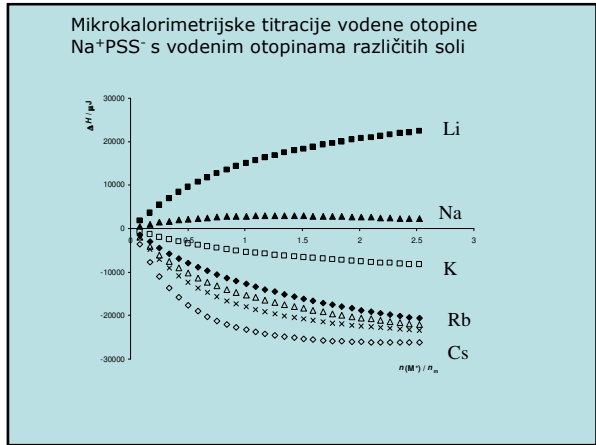
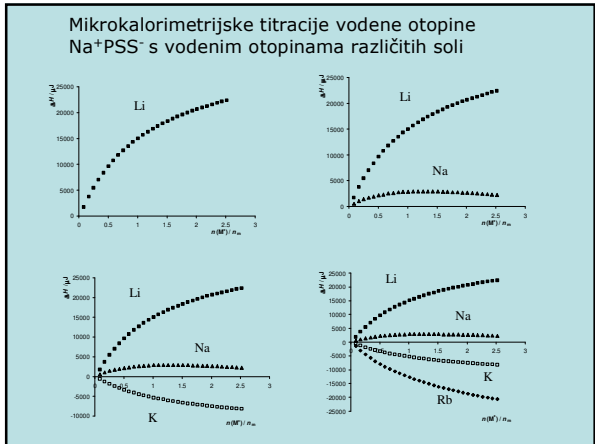
$M_w = 70\,000\text{ g mol}^{-1}$



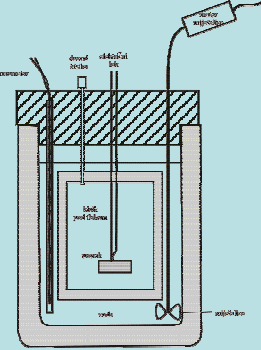
Isothermal titration calorimeter
CSC 4200



Mikrokolorimetrijska titracija vodene otopine Na⁺PSS⁻ s vodenom otopinom CsNO₃



Kombustijski kalorimetar



$$\Delta U = q_v = -C\Delta T$$

$V, T = konst.$

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

Temperaturna ovisnost reakcijske entalpije i unutarnje energije

$$\Delta_r H(T_2) - \Delta_r H(T_1) = \int_{T_1}^{T_2} \Delta_r C_p \, dT \quad \Delta_r C_p = \sum_i \nu_i C_{p,i}$$

$$\Delta_r U(T_2) - \Delta_r U(T_1) = \int_{T_1}^{T_2} \Delta_r C_v \, dT \quad \Delta_r C_v = \sum_i \nu_i C_{v,i}$$

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 $\Delta_r H = -\sum_i \nu_i \Delta_{at} H_i$

DRUGI ZAKON TERMODINAMIKE

ENTROPIJA

Entropija svemira raste.

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

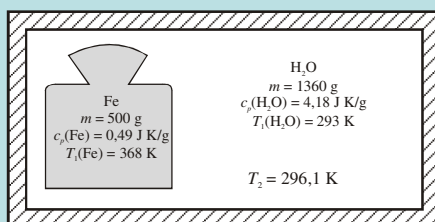
Spontani procesi $\Delta S > 0$

Primjeri:

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



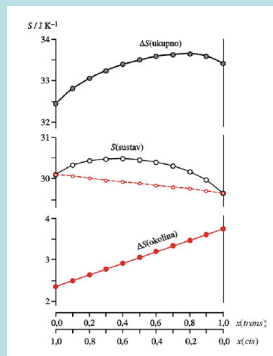
Spontani procesi u izoliranom sustavu popraćeni su povećanjem ukupne entropije.



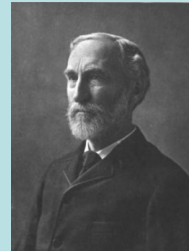
TREĆI ZAKON TERMODINAMIKE

Entropija elemenata i savršenih kristala je nula pri apsolutnoj nuli.

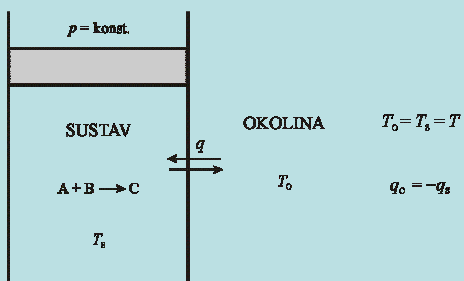
$$S_m(T = 0 \text{ K}) = 0$$



Josiah Willard Gibbs



Gibbsova energija, G



$$G = H - TS$$

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

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

$\Delta_r G > 0$ Povratna reakcija

$\Delta_r G = 0$ Ravnoteža

$\Delta_r G < 0$ Spontana, napredna reakcija

$$G = H - TS$$

$$p = konst.$$

$$T = konst.$$

$$dG = d(H - TS) = dH - d(TS) = dH - TdS - SdT$$

$$dG = dH - TdS$$

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

$$dG = dU + pdV - TdS$$

$$dG = dq + dw' - pdV + pdV - TdS$$

Maksimalni neekspanzijski rad

$$dG = dw'$$

$$G = H - TS$$

$$dG = d(H - TS) = dH - d(TS) = dH - TdS - SdT$$

$$H = U + pV$$

$$dH = dU + d(pV) = dU + pdV + Vdp$$

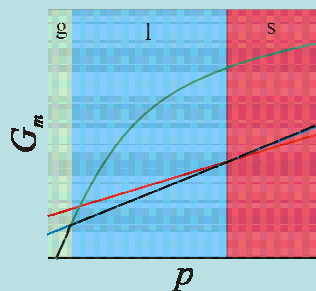
$$dG = dU + pdV + Vdp - TdS - SdT$$

$$dG = dq - pdV + pdV + Vdp - dq - SdT$$

$$dG = Vdp - SdT$$

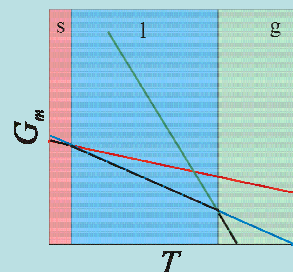
$$dG = Vdp - SdT$$

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



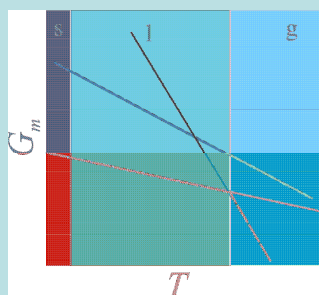
$$dG = Vdp - SdT$$

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



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

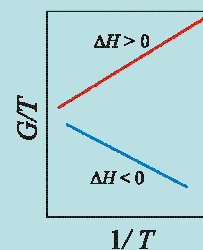
Sublimacija: $A(s) \rightarrow A(g)$



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

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

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



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

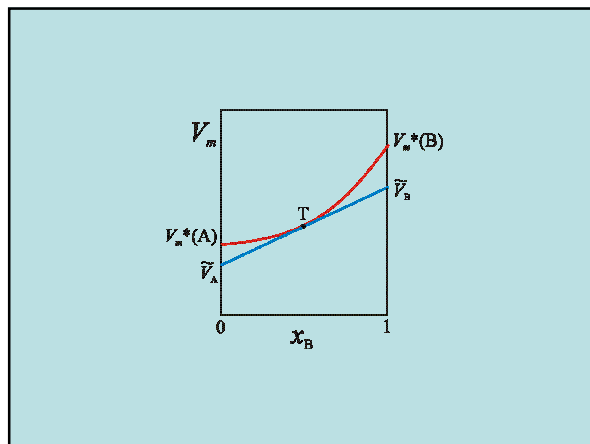
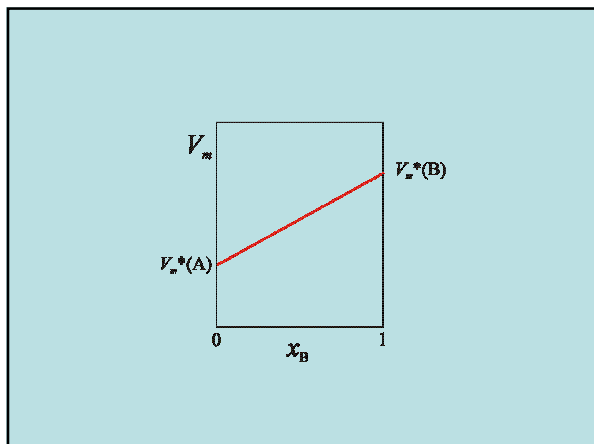
$$\Delta V = 18 \text{ cm}^3$$

$$\tilde{V}(H_2O) = 18 \text{ cm}^3 \text{ mol}^{-1}$$

1 mol H_2O u C_2H_5OH

$$\Delta V = 14 \text{ cm}^3$$

$$\tilde{V}(H_2O) = 14 \text{ cm}^3 \text{ mol}^{-1}$$



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

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

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

Kemijski potencijal

$$\mu_B = \left(\frac{\partial G}{\partial n_B} \right)_{p,T,n_{j \neq B}}$$

1) Čista tvar*

$$\mu_B^* = G_m(B)$$

Čisti plin

$$dG = Vdp - SdT \quad T = \text{konst.} \Rightarrow dG = Vdp$$

$$\int_{G(p_1)}^{G(p_2)} dG = \int_{p_1}^{p_2} Vdp$$

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

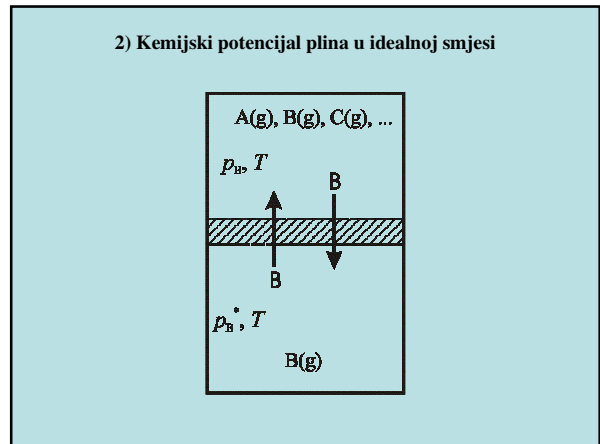
$$\mu(p_2) - \mu(p_1) = RT \ln \frac{p_2}{p_1}$$

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

$$p_2 = p$$

Kemijski potencijal čistog idealnog plina

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



RAVNOTEŽA

$$p_B^* = p_B \quad dG = 0 \quad \mu_B^* = \mu_B$$

Kemijski potencijal čistog idealnog plina:

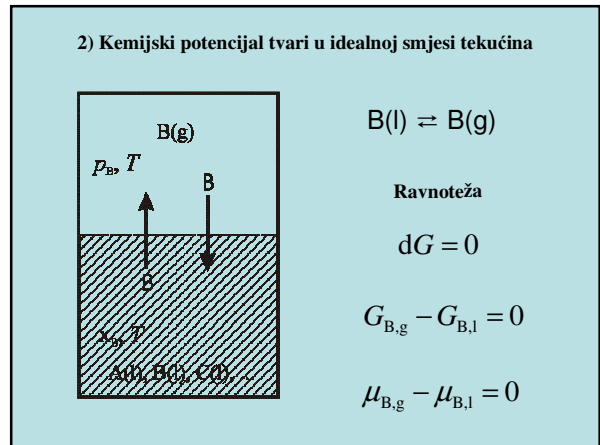
$$\mu_B = \mu^\ominus + RT \ln \frac{p_B}{p^\ominus}$$

Daltonov zakon

$$p_B = x_B p$$

Kemijski potencijal plina u idealnoj smjesi:

$$\mu_B = \mu^\ominus + RT \ln x_B + RT \ln \frac{p}{p^\ominus}$$



Raoultov zakon:
$$p_B = x_B p_B^*$$

$$\mu_B = \mu^\ominus + RT \ln \frac{p_B}{p^\ominus}$$

$$\mu_{B,g} = \mu_g^\ominus + RT \ln x_B + RT \ln \frac{p_B}{p^\ominus}$$

$$\mu_{B,g}^* = \mu_g^\ominus + RT \ln \frac{p_B}{p^\ominus}$$

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

Čista tekućina u ravnoteži:
$$\mu_{B,g}^* = \mu_{B,l}^* \quad \mu_{B,l} = \mu_{B,l}^* + RT \ln x_B$$

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

$$\mu_B = \mu_B^* + RT \ln x_B$$

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

$$p = p^\ominus \quad \mu_B = \mu^\ominus + RT \ln x_B$$

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

$$p \neq p^\ominus \quad \mu_B = \mu^\ominus + RT \ln x_B + \int_{p^\ominus}^p \tilde{V}_B dp$$

$$\mu_B = \mu^\circ + RT \ln x_B + \int_{p^\circ}^p \tilde{V}_B dp$$

$$\mu_B = \mu^\circ + RT \ln x_B + \int_{p^\circ}^p V_{B,m} dp$$

$p \neq p^\circ$

Kemijski potencijal sastojka B u idealnim plinskim smjesama:

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

Kemijski potencijal sastojka B u idealnim kondenziranim smjesama:

$$\mu_B = \mu^\circ + RT \ln x_B + V_{B,m} (p - p^\circ)$$

Kemijski potencijal otopljene tvari B u otopini:

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

$$x_B \approx \frac{n_B}{n_A} = b_B M_A \qquad x_B \approx \frac{n_B}{n_A} = c_B \frac{M_A}{\rho}$$

$$\mu_B = \mu^\circ (p^\circ) + RT \ln \frac{M_A c}{\rho} + RT \ln \frac{c_B}{c^\circ} = \mu^\circ + RT \ln \frac{c_B}{c^\circ}$$

$$\mu_B = \mu^\circ (p^\circ) + RT \ln M_A b^\circ + RT \ln \frac{b_B}{b^\circ} = \mu^\circ + RT \ln \frac{b_B}{b^\circ}$$

IDEALNI SUSTAVI **REALNI SUSTAVI**

INTERAKCIJA MEĐU ČESTICAMA

Plinovi
Tekućine
Krutine
Otopine

Kemijski potencijal realnih sustava

PROMJENE TERMODINAMIČKIH VELIČINA PRILIKOM MIJEŠANJA PLINOVA I TEKUĆINA

Gibbsova energija miješanja

(a) (b)

Razdvojeni plinovi

$$G_1 = n_A \mu_A^* + n_B \mu_B^*$$

(a)

$$\mu_B^* = \left(\mu_B^\circ + RT \ln \frac{p}{p^\circ} \right) \qquad \mu_A^* = \left(\mu_A^\circ + RT \ln \frac{p}{p^\circ} \right)$$

$$G_1 = n_A \left(\mu_A^\circ + RT \ln \frac{p}{p^\circ} \right) + n_B \left(\mu_B^\circ + RT \ln \frac{p}{p^\circ} \right)$$

Pomiješani plinovi

$$G_2 = n_A \mu_A + n_B \mu_B$$

(b)

$$\mu_A = \left(\mu_A^\circ + RT \ln \frac{p_A}{p^\circ} \right) \qquad \mu_B = \left(\mu_B^\circ + RT \ln \frac{p_B}{p^\circ} \right)$$

$$G_2 = n_A \left(\mu_A^\circ + RT \ln \frac{p_A}{p^\circ} \right) + n_B \left(\mu_B^\circ + RT \ln \frac{p_B}{p^\circ} \right)$$

$$G_2 = n_A \left(\mu_A^\circ + RT \ln \frac{p_A}{p^\circ} \right) + n_B \left(\mu_B^\circ + RT \ln \frac{p_B}{p^\circ} \right)$$

$$p_A = x_A p \quad p_B = x_B p$$

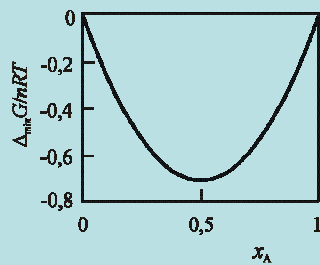
$$G_2 = n_A \left(\mu_A^\circ + RT \ln x_A + RT \ln \frac{p}{p^\circ} \right) + n_B \left(\mu_B^\circ + RT \ln x_B + RT \ln \frac{p}{p^\circ} \right)$$

Gibbsova energija miješanja idealnih plinova:

$$\Delta G_{\text{mix}} = G_1 - G_2$$

$$\Delta G_{\text{mix}} = n_A RT \ln x_A + n_B RT \ln x_B$$

$$\Delta G_{\text{mix}} = nRT (x_A \ln x_A + x_B \ln x_B)$$

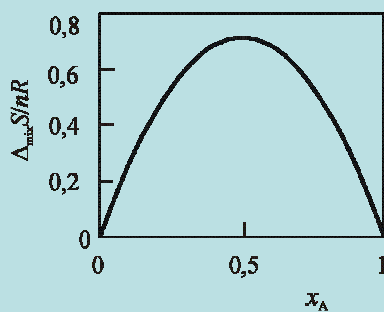


$$dG = VdP - SdT$$

$$\left(\frac{\partial G}{\partial T} \right)_P = -S \quad \Delta S_{\text{mix}} = - \left(\frac{\partial \Delta G_{\text{mix}}}{\partial T} \right)_P$$

$$\Delta S_{\text{mix}} = -n_A R \ln x_A - n_B R \ln x_B$$

$$\Delta S_{\text{mix}} = -nR (x_A \ln x_A + x_B \ln x_B)$$



$$\Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T \Delta S_{\text{mix}} = 0$$

Miješanje tekućina koje tvore idealnu smjesu

$$\Delta G_{\text{mix}} = nRT(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta S_{\text{mix}} = -nR(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta H_{\text{mix}} = 0$$

Promjena Gibbsove energije s napredovanjem kemijske reakcije

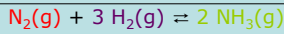
$$\left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j \neq i}} = \tilde{G}_i = \mu_i$$

$$dG_i = \mu_i dn_i$$

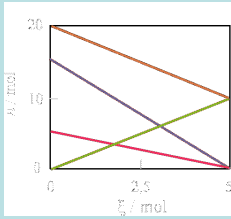
$$dn_i = \nu_i d\xi$$

$$dG_i = \sum_i \nu_i \mu_i d\xi \quad p, T = \text{konst.}$$

SASTAV REAKCIJSKOG SUSTAVA



n_0 / mol	5	15	0
n_i / mol	0	0	10



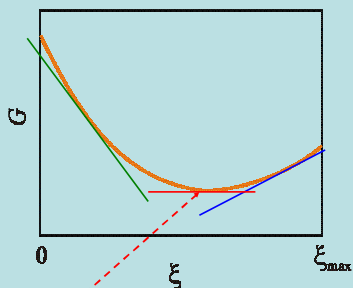
$$\xi_{\text{max}} = 5 \text{ mol}$$

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

Gibbsova energija u reakcijskom sustavu

$$\Delta_r G = \frac{dG}{d\xi} = \sum_i \nu_i \mu_i$$

$$\Delta_r G^\circ = \frac{dG^\circ}{d\xi} = \sum_i \nu_i \mu_i^\circ$$



$$\Delta_r G < 0$$

$$\Delta_r G = 0$$

$$\Delta_r G > 0$$

$$\Delta_r G = \frac{dG}{d\xi} = \sum_i \nu_i \mu_i$$

Gibbsova energija u reakcijskom sustavu

$$\Delta_r G = \frac{dG}{d\xi} = \sum_i \nu_i \mu_i$$

$$\Delta_r G^\circ = \frac{dG^\circ}{d\xi} = \sum_i \nu_i \mu_i^\circ$$

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

$$\Delta_r G = \sum_i \nu_i (\mu_i^\circ + RT \ln a_i)$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln \prod_i a_i^{\nu_i}$$

$$\prod_i a_i^{\nu_i} = Q$$

Standardna konstanta ravnoteže

$$\Delta_r G^{\text{eq}} = 0$$

$$\Delta_r G^\circ + RT \ln \prod_i (a_i^{v_i})^{\text{eq}} = 0$$

$$\Delta_r G^\circ = -RT \ln \prod_i (a_i^{v_i})^{\text{eq}}$$

Standardna konstanta ravnoteže

$$\prod_i a_i^{v_i} = Q$$

$$\prod_i (a_i^{v_i})^{\text{eq}} = Q_e$$

$$\prod_i (a_i^{v_i})^{\text{eq}} = K^\circ$$

$$\Delta_r G^\circ = -RT \ln K^\circ$$

EMPIRIJSKE KONSTANTE RAVNOTEŽA

Tlačna konstanta ravnoteže

$$K_p = \prod_i (p_i^{\text{eq}})^{v_i}$$

$$K^\circ = K_p (p^\circ)^{-\sum_i v_i} \prod_i (y_i^{\text{eq}})^{v_i}$$

Racionalna konstanta ravnoteže

$$K_x = \prod_i (x_i^{\text{eq}})^{v_i}$$

$$K^\circ = K_x \prod_i (y_i^{\text{eq}})^{v_i}$$

Koncentracijska konstanta ravnoteže

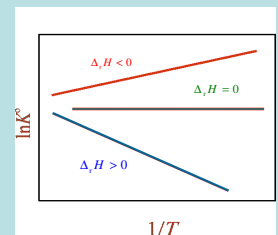
$$K_c = \prod_i (c_i^{\text{eq}})^{v_i}$$

$$K^\circ = K_c (c^\circ)^{-\sum_i v_i} \prod_i (y_i^{\text{eq}})^{v_i}$$

Ovisnost standardne konstante ravnoteže o temperaturi

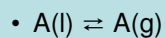
$$-RT \ln K^\circ = \Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

$$\ln K^\circ = -\frac{\Delta_r H^\circ}{R} \cdot \frac{1}{T} + \frac{\Delta_r S^\circ}{R}$$



Koligativna svojstva

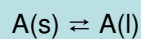
Tlak para otopala



$$p_A = p_A^* x_A \quad \Delta p_A = p_A^* - p_A = p_A^* x_B$$

$$p_A = p_A^* (1 - x_B)$$

Talište otopine



$$-\mu(s) + \mu(l) = 0$$

$$\mu^\ominus(l) + RT_f \ln x_1 = \mu^\ominus(s) + RT_f \ln x_s$$

$$-RT_f \ln x_1 = \mu^\ominus(l) - \mu^\ominus(s) =$$

$$= \Delta_{\text{fus}} G^\ominus = \Delta_{\text{fus}} H^\ominus - T_f \Delta_{\text{fus}} S^\ominus$$

$$T_f = \frac{\Delta_{\text{fus}} H^\ominus}{\Delta_{\text{fus}} S^\ominus - R \ln x_1}$$

krioskopska konstanta

$$K_f = \frac{M_A RT_f^{*2}}{\Delta_{\text{fus}} H^\ominus}$$

$$M_B = \frac{K_f m_B}{\Delta T_f m_A}$$

krioskopska konstanta

određivanje molarne
mase otopljene tvari
krioskopijom

Vrelište otopine

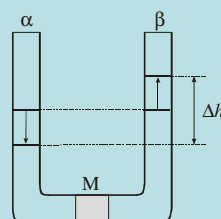
$$K_b = \frac{M_A RT_b^{*2}}{\Delta_{\text{vap}} H^\ominus}$$

$$M_B = \frac{K_b m_B}{\Delta T_b m_A}$$

ebulioskopska konstanta

određivanje molarne
mase otopljene tvari
ebulioskopijom

osmotski tlak



osmotski tlak

Osmotska ravnoteža: $\mu_A^*(p^\alpha) = \mu_A(p^\beta, c_B)$

$$-RT \ln x_A^\beta = \Pi V_{m,A}$$

$$RT x_B = \Pi V_{m,A}$$

osmotski tlak

$$x_B = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A} \quad (n_B \ll n_A)$$

$$V_{A,m} = V/n_A$$

$$\Pi = c_B RT$$

$$M_B = \frac{RT m_B}{\Pi V} = \frac{RT}{\Pi} \gamma_B$$

osmometrijsko određivanje molarne mase tvari B