Kemijska ravnoteža

Uvjeti kemijske ravnoteže

Prvi zakon termodinamike – bilančne jednadžbe po atomima

$$CH_3COOH + C_2H_5OH \leftrightarrow CH_3COOC_2H_5 + H_2O$$

2 mol 1 mol 0,03 mol 0,02 mol

nk=4 ne=3

Ugljik: $2*2+1*2+0,03*4+0,02*0$

$$b_C^F = \sum_{i=1}^{nk} n_i^F \beta_{iC}$$

$$\sum_{i=1}^{nk} n_i^F \beta_{ie} = \sum_{i=1}^{nk} n_i^O \beta_{ie}$$

Broj atoma na ulazu jednak je broju u bilo kojem trenutku, pa tako i u ravnoteži

Uvjeti kemijske ravnoteže

Prvi zakon termodinamike – bilančne jednadžbe po atomima

Kod heterogene ravnoteže

$$\sum_{i=1}^{nk} n_i^{\mathrm{F}} \beta_{ie} = \sum_{i=1}^{nk} n_i^{\mathrm{I}} \beta_{ie} + \sum_{i=1}^{nk} n_i^{\mathrm{II}} \beta_{ie} + \cdots + \sum_{i=1}^{nk} n_i^{nf} \beta_{ie}$$

$$\sum_{j=1}^{ne} \sum_{i=1}^{nk} n_i^{\mathrm{F}} \beta_{ij} = \sum_{j=1}^{ne} \sum_{i=1}^{nk} n_i^{\mathrm{I}} \beta_{ij} + \sum_{j=1}^{ne} \sum_{i=1}^{nk} n_i^{\mathrm{II}} \beta_{ij} + L + \sum_{j=1}^{ne} \sum_{i=1}^{nk} n_i^{nf} \beta_{ij}$$

$$\sum_{i=1}^{nk} x_i^{\mathrm{I}} = \sum_{i=1}^{nk} x_i^{\mathrm{II}} = \cdots = \sum_{i=1}^{nk} x_i^{nf} = 1$$

Uvjeti kemijske ravnoteže

Prvi zakon termodinamike – bilance energije

$$H^{\mathrm{F}} = \sum_{i=1}^{nk} n_i^{\mathrm{F}} h_i^{\mathrm{F}}$$ Ulaz

$$H^{\mathrm{O}} = \sum_{i=1}^{nk} n_i^{\mathrm{O}} h_i^{\mathrm{O}}$$ Ravnoteža

$$H^{\mathrm{O}} = \sum_{i=1}^{nk} n_i^{\mathrm{I}} h_i^{\mathrm{I}} + \sum_{i=1}^{nk} n_i^{\mathrm{II}} h_i^{\mathrm{II}} + \cdots \sum_{i=1}^{nk} n_i^{nf} h_i^{nf}$$ Višefazni sustavi

Adijabatski $$H^{\mathrm{F}} = H^{\mathrm{O}}$$ $$\sum_{i=1}^{nk} n_i^{\mathrm{F}} h_i^{\mathrm{F}} = \sum_{i=1}^{nk} n_i^{\mathrm{O}} h_i^{\mathrm{O}}$$

$$\sum_{i=1}^{nk} n_i^{\mathrm{F}} h_i^{\mathrm{F}} = \sum_{i=1}^{nk} n_i^{\mathrm{I}} h_i^{\mathrm{I}} + \sum_{i=1}^{nk} n_i^{\mathrm{II}} h_i^{\mathrm{II}} + \cdots \sum_{i=1}^{nk} n_i^{nf} h_i^{nf}$$

Uz izmjenu $$H^{\mathrm{F}} = H^{\mathrm{O}} + Q$$

Uvjeti kemijske ravnoteže

Entalpije pojedinih komponenata iz entalpija nastajanja

$$h = \Delta h_{\mathrm{f}}^{\circ} + \int_{T^{\circ}}^{T} c_{p^{\circ}}(T)\,dT + \sum h^{\mathrm{fp}} + \int_{p^{\circ}}^{p} \left(\frac{\partial h}{\partial p}\right)_{T} dp$$

Neidealni sustavi

$$\sum_{i=1}^{nk} n_i^{\mathrm{F}} h_i^{\mathrm{F}} + H^{\mathrm{ex,F}} = \sum_{i=1}^{nk} n_i^{\mathrm{O}} h_i^{\mathrm{O}} + H^{\mathrm{ex,O}}$$

Jedna faza

$$\sum_{i=1}^{nk} n_i^{\mathrm{F}} h_i^{\mathrm{F}} + H^{\mathrm{ex,F}} = \sum_{i=1}^{nk} n_i^{\mathrm{I}} h_i^{\mathrm{I}} + H^{\mathrm{ex,I}} + \sum_{i=1}^{nk} n_i^{\mathrm{II}} h_i^{\mathrm{II}} + H^{\mathrm{ex,II}} + \cdots \sum_{i=1}^{nk} n_i^{nf} h_i^{nf} + H^{\mathrm{ex},nf}$$

Više faza

Uvjeti kemijske ravnoteže

Drugi zakon termodinamike

$$S = \max \quad \Rightarrow \quad dS = 0$$

Maksimum entropije izoliranih sustava

$$G = \min \quad \Rightarrow \quad dG = 0$$

Minimum Gibbsove energije zatvorenih sustava pri *p, T*=konst.

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

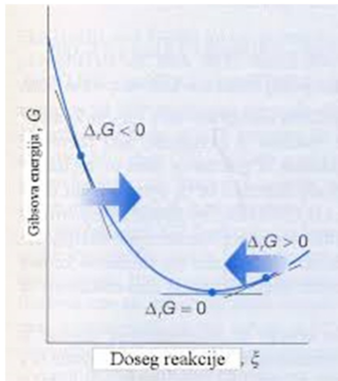
$$dG = \sum_{i=1}^{nk} \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j\neq i}} dn_i$$

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

$$dn_i = \nu_i d\xi$$

$$dG = \left(\sum_{i=1}^{nk} \mu_i \nu_i\right) d\xi \qquad \frac{dG}{d\xi} = 0$$

Ravnotežni doseg



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

Stehiometrijska suma kemijskih potencijala

Uvjeti kemijske ravnoteže

$$\sum_{i=1}^{nk} \mu_i \nu_i = 0$$ Stehiometrijska suma kemijskih potencijala

$$\mu_i = \mu_i^\circ + RT \ln a_i \qquad \mu_i^\circ = g_i$$ Standardno stanje
Čista tvar

Najčešći podaci: $\Delta g_\mathrm{f}^\circ$ i $\Delta h_\mathrm{f}^\circ$ pri standardnim uvjetima od 1 bar i 298,15 K

Standardna temperatura $$G = H - TS \qquad \Delta s_\mathrm{f}^\circ = \frac{\Delta h_\mathrm{f}^\circ - \Delta g_\mathrm{f}^\circ}{T^\circ}$$

Integriranje $$h_i = \Delta h_\mathrm{f}^\circ + \int_{T^\circ}^{T} c_{p^\circ}(T)\,dT \qquad s_i = \Delta s_\mathrm{f}^\circ + \int_{T^\circ}^{T} \frac{c_{p^\circ}(T)}{T}\,dT$$

Konačna temperatura $$g_i = h_i - Ts_i$$

Za realne plinove ovisnost o tlaku putem aktivnosti $$a_i = \frac{\hat{f}_i}{f_i^\circ} = \frac{\hat{\varphi}_i p y_i}{\varphi_i^\circ p^\circ}$$

Za realne otopine ovisnost o tlaku zanemariva $$a_i = x_i \gamma_i$$

Kemijske reakcije

Jednostavne reakcije

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

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$$

$$CH_3COOH + C_2H_5OH \leftrightarrow CH_3COOC_2H_5 + H_2O$$

Dopuštene su linearne transformacije kemijskih jednadžbi

Ekvivalentno

$$3/2\,H_2 + 1/2\,N_2 \leftrightarrow NH_3$$

$$4CH_4 + 8O_2 \leftrightarrow 4CO_2 + 8H_2O$$

$$CH_3COOC_2H_5 + H_2O\text{-}C_2H_5OH \leftrightarrow CH_3COOH$$

Položaj kemijske ravnoteže u reakcijskom sustavu ne ovise o obliku zapisa

Kemijske reakcije

Esterifikacija

$$CH_3COOH + C_2H_5OH \leftrightarrow CH_3COOC_2H_5 + H_2O$$

Linearna transformacija – dodaju se kemijski elementi

$$CH_3COOH + C_2H_5OH + 4C + 3/2\,O_2 + 5H_2 \leftrightarrow CH_3COOC_2H_5 + H_2O + 4C + 3/2\,O_2 + 5H_2$$

E

Linearna kombinacija (manipulacija)

A $2C + O_2 + 2H_2 \leftrightarrow CH_3COOH$

B $2C + 1/2\,O_2 + 3H_2 \leftrightarrow C_2H_5OH$

C $4C + O_2 + 4H_2 \leftrightarrow CH_3COOC_2H_5$

D $1/2\,O_2 + H_2 \leftrightarrow H_2O$

$$E = C + D - A - B$$

$$\Delta g_{\mathrm{r}}^{\circ}(\text{esterifikacija}) = \Delta g_{\mathrm{f}}^{\circ}(CH_3COOC_2H_5) + \Delta g_{\mathrm{f}}^{\circ}(H_2O) - \Delta g_{\mathrm{f}}^{\circ}(CH_3COOH) - \Delta g_{\mathrm{f}}^{\circ}(C_2H_5OH)$$

$$\Delta g_{\mathrm{r}}^{\circ} = \sum_{i=1}^{nk} \nu_i \Delta g_{\mathrm{f},i}^{\circ}$$

Kemijske reakcije

Esterifikacija

$$CH_3COOH + C_2H_5OH \leftrightarrow CH_3COOC_2H_5 + H_2O$$

Linearna transformacija – dodaju se termodinamički nestabilne specije – atomi

$$CH_3COOH + C_2H_5OH + 4C + 3O + 10H \leftrightarrow CH_3COOC_2H_5 + H_2O + 4C + 3O + 10H$$

E

Linearna kombinacija (manipulacija)

A $2C + 2O + 4H \leftrightarrow CH_3COOH$

B $2C + O + 6H \leftrightarrow C_2H_5OH$

C $4C + 2O + 8H \leftrightarrow CH_3COOC_2H_5$

D $O + 2H \leftrightarrow H_2O$

$$E = C + D - A - B$$

Kemijske reakcije

Metoda matrične eliminacije

Određivanje minimalnoga broja kemijskih reakcija

A: $4NH_3 + 5O_2 \leftrightarrow 4NO + 6H_2O$,

B: $4NH_3 + 3O_2 \leftrightarrow 2N_2 + 6H_2O$,

C: $4NH_3 + 6NO \leftrightarrow 5N_2 + 6H_2O$,

D: $2NO + O_2 \leftrightarrow 2NO_2$,

E: $2NO \leftrightarrow N_2 + O_2$,

F: $N_2 + 2O_2 \leftrightarrow 2NO_2$.

Kod složenih reakcija često nije moguće *a priori* odrediti broj neovisnih kemijskih reakcija u sustavu

Matrica stehiometrijskih koeficijenata

	NH_3	O_2	NO	H_2O	N_2	NO_2
A	-4	-5	4	6	0	0
B	-4	-3	0	6	2	0
C	-4	0	-6	6	5	0
D	0	-1	-2	0	0	2
E	0	1	-2	0	1	0
F	0	-2	0	0	-1	2

	NH_3	O_2	NO	H_2O	N_2	NO_2
A/(-4)	1	5/4	-1	-3/2	0	0
B	-4	-3	0	6	2	0
C	-4	0	-6	6	5	0
D	0	-1	-2	0	0	2
E	0	1	-2	0	1	0
F	0	-2	0	0	-1	2

Dijagonala traži jedinicu

Neovisne kemijske reakcije u sustavu potrebno je odrediti radi stabilnosti numeričkih postupaka proračuna ravnoteže

Kemijske reakcije

Metoda matrične eliminacije

Određivanje minimalnoga broja kemijskih reakcija

			NH_3	O_2	NO	H_2O	N_2	NO_2
A/(-4)	=	-A/4	1	5/4	-1	-3/2	0	0
{[A/(-4)]×(-4)}-B	=	A-B	0	-2	4	0	-2	0
{[A/(-4)]×(-4)}-C	=	A-C	0	-5	10	0	-5	0
{[A/(-4)]×0}-D	=	-D	0	1	2	0	0	-2
{[A/(-4)]×0}-E	=	-E	0	-1	2	0	-1	0
{[A/(-4)]×0}-F	=	-F	0	2	0	0	1	-2

Pod dijagonalom traže se nule

	NH_3	O_2	NO	H_2O	N_2	NO_2
A/(-4)	1	5/4	-1	-3/2	0	0
(A-B)/(-2)	0	1	-2	0	1	0
A-C	0	-5	10	0	-5	0
-D	0	1	2	0	0	-2
-E	0	-1	2	0	-1	0
-F	0	2	0	0	1	-2

Dijagonala traži jedinicu

			NH_3	O_2	NO	H_2O	N_2	NO_2
-A/4	=	-A/4	1	5/4	-1	-3/2	0	0
(A-B)/(-2)	=	(B-A)/2	0	1	-2	0	1	0
[(A-B)/(-2)]×(-5)-(A-C)	=	(A-B)×5/2+C-A	0	0	0	0	0	0
[(A-B)/(-2)]×1-(-D)	=	(B-A)/2+D	0	0	-4	0	1	2
[(A-B)/(-2)]×(-1)-(-E)	=	(A-B)/2+E	0	0	0	0	0	0
[(A-B)/(-2)]×2-(-F)	=	B-A+F	0	0	-4	0	1	2

Pod dijagonalom traže se nule

Kemijske reakcije

Metoda matrične eliminacije

Određivanje minimalnoga broja kemijskih reakcija

	NH_3	O_2	NO	H_2O	N_2	NO_2
-A/4	1	5/4	-1	-3/2	0	0
(B-A)/2	0	1	-2	0	1	0
(B-A)/2+D	0	0	-4	0	1	2
B-A+F	0	0	-4	0	1	2

Eliminiranje praznih redaka

	NH_3	O_2	NO	H_2O	N_2	NO_2
-A/4	1	5/4	-1	-3/2	0	0
(B-A)/2	0	1	-2	0	1	0
[(B-A)/2+D]/(-4)	0	0	1	0	-1/4	-1/2
B-A+F	0	0	-4	0	1	2

Dijagonala traži jedinicu

			NH_3	O_2	NO	H_2O	N_2	NO_2
-A/4	=	-A/4	1	5/4	-1	-3/2	0	0
(B-A)/2	=	(B-A)/2	0	1	-2	0	1	0
[(B-A)/2+D]/(-4)	=	[(A-B)/2-D]/4	0	0	1	0	-1/4	-1/2
[(B-A)/2+D]/(-4)×(-4)-(B-A+F)	=	(A-B)/2+D-F	0	0	0	0	0	0

Pod dijagonalom traže se nule

Kemijske reakcije

Metoda matrične eliminacije

Određivanje minimalnoga broja kemijskih reakcija

	NH_3	O_2	NO	H_2O	N_2	NO_2
-A/4	1	5/4	-1	-3/2	0	0
(B-A)/2	0	1	-2	0	1	0
[(A-B)/2-D]/4	0	0	1	0	-1/4	-1/2

Eliminiranje praznih redaka

-A/4: $NO + 3/2\,H_2O \leftrightarrow NH_3 + 5/4\,O_2$

(B-A)/2: $2NO \leftrightarrow O_2 + N_2$

[(A-B)/2-D]/4: $1/4\,N_2 + 1/2\,NO_2 \leftrightarrow NO$

Rješenje

	NH_3	O_2	NO	H_2O	N_2	NO_2
G:	1	0	0	-3/2	-7/8	3/4
H:	0	1	0	0	1/2	-1
I:	0	0	1	0	-1/4	-1/2

Wolfram Mathematica **RowReduce**

G: $3/2\,H_2O + 7/8\,N_2 \leftrightarrow NH_3 + 3/4\,NO_2$

H: $NO_2 \leftrightarrow O_2 + 1/2\,N_2$

I: $1/4\,N_2 + 1/2\,NO_2 \leftrightarrow NO$

Ekvivalentno rješenje

Kemijske reakcije

Denbighova metoda

1. oblikovanje komponenata iz atoma
2. eliminiranje termodinamički nestabilnih specija

J:	$N + 3H \leftrightarrow NH_3$,
K:	$2O \leftrightarrow O_2$,
L:	$N + O \leftrightarrow NO$,
M:	$2H + O \leftrightarrow H_2O$,
N:	$2N \leftrightarrow N_2$,
O:	$N + 2O \leftrightarrow NO_2$.

Eliminiranje npr. N

K:	$2O \leftrightarrow O_2$,
L-J:	$O - 3H \leftrightarrow NO - NH_3$,
M:	$2H + O \leftrightarrow H_2O$,
N-2×J:	$-6H \leftrightarrow N_2 - 2NH_3$,
O-J:	$2O - 3H \leftrightarrow NO_2 - NH_3$.

Eliminiranje npr. O

L-J-K/2:	$-3H \leftrightarrow NO - NH_3 - 1/2\,O_2$,
M-K/2:	$2H \leftrightarrow H_2O - 1/2\,O_2$,
N-2×J:	$-6H \leftrightarrow N_2 - 2NH_3$,
O-J-K:	$-3H \leftrightarrow NO_2 - NH_3 - O_2$.

Eliminiranje H

M-K/2+2/3×(L-J-K/2):	$0 \leftrightarrow H_2O - 5/6\,O_2 + 2/3\,NO - 2/3\,NH_3$,
N-2×J-2×(L-J-K/2):	$0 \leftrightarrow N_2 - 2NO + O_2$,
O-J-K-(L-J-K/2):	$0 \leftrightarrow NO_2 - NO - 1/2\,O_2$.

Ekvivalentno rješenje

$$5/6\,O_2 + 2/3\,NH_3 \leftrightarrow H_2O + 2/3\,NO\,,$$
$$2NO \leftrightarrow N_2 + O_2\,,$$
$$NO + 1/2\,O_2 \leftrightarrow NO_2\,.$$

Homogena kemijska ravnoteža

Jedna kemijska reakcija

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

$$\mu_i = g_i + RT \ln a_i$$ Standardno stanje čista tvar

$$\sum_{i=1}^{nk} \nu_i \mu_i = \sum_{i=1}^{nk} \nu_i g_i + RT \sum_{i=1}^{nk} \nu_i \ln a_i = 0$$

$$-\sum_{i=1}^{nk} \nu_i g_i = RT \ln \prod_{i=1}^{nk} (a_i)^{\nu_i}$$

$$-\sum_{i=1}^{nk} \nu_i \left(\Delta g_\mathrm{f}^\circ\right) = RT \ln \prod_{i=1}^{nk} (a_i)^{\nu_i}$$ Uvođenje Gibbsovih energija nastajanja

$$-\sum_{i=1}^{nk} \nu_i \left(\Delta g_\mathrm{f}^\circ\right) = -\Delta g_\mathrm{r}^\circ$$

Standardna Gibbsova Reakcijska energija

$$\prod_{i=1}^{nk} (a_i)^{\nu_i} = K_\mathrm{r}$$

Konstanta ravnoteže

$$-\Delta g_\mathrm{r}^\circ = RT \ln K_\mathrm{r}$$

Ravnotežna jednadžba II

Homogena kemijska ravnoteža

Jedna kemijska reakcija

$$-\Delta g_{\mathrm{r}}^{\circ} = RT \ln \prod_{i=1}^{nk} \left(\frac{\hat{f}_i}{f_i^{\circ}} \right)^{\nu_i}$$

Realni plinovi

$$-\Delta g_{\mathrm{r}}^{\circ} = RT \ln \prod_{i=1}^{nk} \left(\frac{\hat{\varphi}_i p y_i}{\varphi_i^{\circ} p^{\circ}} \right)^{\nu_i}$$

$$-\Delta g_{\mathrm{r}}^{\circ} = RT \ln \prod_{i=1}^{nk} \left(\frac{p y_i}{p^{\circ}} \right)^{\nu_i}$$

Idealni plinovi

$$-\Delta g_{\mathrm{r}}^{\circ} = RT \ln \prod_{i=1}^{nk} \left(\frac{p_i}{p^{\circ}} \right)^{\nu_i}$$

Parcijalni tlakovi

$$-\Delta g_{\mathrm{r}}^{\circ} = RT \ln \prod_{i=1}^{nk} \left(x_i \gamma_i \right)^{\nu_i}$$

Realne otopine

$$-\Delta g_{\mathrm{r}}^{\circ} = RT \ln \prod_{i=1}^{nk} \left(x_i \right)^{\nu_i}$$

Idealne otopine

Homogena kemijska ravnoteža

Jedna kemijska reakcija – 1. primjer

Stehiometrijska smjesa vodika i dušika (3:1) ulazi u kemijski reaktor, pri 450 K i 4 atm, u kojem se zadržava dovoljno dugo da se postigne kemijska ravnoteža. Odrediti molarne udjele dušika, vodika i amonijaka u izlaznoj struji! Pretpostaviti idealno ponašanje plinske smjese u ravnoteži! (Prema Sandleru!)

$$1/2\,N_2 + 3/2\,H_2 \rightarrow NH_3$$

Kemijska reakcija

$$\nu(NH_3) = 1$$
$$\nu(N_2) = -1/2$$
$$\nu(H_2) = -3/2$$

Stehiometrijski koeficijenti

$$\Delta h_f^\circ(NH_3) = -45857\ \mathrm{J\ mol^{-1}}$$
$$\Delta g_f^\circ(NH_3) = -16330\ \mathrm{J\ mol^{-1}}$$

Termodinamički podaci

$$c_p(NH_3) = \left(6{,}5846 + 6{,}1251\cdot10^{-3}\frac{T}{\mathrm{K}} + 2{,}3663\cdot10^{-6}\frac{T^2}{\mathrm{K}^2} - 1{,}5981\cdot10^{-9}\frac{T^3}{\mathrm{K}^3}\right)\cdot 4{,}184\ \mathrm{J\ mol^{-1}K^{-1}}$$
$$c_p(H_2) = \left(6{,}952 - 4{,}576\cdot10^{-4}\frac{T}{\mathrm{K}} + 9{,}563\cdot10^{-7}\frac{T^2}{\mathrm{K}^2} - 2{,}079\cdot10^{-10}\frac{T^3}{\mathrm{K}^3}\right)\cdot 4{,}184\ \mathrm{J\ mol^{-1}K^{-1}}$$
$$c_p(N_2) = \left(6{,}903 - 3{,}753\cdot10^{-4}\frac{T}{\mathrm{K}} + 1{,}930\cdot10^{-6}\frac{T^2}{\mathrm{K}^2} - 6{,}861\cdot10^{-10}\frac{T^3}{\mathrm{K}^3}\right)\cdot 4{,}184\ \mathrm{J\ mol^{-1}K^{-1}}$$

Homogena kemijska ravnoteža

Jedna kemijska reakcija – 1. primjer

$$\Delta c_p(T) = \sum_{i=1}^{nk} \nu_i c_{pi}(T) =$$

$$= \begin{bmatrix} \left(6,5846 - \frac{6,903}{2} - \frac{3\cdot 6,952}{2}\right) \\ + \left(6,1251\cdot 10^{-3} + \frac{3,753\cdot 10^{-4}}{2} + \frac{3\cdot 4,576\cdot 10^{-4}}{2}\right)\cdot \frac{T}{\mathrm{K}} + \\ + \left(2,3663\cdot 10^{-6} - \frac{1,930\cdot 10^{-6}}{2} - \frac{3\cdot 9,563\cdot 10^{-7}}{2}\right)\cdot \frac{T^2}{\mathrm{K}^2} + \\ + \left(-1,5981\cdot 10^{-9} + \frac{6,861\cdot 10^{-10}}{2} + \frac{3\cdot 2,079\cdot 10^{-10}}{2}\right)\cdot \frac{T^3}{\mathrm{K}^3} \end{bmatrix} \cdot 4,184\ \mathrm{J\ mol^{-1} K^{-1}} =$$

Toplinska funkcija

$$= \left(-30,5219 + 2,92844\cdot 10^{-2}\cdot \frac{T}{\mathrm{K}} - 1,387\cdot 10^{-7}\cdot \frac{T^2}{\mathrm{K}^2} - 3,94635\cdot 10^{-9}\cdot \frac{T^3}{\mathrm{K}^3}\right)\ \mathrm{J\ mol^{-1} K^{-1}}$$

$$\Delta h_\mathrm{r}^\circ = \sum_{i=1}^{nk} \nu_i \Delta h_{\mathrm{f},i}^\circ = 1\cdot\left(-45857\ \mathrm{J\ mol^{-1}}\right) - 1/2\cdot 0 - 3/2\cdot 0 = -45857\ \mathrm{J\ mol^{-1}}$$

Standardna reakcijska entalpija pri 298,15K

$$\Delta s_\mathrm{r}^\circ = \frac{\Delta h_\mathrm{r}^\circ - \Delta g_\mathrm{r}^\circ}{T^\circ} = \frac{-45857 - (-16330)}{298,2} = 99,0174\ \mathrm{J\ mol^{-1} K^{-1}}$$

Standardna reakcijska entropija pri 298,15K

$$\Delta g_\mathrm{r}^\circ = \sum_{i=1}^{nk} \nu_i \Delta g_{\mathrm{f},i}^\circ = -16330\ \mathrm{J\ mol^{-1}}$$

Standardna reakcijska Gibbsova energija pri 298,15K

Homogena kemijska ravnoteža

Jedna kemijska reakcija – 1. primjer

$$\Delta h_{\mathrm{r}} = \Delta h_{\mathrm{r}}^{\circ} + \int_{T^{\circ}}^{T} \Delta c_p(T)\, dT = -45857 + \int_{298.2}^{450} \begin{pmatrix} -30{,}5219 \\ +2{,}92844\cdot 10^{-2}\cdot T \\ -1{,}387\cdot 10^{-7}\cdot T^2 \\ -3{,}94635\cdot 10^{-9}\cdot T^3 \end{pmatrix} dT = -48862{,}8\ \mathrm{J\ mol^{-1}}$$

Reakcijska entalpija pri 450K

$$\Delta s_{\mathrm{r}} = \Delta s_{\mathrm{r}}^{\circ} + \int_{T^{\circ}}^{T} \frac{\Delta c_p(T)}{T}\, dT = 99{,}0174 + \int_{298.2}^{450} \begin{pmatrix} -30{,}5219/T \\ +2{,}92844\cdot 10^{-2} \\ -1{,}387\cdot 10^{-7}\cdot T \\ -3{,}94635\cdot 10^{-9}\cdot T^2 \end{pmatrix} dT = -107{,}224\ \mathrm{J\ mol^{-1}K^{-1}}$$

Reakcijska entropija pri 450K

$$\Delta g_{\mathrm{r}} = \Delta h_{\mathrm{r}} - T\Delta s_{\mathrm{r}} = -48862{,}8 - 450\cdot(-107{,}224) = -611{,}974\ \mathrm{J\ mol^{-1}}$$

Reakcijska Gibbsova energija pri 450K

Bilanca tvari preko stehiometrijske tablice

Tvar	Početno stanje	Ravnotežno stanje	Molarni udio
NH_3	0	ξ	ξ / (2-ξ)
N_2	0,5	0,5(1-ξ)	0,5(1-ξ) / (2-ξ)
H_2	1,5	1,5(1-ξ)	1,5(1-ξ) / (2-ξ)
ukupno	2	2-ξ	1

Homogena kemijska ravnoteža

Jedna kemijska reakcija – 1. primjer

$$-\Delta g_\mathrm{r} = RT\ln\prod_{i=1}^{nk}\left(\frac{\hat{\varphi}_i p y_i}{\varphi_i^\circ p^\circ}\right)^{\nu_i}$$ Ravnoteža u plinskoj fazi

$$-\Delta g_\mathrm{r} = RT\ln\prod_{i=1}^{nk}\left(\frac{p y_i}{p^\circ}\right)^{\nu_i}$$ Idealni plin

$$-(-611{,}974) = 8{,}314\cdot 450\cdot\ln\left[\left(\frac{4\cdot 101325}{101325}\cdot\frac{\xi}{2-\xi}\right)\cdot\left(\frac{4\cdot 101325}{101325}\cdot\frac{0{,}5\cdot(1-\xi)}{2-\xi}\right)^{-0{,}5}\cdot\left(\frac{4\cdot 101325}{101325}\cdot\frac{1{,}5\cdot(1-\xi)}{2-\xi}\right)^{-1{,}5}\right]$$

Uvrsti se bilanca tvari (stehiometrijska tablica)

.

$\underline{\xi_1 = 0{,}625223,}$ $\xi_2 = 1{,}37478$ Dva rješenja nelinearne jednadžbe

$$y(\mathrm{NH_3}) = \frac{\xi}{2-\xi} = \frac{0{,}625223}{2-0{,}625223} = 0{,}454781 \qquad y(\mathrm{N_2}) = \frac{1}{2}\cdot\frac{1-\xi}{2-\xi} = \frac{1}{2}\cdot\frac{1-0{,}625223}{2-0{,}625223} = 0{,}136305 \qquad y(\mathrm{H_2}) = \frac{3}{2}\cdot\frac{1-\xi}{2-\xi} = \frac{3}{2}\cdot\frac{1-0{,}625223}{2-0{,}625223} = 0{,}408194$$

Homogena kemijska ravnoteža

Jedna kemijska reakcija – 2. primjer

Izračunati ravnotežne molarne udjele svih komponenata za reakciju redukcije ugljičnog dioksida u monoksid pomoću vodika pri 1000 K i 500 atm. Konstanta ravnoteže određena je eksperimentom i iznosi 0,693. Inicijalno, CO_2 i H_2 se nalaze u ekvimolarnim količinama. (Prema Sandleru!)

$$\mathrm{CO_2 + H_2 \rightarrow CO + H_2O}$$

Kemijska reakcija

$$\nu(\mathrm{CO_2}) = -1$$
$$\nu(\mathrm{H_2}) = -1$$
$$\nu(\mathrm{CO}) = 1$$
$$\nu(\mathrm{H_2O}) = 1$$

Stehiometrijski koeficijenti

$$-\Delta g_\mathrm{r} = RT \ln \prod_{i=1}^{nk} \left(\frac{\hat{\varphi}_i p y_i}{\varphi_i^\circ p^\circ} \right)^{\nu_i}$$

Kemijska ravnoteža plinovi

$$K_\mathrm{r} = \prod_{i=1}^{nk} \left(\frac{\hat{\varphi}_i p y_i}{\varphi_i^\circ p^\circ} \right)^{\nu_i}$$

$$K_\mathrm{r} = \prod_{i=1}^{nk} \left(\frac{\hat{\varphi}_i p y_i}{p^\circ} \right)^{\nu_i}$$

$$K_\mathrm{r} = \prod_{i=1}^{nk} y_i^{\nu_i} \times \prod_{i=1}^{nk} \hat{\varphi}_i^{\nu_i} \times \left(\frac{p}{p^\circ} \right)^{\sum \nu_i}$$

nepoznanice — neidealnost — Utjecaj tlaka na ravnotežu

$$K_\mathrm{r} = \prod_{i=1}^{nk} y_i^{\nu_i} \times \prod_{i=1}^{nk} \hat{\varphi}_i^{\nu_i}$$

Homogena kemijska ravnoteža

Jedna kemijska reakcija – 2. primjer

Bilanca tvari preko stehiometrijske tablice

Tvar	Početno stanje	Ravnotežno stanje	Molarni udio
CO_2	1	$1-\xi$	$(1-\xi)/2$
H_2	1	$1-\xi$	$(1-\xi)/2$
CO	0	ξ	$\xi/2$
H_2O	0	ξ	$\xi/2$
ukupno	2	2	1

Prva pretpostavka – idealna plinska smjesa

$$0,693 = \prod_{i=1}^{nk} y_i^{\nu_i} \times \prod_{i=1}^{nk} \hat{\varphi}_i^{\nu_i}$$

$$y_i = \left\{ \frac{1-\xi}{2} \quad \frac{1-\xi}{2} \quad \frac{\xi}{2} \quad \frac{\xi}{2} \right\}$$

$$\hat{\varphi}_i = \{1 \quad 1 \quad 1 \quad 1\}$$

$$\xi = 0,454287$$

$$y_i = \{0,272856 \quad 0,272856 \quad 0,227144 \quad 0,227144\}$$

Homogena kemijska ravnoteža

Jedna kemijska reakcija – 2. primjer

Iz procijenjenih sastava moguće je izračunati parcijalne koeficijente fugacitivnosti

$a=\dfrac{\Omega_a R^2 T_k^2}{p_k}$ $\Omega_a=0{,}45724$ $b=\dfrac{\Omega_b R T_k}{p_k}$ $\Omega_b=0{,}07780$

$\alpha=\left(1+\kappa\left(1-\sqrt{T_r}\right)\right)^2$ $\kappa=0{,}37464+1{,}54226\omega-0{,}26992\omega^2$

vodik : $\alpha=1{,}202\exp\left(-0{,}30288T_r\right)$

$(a\alpha)_M=\sum y_i y_j (a\alpha)_{ij}$ $b_M=\sum y_i b_i$

$(a\alpha)_{ij}=\left(1-k_{ij}\right)\sqrt{(a\alpha)_1 (a\alpha)_2}$

$A_M=\dfrac{(a\alpha)_M p}{R^2T^2}$ $B_M=\dfrac{b_M p}{RT}$

$z^3-(1-B_M)z^2+\left(A_M-3B_M^2-2B_M\right)z-\left(A_M B_M-B_M^2-B_M^3\right)=0$

$$\ln\hat{\varphi}_i=\frac{b_i}{b_M}(z-1)-\ln\left[z\left(1-\frac{b_M}{v}\right)\right]+\frac{(a\alpha)_M}{RT2\sqrt{2}b_M}\left(\frac{b_i}{b_M}-\frac{2}{(a\alpha)_M}\sum_j y_j (a\alpha)_{ij}\right)\ln\frac{v+b_M\left(1+\sqrt{2}\right)}{v+b_M\left(1-\sqrt{2}\right)}$$

Peng - Robinson

Slijed: sastav – neidealnost –
sastav – neidealnost –
sastav – neidealnost –
sastav – neidealnost –
sastav – neidealnost –…

$$0,693=\prod_{i=1}^{nk} y_i^{\nu_i}\times\prod_{i=1}^{nk}\hat{\varphi}_i^{\nu_i}$$

Rješenje

$$y_i=\left\{\frac{1-\xi}{2}\quad\frac{1-\xi}{2}\quad\frac{\xi}{2}\quad\frac{\xi}{2}\right\}$$

$$\hat{\varphi}_i=\{1{,}13255\quad 1{,}14544\quad 1{,}16356\quad 0{,}960411\}$$

$$\xi=0,472833$$

$$y_i=\{0,263584\quad 0,263584\quad 0,236416\quad 0,236416\}$$

Homogena kemijska ravnoteža

Jedna kemijska reakcija – 3. primjer

Treba izračunati adijabatsku temperaturu plamena za sagorijevanje metana u zraku, pri 1 atm i 298,15 K, u ovisnosti o ulaznome omjeru zrak/metan.

A: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$.

B: $CH_4(g) + 3/2\,O_2(g) \rightarrow CO(g) + 2H_2O(g)$.

C: $CO(g) + 1/2\,O_2(g) \rightarrow CO_2(g)$.

C = A – B , dvije neovisne reakcije

Matrica stehiometrijskih koeficijenata

	Ar	CH_4	CO	CO_2	H_2O	N_2	O_2
A	0	-1	0	1	2	0	-2
B	0	-1	1	0	2	0	-3/2
C	0	0	-1	1	0	0	-1/2

Termodinamički podaci

tvar	$\Delta h_{f0}°$/ (kJ mol^{-1})	$\Delta g_{f0}°$/ (kJ mol^{-1})	a	$b\times10^3$	$c\times10^6$	$d\times10^{-5}$
Ar	0	0	2,5	-	-	-
CH_4	-74,52	-50,45	1,702	9,081	-2,164	0
CO	-110,53	-137,16	3,376	0,557	-	-0,031
CO_2	-393,51	-394,38	5,457	1,045	-	-1,157
H_2O	-241,81	-228,42	3,470	1,450	-	0,121
N_2	0	0	3,280	0,593	-	0,040
O_2	0	0	3,639	0,506	-	-0,227

$$\left(c_p^{\mathrm{id}}/R\right) = a + b\left(T/\mathrm{K}\right) + c\left(T/\mathrm{K}\right)^2 + d\left(T/\mathrm{K}\right)^{-2}$$

Stand. Gibbsove reakcijske energije i konstante ravnoteže

$$\Delta g_r^\circ(\mathrm{A}) = \sum_{i=1}^{nk} \nu_{\mathrm{A},i}\Delta g_{\mathrm{f},i}^\circ = -800{,}77\cdot10^3 \qquad K_r(\mathrm{A}) = \exp\left[\frac{-\Delta g_r^\circ(\mathrm{A})}{RT}\right] = 1{,}94\cdot10^{140}$$

$$\Delta g_r^\circ(\mathrm{B}) = \sum_{i=1}^{nk} \nu_{\mathrm{B},i}\Delta g_{\mathrm{f},i}^\circ = -543{,}55\cdot10^3 \qquad K_r(\mathrm{B}) = \exp\left[\frac{-\Delta g_r^\circ(\mathrm{B})}{RT}\right] = 1{,}68\cdot10^{95}$$

$$\Delta g_r^\circ(\mathrm{C}) = \sum_{i=1}^{nk} \nu_{\mathrm{C},i}\Delta g_{\mathrm{f},i}^\circ = -257{,}22\cdot10^3 \qquad K_r(\mathrm{C}) = \exp\left[\frac{-\Delta g_r^\circ(\mathrm{C})}{RT}\right] = 1{,}16\cdot10^{45}$$

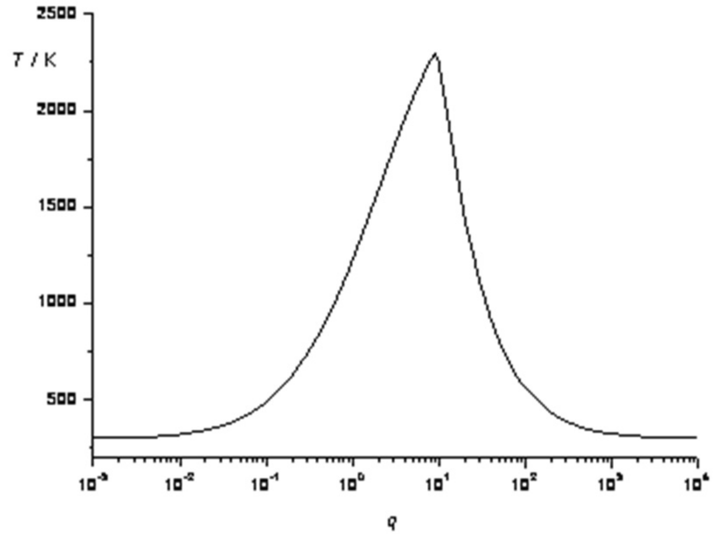
Homogena kemijska ravnoteža

Jedna kemijska reakcija – 3. primjer

Baza 1 mol CH_4, količina zraka *q*

Stehiometrijska tablica

Tvar	Početno stanje	Ravnotežno stanje uz manjak zraka (0,21 *q*<2)	Ravnotežno stanje uz suvišak zraka (0,21 *q*>2)
Ar	0,01 *q*	0,01 *q*	0,01 *q*
CH_4	1	1-0,21 *q*/2	0
CO	0	0	0
CO_2	0	0,21 *q*/2	1
H_2O	0	0,21 *q*	2
N_2	0,78 *q*	0,78 *q*	0,78 *q*
O_2	0,21 *q*	0	0,21 *q*-2
ukupno	1+*q*	1+*q*	1+*q*



Adijabatsko sagorijevanje

$$\sum_{i=1}^{nk} n_i^{\mathrm{F}} h_i^{\mathrm{F}} = \sum_{i=1}^{nk} n_i^{\mathrm{O}} h_i^{\mathrm{O}}$$

Jedna nepoznanica – izlazna temperatura

$$\sum_{i=1}^{nk} n_i^{\mathrm{F}} \Delta h_{\mathrm{f},i}^{\circ} = \sum_{i=1}^{nk} n_i^{\mathrm{O}} \left(\Delta h_{\mathrm{f},i}^{\circ} + \int_{298,15}^{T} c_p^{\mathrm{id}}(T)\, dT \right)$$

Homogena kemijska ravnoteža

Više kemijskih reakcija

$$-\frac{\Delta g_{\mathrm{r}}}{RT} = \ln K_{\mathrm{r}} = \ln \prod_{i=1}^{nk} (a_i)^{\nu_i} = \ln \prod_{i=1}^{nk} \left(\frac{f_i}{f_i^{\circ}} \right)^{\nu_i} \Bigg|_{\text{reakcija I}}$$

Ravnotežne jednadžbe

$$\vdots$$

$$-\frac{\Delta g_{r}}{RT} = \ln K_{r} = \ln \prod_{i=1}^{nk} (a_i)^{\nu_i} = \ln \prod_{i=1}^{nk} \left(\frac{f_i}{f_i^{\circ}} \right)^{\nu_i} \Bigg|_{\text{reakcija N}}$$

Bilančne jednadžbe – stehiometrijska tablica

Homogena kemijska ravnoteža

Više kemijskih reakcija – 1. primjer

Treba izračunati sastav plinske smjese CH_4, H_2O, CO, CO_2 i H_2 u reakciji koksa i vodene pare, pri 1 bar i 1000 K, na osnovi podataka o Gibbsovim energijama nastajanja pri zadanoj temperaturi. (prema Sandleru)

$$C + H_2O \rightarrow CO + H_2$$

Proizvodnja vodenog (sintetskog) plina

$$C + 2H_2O \rightarrow CO_2 + 2H_2$$

$$C + H_2O \rightarrow CO + H_2$$

$$C + CO_2 \rightarrow 2CO$$

$$C + 2H_2 \rightarrow CH_4$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Karakteristične reakcije

Denbighova metoda

Neovisne reakcije

B-2×(A-E): $C + 2H_2O \rightarrow CO_2 + 2H_2$

C-(A-E): $C + H_2O \rightarrow CO + H_2$

D-2×E: $C + 2H_2 \rightarrow CH_4$

Matrica stehiometrijskih koeficijenata

reakcija	CH_4	H_2O	CO	CO_2	H_2	C
$B-2\times(A-E)$	0	-2	0	1	2	-1
$C-(A-E)$	0	-1	1	0	1	-1
$D-2\times E$	1	0	0	0	-2	-1

Homogena kemijska ravnoteža

Više kemijskih reakcija – 1. primjer

Termodinamički podaci

	CH_4	H_2O	CO	CO_2	H_2	C
Δg_f° / J mol^{-1}	19720	-192420	-200240	-395790	0	0
n_0 / mol	0	1	0	0	0	∞

Gibbsove energije nastajanja pri 1000 K i 1 bar

Konstante ravnoteže

$$K_r = \exp\left(-\frac{\sum_{i=1}^{nk} \nu_i \Delta g_{f,i}}{RT}\right) = \prod_{i=1}^{nk} (a_i)^{\nu_i}$$

$$K_{r1} = \exp\left[-\frac{0 \cdot 19720 - 2 \cdot (-192420) + 0 \cdot (-200240) + 1 \cdot 395790 + 2 \cdot 0 - 1 \cdot 0}{8{,}314 \cdot 1000}\right] = $$
$$= a_{CH_4}^{0} a_{H_2O}^{-2} a_{CO}^{0} a_{CO_2}^{1} a_{H_2}^{2} a_{C}^{-1}$$

$$K_{r2} = \exp\left[-\frac{0 \cdot 19720 - 1 \cdot (-192420) + 1 \cdot (-200240) + 0 \cdot 395790 + 1 \cdot 0 - 1 \cdot 0}{8{,}314 \cdot 1000}\right] = $$
$$= a_{CH_4}^{0} a_{H_2O}^{-1} a_{CO}^{1} a_{CO_2}^{0} a_{H_2}^{1} a_{C}^{-1}$$

$$K_{r3} = \exp\left[-\frac{1 \cdot 19720 - 0 \cdot (-192420) + 0 \cdot (-200240) + 0 \cdot 395790 - 2 \cdot 0 - 1 \cdot 0}{8{,}314 \cdot 1000}\right] = $$
$$= a_{CH_4}^{1} a_{H_2O}^{0} a_{CO}^{0} a_{CO_2}^{0} a_{H_2}^{-2} a_{C}^{-1}$$

$$3{,}73242 = \frac{a_{CO_2} a_{H_2}^2}{a_C a_{H_2O}^2} \qquad 2{,}56147 = \frac{a_{CO} a_{H_2}}{a_C a_{H_2O}} \qquad 0{,}093303 = \frac{a_{CH_4}}{a_C a_{H_2}^2}$$

Homogena kemijska ravnoteža

Više kemijskih reakcija – 1. primjer

Stehiometrijska tablica

Tvar	Početno stanje	Ravnotežno stanje	Molarni udio
CH_4	0	ξ_{r3}	$\xi_{r3}/(1+\xi_{r1}+\xi_{r2}-\xi_{r3})$
H_2O	1	$1-2\xi_{r1}-\xi_{r2}$	$(1-2\xi_{r1}-\xi_{r2})/(1+\xi_{r1}+\xi_{r2}-\xi_{r3})$
CO	0	ξ_{r2}	$\xi_{r2}/(1+\xi_{r1}+\xi_{r2}-\xi_{r3})$
CO_2	0	ξ_{r1}	$\xi_{r1}/(1+\xi_{r1}+\xi_{r2}-\xi_{r3})$
H_2	0	$2\xi_{r1}+\xi_{r2}-2\xi_{r3}$	$(2\xi_{r1}+\xi_{r2}-2\xi_{r3})/(1+\xi_{r1}+\xi_{r2}-\xi_{r3})$
C	∞	∞	∞
Σ	1	$1+\xi_{r1}+\xi_{r2}-\xi_{r3}$	

$$\prod_{i=1}^{nk} a_i^{\nu_i} = \prod_{i=1}^{nk}\left(\frac{\hat{\varphi}_i p y_i}{\varphi_i^\circ p^\circ}\right)^{\nu_i}$$

Stehiom. Produkt aktivnosti

$$\prod_{i=1}^{nk} a_i^{\nu_i} = \prod_{i=1}^{nk} y_i^{\nu_i}$$

Tlak jednak standardnom

$$\prod_{i=1}^{nk} a_i^{\nu_i} = \prod_{i=1}^{nk}\left(\frac{p y_i}{p^\circ}\right)^{\nu_i}$$

Idealni plin

Homogena kemijska ravnoteža

Više kemijskih reakcija – 1. primjer

Ravnotežne jednadžbe

$$3{,}73242 = \frac{y_{CO_2} y_{H_2}^2}{1 \cdot y_{H_2O}^2} \quad 2{,}56147 = \frac{y_{CO} y_{H_2}}{1 \cdot y_{H_2O}} \quad 0{,}093303 = \frac{y_{CH_4}}{1 \cdot y_{H_2}^2}$$

$$3{,}73242 \cdot \left(1 - 2\xi_{r1} - \xi_{r2}\right)^2 \left(1 + \xi_{r1} + \xi_{r2} - \xi_{r3}\right) = \xi_{r1} \left(2\xi_{r1} + \xi_{r2} - 2\xi_{r3}\right)^2$$

$$2{,}56147 \cdot \left(1 - 2\xi_{r1} - \xi_{r2}\right)\left(1 + \xi_{r1} + \xi_{r2} - \xi_{r3}\right) = \xi_{r2} \left(2\xi_{r1} + \xi_{r2} - 2\xi_{r3}\right)$$

$$0{,}093303 \cdot \left(2\xi_{r1} + \xi_{r2} - 2\xi_{r3}\right)^2 = \xi_{r3} \left(1 + \xi_{r1} + \xi_{r2} - \xi_{r3}\right)$$

Fizikalno smislena rješenja

$$0 \le \xi_{r1} \le 1$$
$$0 \le \xi_{r2} \le 1$$
$$0 \le \xi_{r3} \le 1$$

$$2\xi_{r1} + \xi_{r2} \le 1 \quad (\text{voda})$$
$$0 \le 2\xi_{r3} \le 2\xi_{r1} + \xi_{r2} \quad (\text{vodik})$$

$$y_{CH_4} = \frac{\xi_{r3}}{\left(1 + \xi_{r1} + \xi_{r2} - \xi_{r3}\right)} = 0{,}0208564$$

$$y_{H_2O} = \frac{\left(1 - 2\xi_{r1} - \xi_{r2}\right)}{\left(1 + \xi_{r1} + \xi_{r2} - \xi_{r3}\right)} = 0{,}0671625$$

$$y_{CO} = \frac{\xi_{r2}}{\left(1 + \xi_{r1} + \xi_{r2} - \xi_{r3}\right)} = 0{,}363869$$

$$y_{CO_2} = \frac{\xi_{r3}}{\left(1 + \xi_{r1} + \xi_{r2} - \xi_{r3}\right)} = 0{,}0753184$$

$$y_{H_2} = \frac{2\xi_{r1} + \xi_{r2} - 2\xi_{r3}}{\left(1 + \xi_{r1} + \xi_{r2} - \xi_{r3}\right)} = 0{,}472793$$

Rješenja

$$\xi_{r1} = 0{,}129487$$
$$\xi_{r2} = 0{,}625561$$
$$\xi_{r3} = 0{,}0358561$$

Minimiziranje Gibbsove energije

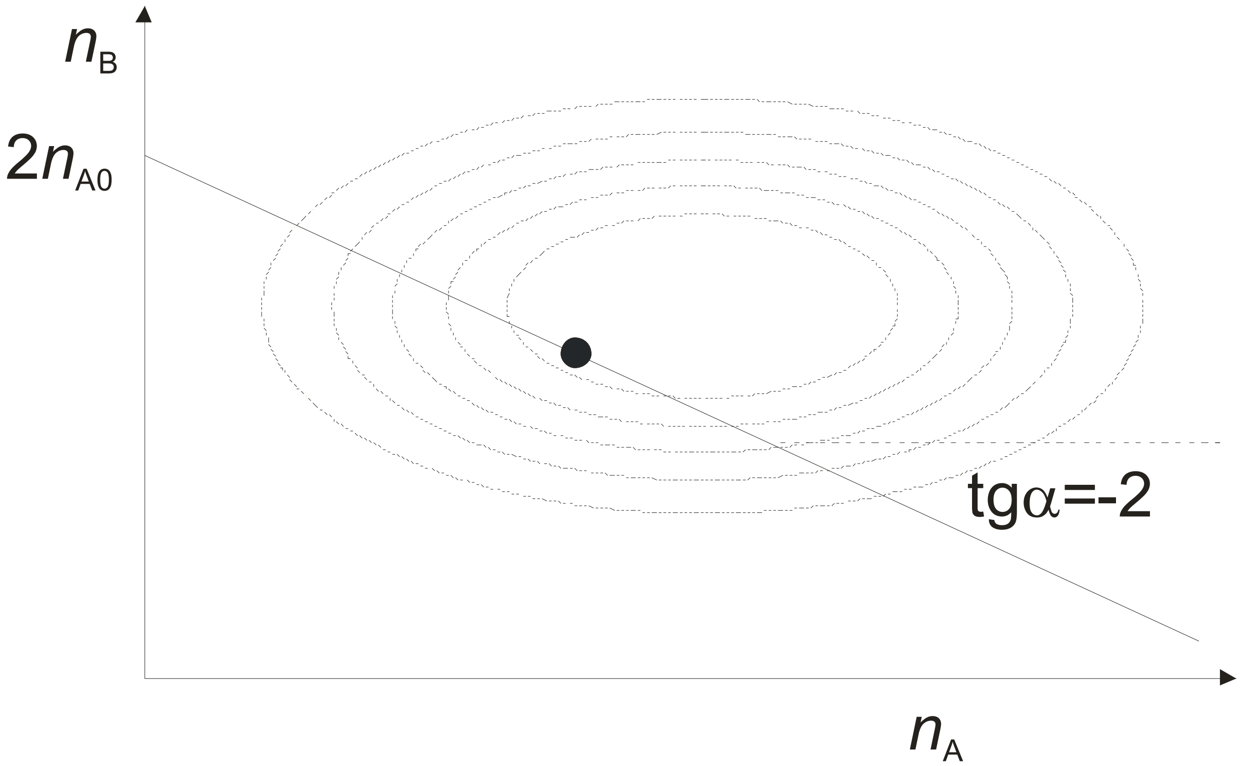
$$G = G\left(n_1, n_2, n_3, \ldots, n_{\mathrm{nk}}\right)_{p,T} \rightarrow \min$$

Minimum Gibbsove energije

Ograničeni minimum

$$\mathrm{A} \rightarrow 2\mathrm{B}$$

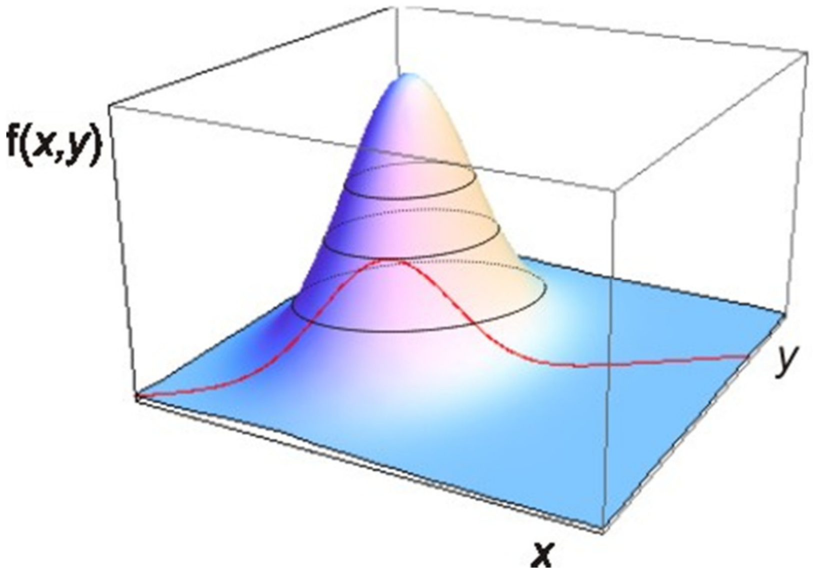
$$n_{\mathrm{A0}} = n_{\mathrm{A}} + n_{\mathrm{B}}/2$$

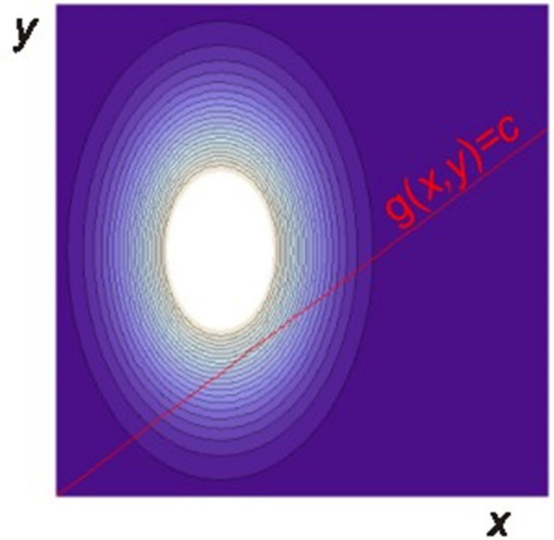


Minimiziranje Gibbsove energije

Metoda neodređenih Lagrangeovih množitelja

Traženje ekstrema funkcija uz ograničenja iznosa varijabli





$$\mathrm{f}(x,y)=d$$ Izvorna jednadžba

$$\mathrm{g}(x,y)=c$$ Izvorno ograničenje

$$\mathrm{F}(x,y,\lambda)=\mathrm{f}(x,y)+\lambda\left[\mathrm{g}(x,y)-c\right]$$

Nova jednadžba

Novi sustav jednadžbi

$$\frac{\partial \mathrm{F}}{\partial x}=\frac{\partial \mathrm{f}}{\partial x}+\lambda\frac{\partial \mathrm{g}}{\partial x}=0$$

$$\frac{\partial \mathrm{F}}{\partial y}=\frac{\partial \mathrm{f}}{\partial y}+\lambda\frac{\partial \mathrm{g}}{\partial y}=0$$

Izvorno ograničenje $$\frac{\partial \mathrm{F}}{\partial \lambda}=\mathrm{g}(x,y)-c=0$$

Minimiziranje Gibbsove energije

Primjer

Treba izračunati sastav plinske smjese CH_4, H_2O, CO, CO_2 i H_2 pri 1 bar i 1000 K, na osnovi podataka o Gibbsovim energijama nastajanja pri zadanoj temperaturi. Prije zagrijavanja na reakcijsku temperaturu, smjesa sadrži 2 mol CH_4 i 3 mol H_2O. Pretpostavit će se idealno vladanje plinske smjese, te da je 1 bar približno jednak 1 atm (prema Sandleru).

$$CH_4 + H_2O \rightarrow CO + 3\,H_2$$

Proizvodnja vodenog (sintetskog) plina
(za sintezu amonijaka, za sintezu metanola)

Termodinamički podaci

	CH_4	H_2O	CO	CO_2	H_2
Δg_f° / Jmol^{-1}	19720	-192420	-200240	-395790	0
n_0 / mol	2	3	0	0	0
β_C	1	0	1	1	0
β_O	0	1	1	2	0
β_H	4	2	0	0	2

Izvorno ograničenje
Ukupna količina atoma

$$b_j = \sum_{i=1}^{nk} n_{0i}\beta_{ij}$$

$$b_C = 2\cdot 1 + 3\cdot 0 + 0\cdot 1 + 0\cdot 1 + 0\cdot 0 = 2\text{ mol}$$

$$b_O = 2\cdot 0 + 3\cdot 1 + 0\cdot 1 + 0\cdot 2 + 0\cdot 0 = 3\text{ mol}$$

$$b_H = 2\cdot 4 + 3\cdot 2 + 0\cdot 0 + 0\cdot 0 + 0\cdot 2 = 14\text{ mol}$$

Minimiziranje Gibbsove energije

Metoda Lagrangeovih množitelja

$$\mathrm{f}(x,y)=d$$
$$\mathrm{g}(x,y)=c$$
$$\mathrm{F}(x,y,\lambda)=\mathrm{f}(x,y)+\lambda[\mathrm{g}(x,y)-c]$$

Izvorna funkcija

$$G=G(n_1,n_2,n_3,\ldots,n_{nk})_{p,T}\rightarrow \min$$ Minimum Gibbsove energije

$$\sum_{i=1}^{nk} n_i\beta_{ji}-b_j=0$$ Ograničenja – atomne bilance

$$\lambda_j\left(\sum_{i=1}^{nk} n_i\beta_{ji}-b_j\right)=0$$ Uvođenje množitelja

$$\sum_{j=1}^{ne}\lambda_j\left(\sum_{i=1}^{nk} n_i\beta_{ji}-b_j\right)=0$$ Zbrajanje bilanci

$$F=G+\sum_{j=1}^{ne}\lambda_j\left(\sum_{i=1}^{nk} n_i\beta_{ji}-b_j\right)\rightarrow \min$$ Formuliranje osnovne funkcije

Minimiziranje Gibbsove energije

Metoda Lagrangeovih množitelja $\frac{\partial F}{\partial x} = \frac{\partial f}{\partial x} + \lambda \frac{\partial g}{\partial x} = 0$ $\frac{\partial F}{\partial y} = \frac{\partial f}{\partial y} + \lambda \frac{\partial g}{\partial y} = 0$ $\frac{\partial F}{\partial \lambda} = g(x, y) - c = 0$

Diferenciranje po nepoznanicama – količinama tvari

$$\left(\frac{\partial F}{\partial n_i}\right)_{p,T,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j} + \sum_{j=1}^{ne} \lambda_j \beta_{ji} = 0$$

Diferenciranje po Lagrangeovim množiteljima – rekonstruiranje osnovnih ograničenja

$$\left(\frac{\partial F}{\partial \lambda_j}\right)_{p,T,n_i} = \sum_{i=1}^{nk} n_i \beta_{ji} - b_j = 0$$

U sustavu s nk komponenti i ne različitih elemenata (atoma) dobiva se
nk+ne jednadžbi s ***nk+ne*** nepoznanica:
nk ravnotežnih količina tvari
ne Lagrangeovih množitelja

Minimiziranje Gibbsove energije

Primjer

Diferenciranje po nepoznanicama

$$\left(\frac{\partial F}{\partial n_i}\right)_{p,T,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j} + \sum_{j=1}^{ne} \lambda_j \beta_{ji} = 0$$

Kemijski potencijal

$$g_i + RT \ln \frac{\hat{\varphi}_i p y_i}{\varphi_i^\circ p^\circ} + \sum_{j=1}^{ne} \lambda_j \beta_{ji} = 0$$

Standardno stanje – čista tvar

$$g_i + RT \ln \left(\frac{\hat{\varphi}_i p}{\varphi_i^\circ p^\circ} \cdot \frac{n_i}{\sum_{i=1}^{nk} n_i} \right) + \sum_{j=1}^{ne} \lambda_j \beta_{ji} = 0$$

Definicija molarnog udjela

$$\Delta g_{\mathrm{f},i} + RT \ln \left(\frac{p}{p^\circ} \cdot \frac{n_i}{\sum_{i=1}^{nk} n_i} \right) + \sum_{j=1}^{ne} \lambda_j \beta_{ji} = 0$$

Za idealne plinove

$$19720 + 8,314 \cdot 1000 \cdot \ln\left(\frac{1}{1} \cdot \frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_\mathrm{C} \cdot 1 + \lambda_\mathrm{O} \cdot 0 + \lambda_\mathrm{H} \cdot 4 = 0$$

$$-192420 + 8,314 \cdot 1000 \cdot \ln\left(\frac{1}{1} \cdot \frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_\mathrm{C} \cdot 0 + \lambda_\mathrm{O} \cdot 1 + \lambda_\mathrm{H} \cdot 2 = 0$$

$$-200240 + 8,314 \cdot 1000 \cdot \ln\left(\frac{1}{1} \cdot \frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_\mathrm{C} \cdot 1 + \lambda_\mathrm{O} \cdot 1 + \lambda_\mathrm{H} \cdot 0 = 0$$

$$-395790 + 8,314 \cdot 1000 \cdot \ln\left(\frac{1}{1} \cdot \frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_\mathrm{C} \cdot 1 + \lambda_\mathrm{O} \cdot 2 + \lambda_\mathrm{H} \cdot 0 = 0$$

$$0 + 8,314 \cdot 1000 \cdot \ln\left(\frac{1}{1} \cdot \frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_\mathrm{C} \cdot 0 + \lambda_\mathrm{O} \cdot 0 + \lambda_\mathrm{H} \cdot 2 = 0$$

$$19720 + 8314 \cdot \ln\left(\frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_\mathrm{C} + 4 \cdot \lambda_\mathrm{H} = 0$$

$$-192420 + 8314 \cdot \ln\left(\frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_\mathrm{O} + 2 \cdot \lambda_\mathrm{H} = 0$$

$$-200240 + 8314 \cdot \ln\left(\frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_\mathrm{C} + \lambda_\mathrm{O} = 0$$

$$-395790 + 8314 \cdot \ln\left(\frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_\mathrm{C} + 2 \cdot \lambda_\mathrm{O} = 0$$

$$8314 \cdot \ln\left(\frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + 2 \cdot \lambda_\mathrm{H} = 0$$

Minimiziranje Gibbsove energije

Primjer

Diferenciranje po Lagrangeovim množiteljima rekonstruira atomne bilance

$$\left(\frac{\partial F}{\partial \lambda_j}\right)_{p,T,n_i} = \sum_{i=1}^{nk} n_i \beta_{ji} - b_j = 0$$

$$\sum_{i=1}^{nk} n_i \beta_{ij} - b_j = 0$$

$$n_1 \cdot 1 + n_2 \cdot 0 + n_3 \cdot 1 + n_4 \cdot 1 + n_5 \cdot 0 - 2\ \text{mol} = 0$$

$$n_1 \cdot 0 + n_2 \cdot 1 + n_3 \cdot 1 + n_4 \cdot 2 + n_5 \cdot 0 - 3\ \text{mol} = 0$$

$$n_1 \cdot 4 + n_2 \cdot 2 + n_3 \cdot 0 + n_4 \cdot 0 + n_5 \cdot 2 - 14\ \text{mol} = 0$$

$$n_1 + n_3 + n_4 - 2\ \text{mol} = 0$$

$$n_2 + n_3 + 2 \cdot n_4 - 3\ \text{mol} = 0$$

$$4 \cdot n_1 + 2 \cdot n_2 + 2 \cdot n_5 - 14\ \text{mol} = 0$$

Osam jednadžbi s osam nepoznanica

$$n_1 \rightarrow 0{,}169605$$

$$n_2 \rightarrow 0{,}848531$$

$$n_3 \rightarrow 1{,}50932$$

$$n_4 \rightarrow 0{,}321074$$

$$n_5 \rightarrow 5{,}81226$$

$$\lambda_\text{C} \rightarrow 6347{,}83$$

$$\lambda_\text{O} \rightarrow 208418$$

$$\lambda_\text{H} \rightarrow 1657{,}96$$

Nisu razmatrane stvarne jednadžbe, već jednadžbe nastajanja iz elemenata

Heterogena kemijska ravnoteža

$$\mathrm{mA} + \mathrm{nB} \leftrightarrow \mathrm{pC} + \mathrm{qD}$$

Općenita reakcija

$$p\mu_{\mathrm{C}}^{\mathrm{I}} + q\mu_{\mathrm{D}}^{\mathrm{I}} = m\mu_{\mathrm{A}}^{\mathrm{I}} + n\mu_{\mathrm{B}}^{\mathrm{I}}$$

Stehiometrijska suma kemijskih potencijala u fazi I

$$\mu_{\mathrm{A}}^{\mathrm{I}} = \mu_{\mathrm{A}}^{\mathrm{II}} \quad \mu_{\mathrm{B}}^{\mathrm{I}} = \mu_{\mathrm{B}}^{\mathrm{II}} \quad \mu_{\mathrm{C}}^{\mathrm{I}} = \mu_{\mathrm{C}}^{\mathrm{II}} \quad \mu_{\mathrm{D}}^{\mathrm{I}} = \mu_{\mathrm{D}}^{\mathrm{II}}$$

Jednadžbe fazne ravnoteže

$$p\mu_{\mathrm{C}}^{\mathrm{II}} + q\mu_{\mathrm{D}}^{\mathrm{II}} = m\mu_{\mathrm{A}}^{\mathrm{II}} + n\mu_{\mathrm{B}}^{\mathrm{II}}$$

Stehiometrijska suma kemijskih potencijala u fazi II
Fazna ravnoteža je automatski zadovoljena

Bilančne jednadžbe prema potrebi

$$\sum_{j=1}^{ne}\sum_{i=1}^{nk} n_i^{\mathrm{F}}\beta_{ij} = \sum_{j=1}^{ne}\sum_{i=1}^{nk} n_i^{\mathrm{I}}\beta_{ij} + \sum_{j=1}^{ne}\sum_{i=1}^{nk} n_i^{\mathrm{II}}\beta_{ij} + \cdots + \sum_{j=1}^{ne}\sum_{i=1}^{nk} n_i^{nf}\beta_{ij}$$

$$\sum_{i=1}^{nk} n_i^{\mathrm{F}}\beta_{ie} = \sum_{i=1}^{nk} n_i^{\mathrm{I}}\beta_{ie} + \sum_{i=1}^{nk} n_i^{\mathrm{II}}\beta_{ie} + \cdots + \sum_{i=1}^{nk} n_i^{nf}\beta_{ie}$$

$$\sum_{i=1}^{nk} x_i^{\mathrm{I}} = \sum_{i=1}^{nk} x_i^{\mathrm{II}} = \cdots = \sum_{i=1}^{nk} x_i^{nf} = 1$$

Heterogena kemijska ravnoteža

Primjer

U zatvoreni spremnik pri stalnoj temperaturi od 25°C i stalnom tlaku od 13,33 kPa uvedena je smjesa od 3 mola vodika, 1 mola dušika i 5 mola vode. Primjenom prikladnog katalizatora inicirana je reakcija sinteze amonijaka i dovedena do stanja fazno-kemijske ravnoteže. Treba izračunati ukupnu količinu i sastave plinske, odnosno vodene faze, zanemarujući pritom reakciju amonijaka s vodom uz nastajanje amonijevog hidroksida i njegovu naknadnu ionizaciju (prema Sandleru).

Pretpostavke — Idealna plinska faza
Topljivost prema Henryjevu zakonu

Termodinamički podaci — pri 25 °C

$p^\bullet(H_2O)=3{,}167$ kPa,
$k_H(N_2)=9{,}224\cdot10^7$ kPa,
$k_H(H_2)=7{,}158\cdot10^7$ kPa; $k_H(NH_3)=97{,}58$ kPa
$\Delta g_f^\circ(NH_3)=-16450$ J/mol.

Jednadžba

$$1/2\,N_2 + 3/2\,H_2 \rightarrow NH_3$$

Stehiometrijski koeficijenti

$$\nu_{N_2} = -1/2 \quad \nu_{H_2} = -3/2 \quad \nu_{NH_3} = 1$$

Heterogena kemijska ravnoteža

Primjer

Nepoznanice $n_{H_2}^{V}$ $n_{N_2}^{V}$ $n_{NH_3}^{V}$ $n_{H_2O}^{V}$ $n_{H_2}^{L}$ $n_{N_2}^{L}$ $n_{NH_3}^{L}$ $n_{H_2O}^{L}$

Kemijska ravnoteža u parnoj fazi

$$\exp\left(-\frac{\sum_{i=1}^{nk}\nu_i \Delta g_{\mathrm{f},i}^{\circ}}{RT}\right) = \prod_{i=1}^{nk}\left(\frac{\hat{f}_i}{f_i^{\circ}}\right)^{\nu_i}$$

Lijeva strana

$$K_{\mathrm{r}} = \exp\left(-\frac{\sum_{i=1}^{nk}\nu_i \Delta g_{\mathrm{f},i}^{\circ}}{RT}\right) = \exp\left(-\frac{-16450\cdot 1 + 0\cdot(-1/2) + 0\cdot(-3/2)}{8,314\cdot(273,2+25)}\right) = 761,4$$

Desna strana

$$\prod_{i=1}^{nk}\left(\frac{\hat{f}_i}{f_i^{\circ}}\right)^{\nu_i} = \prod_{i=1}^{nk}\left(\frac{\hat{\varphi}_i p}{\varphi^{\circ} p^{\circ}}\cdot y_i\right)^{\nu_i}$$

$$\prod_{i=1}^{nk}\left(\frac{\hat{f}_i}{f_i^{\circ}}\right)^{\nu_i} = \prod_{i=1}^{nk}\left(\frac{p}{p^{\circ}}\right)^{\nu_i}\cdot\prod_{i=1}^{nk}(y_i)^{\nu_i} =$$

$$\prod_{i=1}^{nk}\left(\frac{\hat{f}_i}{f_i^{\circ}}\right)^{\nu_i} = \prod_{i=1}^{nk}\left(\frac{p}{p^{\circ}}\cdot y_i\right)^{\nu_i}$$

Idealna para

$$= \left(\frac{p}{p^{\circ}}\right)^{\sum_{i=1}^{nk}\nu_i}\cdot\prod_{i=1}^{nk}(y_i)^{\nu_i}$$

Heterogena kemijska ravnoteža

Primjer

Kemijska ravnoteža u parnoj fazi

$$\prod_{i=1}^{nk}\left(\frac{\hat{f}_i}{f_i^\circ}\right)^{\nu_i}=\left(\frac{13330}{100000}\right)^{1-1/2-3/2}\cdot\frac{y_{NH_3}}{y_{H_2}^{3/2}y_{N_2}^{1/2}}=$$

$$=7,5019\cdot\frac{y_{NH_3}}{y_{H_2}^{3/2}y_{N_2}^{1/2}}$$

Obje strane

$$761,4=7,5019\cdot\frac{y_{NH_3}}{y_{H_2}^{3/2}y_{N_2}^{1/2}}$$

Sniženje ravnotežne konstante uslijed niskog tlaka

$$y_{NH_3}=101,49\cdot y_{H_2}^{3/2}y_{N_2}^{1/2}$$

$$\frac{n_{NH_3}^{V}}{n_{H_2}^{V}+n_{N_2}^{V}+n_{NH_3}^{V}+n_{H_2O}^{V}}=101,49\frac{\left(n_{H_2}^{V}\right)^{3/2}\left(n_{N_2}^{V}\right)^{1/2}}{\left(n_{H_2}^{V}+n_{N_2}^{V}+n_{NH_3}^{V}+n_{H_2O}^{V}\right)^{1/2+3/2}}$$

$$n_{NH_3}^{V}\left(n_{H_2}^{V}+n_{N_2}^{V}+n_{NH_3}^{V}+n_{H_2O}^{V}\right)=101,49\left(n_{H_2}^{V}\right)^{3/2}\left(n_{N_2}^{V}\right)^{1/2}$$

Heterogena kemijska ravnoteža

Primjer

Fazne ravnoteže reaktivnih komponenata

$$\hat{f}_i^{\mathrm{V}} = \hat{f}_i^{\mathrm{L}}$$

$$\hat{\varphi}_i^{\mathrm{V}} y_i p = \gamma_i x_i k_{\mathrm{H}}$$

$$y_i p = x_i k_{\mathrm{H}}$$ Obje faze idealne

$$y_i = \frac{k_{\mathrm{H}}}{p} x_i$$

$$y_{\mathrm{H_2}} = \frac{7{,}158 \cdot 10^7}{13{,}33} x_{\mathrm{H_2}} = 5{,}370 \cdot 10^6 x_{\mathrm{H_2}}$$

$$y_{\mathrm{N_2}} = \frac{9{,}224 \cdot 10^7}{13{,}33} x_{\mathrm{N_2}} = 6{,}920 \cdot 10^6 x_{\mathrm{N_2}}$$

$$y_{\mathrm{NH_3}} = \frac{97{,}58}{13{,}33} x_{\mathrm{NH_3}} = 7{,}32 x_{\mathrm{NH_3}}$$

$$n_{\mathrm{H_2}}^{\mathrm{V}} \left(n_{\mathrm{H_2}}^{\mathrm{L}} + n_{\mathrm{N_2}}^{\mathrm{L}} + n_{\mathrm{NH_3}}^{\mathrm{L}} + n_{\mathrm{H_2O}}^{\mathrm{L}} \right) = 5{,}370 \cdot 10^6 \, n_{\mathrm{H_2}}^{\mathrm{L}} \left(n_{\mathrm{H_2}}^{\mathrm{V}} + n_{\mathrm{N_2}}^{\mathrm{V}} + n_{\mathrm{NH_3}}^{\mathrm{V}} + n_{\mathrm{H_2O}}^{\mathrm{V}} \right)$$

$$n_{\mathrm{N_2}}^{\mathrm{V}} \left(n_{\mathrm{H_2}}^{\mathrm{L}} + n_{\mathrm{N_2}}^{\mathrm{L}} + n_{\mathrm{NH_3}}^{\mathrm{L}} + n_{\mathrm{H_2O}}^{\mathrm{L}} \right) = 6{,}920 \cdot 10^6 \, n_{\mathrm{N_2}}^{\mathrm{L}} \left(n_{\mathrm{H_2}}^{\mathrm{V}} + n_{\mathrm{N_2}}^{\mathrm{V}} + n_{\mathrm{NH_3}}^{\mathrm{V}} + n_{\mathrm{H_2O}}^{\mathrm{V}} \right)$$

$$n_{\mathrm{NH_3}}^{\mathrm{V}} \left(n_{\mathrm{H_2}}^{\mathrm{L}} + n_{\mathrm{N_2}}^{\mathrm{L}} + n_{\mathrm{NH_3}}^{\mathrm{L}} + n_{\mathrm{H_2O}}^{\mathrm{L}} \right) = 7{,}32 \, n_{\mathrm{NH_3}}^{\mathrm{L}} \left(n_{\mathrm{H_2}}^{\mathrm{V}} + n_{\mathrm{N_2}}^{\mathrm{V}} + n_{\mathrm{NH_3}}^{\mathrm{V}} + n_{\mathrm{H_2O}}^{\mathrm{V}} \right)$$

Heterogena kemijska ravnoteža

Primjer

Fazna ravnoteža otapala

$$\hat{f}_i^{\mathrm{V}} = \hat{f}_i^{\mathrm{L}}$$

$$\hat{\varphi}_i^{\mathrm{V}} y_i p = x_i \gamma_i^{\mathrm{L}} \varphi_i^{\bullet} p_i^{\bullet} \left(PF\right)_i$$

$$y_i p = x_i p_i^{\bullet}$$ Obje faze idealne

$$y_i = \frac{p_i^{\bullet}}{p} x_i$$

$$y_{\mathrm{H_2O}} = \frac{3{,}167}{13{,}33} x_{\mathrm{H_2O}} = 0{,}2376 x_{\mathrm{H_2O}}$$

$$n_{\mathrm{H_2O}}^{\mathrm{V}} \left(n_{\mathrm{H_2}}^{\mathrm{L}} + n_{\mathrm{N_2}}^{\mathrm{L}} + n_{\mathrm{NH_3}}^{\mathrm{L}} + n_{\mathrm{H_2O}}^{\mathrm{L}} \right) = 0{,}2376\, n_{\mathrm{H_2O}}^{\mathrm{L}} \left(n_{\mathrm{H_2}}^{\mathrm{V}} + n_{\mathrm{N_2}}^{\mathrm{V}} + n_{\mathrm{NH_3}}^{\mathrm{V}} + n_{\mathrm{H_2O}}^{\mathrm{V}} \right)$$

Heterogena kemijska ravnoteža

Primjer

Bilančne jednadžbe

$$n_{H_2O}^{V} + n_{H_2O}^{L} = 5\ \text{mol}$$

Rezultat identičan bilanci za kisik $\sum_{i=1}^{nk} n_i^F \beta_{ie} = \sum_{i=1}^{nk} n_i^I \beta_{ie} + \sum_{i=1}^{nk} n_i^{II} \beta_{ie} + \cdots + \sum_{i=1}^{nk} n_i^{nf} \beta_{ie}$

$$2\left(n_{N_2}^{V} + n_{N_2}^{L}\right) + \left(n_{NH_3}^{V} + n_{NH_3}^{L}\right) = 2\ \text{mol}$$

Bilanca za dušik $\sum_{i=1}^{nk} n_i^F \beta_{ie} = \sum_{i=1}^{nk} n_i^I \beta_{ie} + \sum_{i=1}^{nk} n_i^{II} \beta_{ie} + \cdots + \sum_{i=1}^{nk} n_i^{nf} \beta_{ie}$

$$n_{H_2}^{V} + n_{H_2}^{L} = 3\left(n_{N_2}^{V} + n_{N_2}^{L}\right)$$

Bilanca potječe iz stehiometrije zadatka
Moguće ju je izvesti linearnom kombinacijom triju atomnih bilanci

Rezultati

$$\begin{aligned}
n_{H_2}^{L} &= 9{,}68252 \cdot 10^{-8} & n_{H_2}^{V} &= 0{,}229722 \\
n_{N_2}^{L} &= 2{,}50461 \cdot 10^{-8} & n_{N_2}^{V} &= 0{,}0765742 \\
n_{NH_3}^{L} &= 0{,}436162 & n_{NH_3}^{V} &= 1{,}41069 \\
n_{H_2O}^{L} &= 4{,}525 & n_{H_2O}^{V} &= 0{,}474996
\end{aligned}$$