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

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

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

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

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

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

# 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.

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

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

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

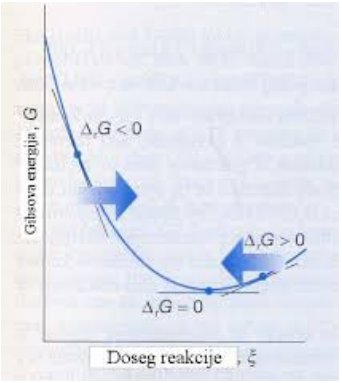
$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j\neq i}}$$

$$dn_i = \nu_i d\xi$$

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

Stehiometrijska suma kemijskih potencijala

Ravnotežni doseg



# 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: $\Delta g_f^\circ$ i $\Delta h_f^\circ$ pri standardnim uvjetima od 1 bar i 298,15 K

Standardna temperatura $G = H - TS \qquad \Delta s_f^\circ = \dfrac{\Delta h_f^\circ - \Delta g_f^\circ}{T^\circ}$

Integriranje $h_i = \Delta h_f^\circ + \int_{T^\circ}^{T} c_{p^\circ}(T)\,dT \qquad s_i = \Delta s_f^\circ + \int_{T^\circ}^{T} \dfrac{c_{p^\circ}(T)}{T}\,dT$

Konačna temperatura $g_i = h_i - Ts_i$

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

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

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

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

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

Položaj kemijske ravnoteže u reakcijskom sustavu ne ovisi o obliku zapisa

# Kemijske reakcije

Esterifikacija

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

Linearna transformacija – dodaju se kemijski elementi

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

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**

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

$$\Delta g_r^\circ(\text{esterifikacija}) = \Delta g_f^\circ(CH_3COOC_2H_5) + \Delta g_f^\circ(H_2O) - \Delta g_f^\circ(CH_3COOH) - \Delta g_f^\circ(C_2H_5OH)$$

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

# 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 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): $0 \leftrightarrow NO_2 - NO - 1/2\,O_2$.

### 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: $-3H \leftrightarrow NO_2 - NH_3 - O_2$.

### 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

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

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

Kemijska reakcija

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

Stehiometrijski koeficijenti

$$\Delta h^\circ_{\mathrm{f0}}(\mathrm{NH_3}) = -45857\ \mathrm{J\ mol^{-1}}$$
$$\Delta g^\circ_{\mathrm{f0}}(\mathrm{NH_3}) = -16330\ \mathrm{J\ mol^{-1}}$$

Termodinamički podaci




$$c_p(\mathrm{NH_3}) = \left(6{,}5846 + 6{,}1251\cdot10^{-3}\frac{T}{\mathrm{K}} + 2{,}3663\cdot10^{-6}\frac{T^2}{\mathrm{K^2}} - 1{,}5981\cdot10^{-9}\frac{T^3}{\mathrm{K^3}}\right)\cdot 4{,}184\ \mathrm{J\ mol^{-1}K^{-1}}$$

$$c_p(\mathrm{H_2}) = \left(6{,}952 - 4{,}576\cdot10^{-4}\frac{T}{\mathrm{K}} + 9{,}563\cdot10^{-7}\frac{T^2}{\mathrm{K^2}} - 2{,}079\cdot10^{-10}\frac{T^3}{\mathrm{K^3}}\right)\cdot 4{,}184\ \mathrm{J\ mol^{-1}K^{-1}}$$

$$c_p(\mathrm{N_2}) = \left(6{,}903 - 3{,}753\cdot10^{-4}\frac{T}{\mathrm{K}} + 1{,}930\cdot10^{-6}\frac{T^2}{\mathrm{K^2}} - 6{,}861\cdot10^{-10}\frac{T^3}{\mathrm{K^3}}\right)\cdot 4{,}184\ \mathrm{J\ mol^{-1}K^{-1}}$$

# Homogena kemijska ravnoteža

Jedna kemijska reakcija – 1. primjer

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

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

Toplinska funkcija

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

$$\Delta h_{r0}^{\circ} = \sum_{i=1}^{nk} \nu_i \Delta h_{f0,i}^{\circ} = 1 \cdot \left(-45857 \text{ J mol}^{-1}\right) - 1/2 \cdot 0 - 3/2 \cdot 0 = -45857 \text{ J mol}^{-1}$$

Standardna reakcijska entalpija pri 298,15K

$$\Delta s_{r0}^{\circ} = \frac{\Delta h_{r0}^{\circ} - \Delta g_{r0}^{\circ}}{T^{\circ}} = \frac{-45857 - (-16330)}{298{,}2} = 99{,}0174 \text{ J mol}^{-1}\text{K}^{-1}$$

Standardna reakcijska entropija pri 298,15K

$$\Delta g_{r0}^{\circ} = \sum_{i=1}^{nk} \nu_i \Delta g_{f0,i}^{\circ} = -16330 \text{ J mol}^{-1}$$

Standardna reakcijska Gibbsova energija pri 298,15K

# Homogena kemijska ravnoteža

Jedna kemijska reakcija – 1. primjer

$$\Delta h_r = \Delta h_{r0}^{\circ} + \int_{T^{\circ}}^{T} \Delta c_p(T)\,dT = -45857 + \int_{298,2}^{450} \begin{pmatrix} -30,5219 \\ +2,92844\cdot 10^{-2}\cdot T \\ -1,387\cdot 10^{-7}\cdot T^2 \\ -3,94635\cdot 10^{-9}\cdot T^3 \end{pmatrix} dT = -48862,8\ \mathrm{J\ mol^{-1}}$$

Reakcijska entalpija pri 450 K

$$\Delta s_r = \Delta s_{r0}^{\circ} + \int_{T^{\circ}}^{T} \frac{\Delta c_p(T)}{T}\,dT = 99,0174 + \int_{298,2}^{450} \begin{pmatrix} -30,5219/T \\ +2,92844\cdot 10^{-2} \\ -1,387\cdot 10^{-7}\cdot T \\ -3,94635\cdot 10^{-9}\cdot T^2 \end{pmatrix} dT = -107,224\ \mathrm{J\ mol^{-1}K^{-1}}$$

Reakcijska entropija pri 450 K

$$\Delta g_r = \Delta h_r - T\Delta s_r = -48862,8 - 450\cdot(-107,224) = -611,974\ \mathrm{J\ mol^{-1}}$$

Reakcijska Gibbsova energija pri 450 K

Bilanca tvari preko stehiometrijske tablice

| Tvar | Početno stanje | Ravnotežno stanje | Molarni udio |
|---|---|---|---|
| $NH_3$ | 0 | $\xi$ | $\xi$ / (2-$\xi$) |
| $N_2$ | 0,5 | 0,5(1-$\xi$) | 0,5(1-$\xi$) / (2-$\xi$) |
| $H_2$ | 1,5 | 1,5(1-$\xi$) | 1,5(1-$\xi$) / (2-$\xi$) |
| ukupno | 2 | 2-$\xi$ | 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

$$-(-611{,}974) = 8{,}314 \cdot 450 \cdot \ln \left[ \begin{array}{l} \left( \frac{4 \cdot 101325}{101325} \cdot \frac{\xi}{2-\xi} \right) \cdot \\ \left( \frac{4 \cdot 101325}{101325} \cdot \frac{0{,}5 \cdot (1-\xi)}{2-\xi} \right)^{-0{,}5} \cdot \\ \left( \frac{4 \cdot 101325}{101325} \cdot \frac{1{,}5 \cdot (1-\xi)}{2-\xi} \right)^{-1{,}5} \end{array} \right]$$ Uvrsti se bilanca tvari (stehiometrijska tablica)

$\xi_1 = 0{,}625223, \quad \xi_2 = 1{,}37478$ 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!)

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

Kemijska reakcija

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

Stehiometrijski koeficijenti

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

Kemijska ravnoteža plinovi

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

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

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

nepoznanice — neidealnost — Utjecaj tlaka na ravnotežu

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



# 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 | $\xi$ | $\xi/2$ |
| $H_2O$ | 0 | $\xi$ | $\xi/2$ |
| 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

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

Iz procijenjenih sastava moguće je izračunati parcijalne koeficijente fugacitivnosti

$$a=\frac{\Omega_a R^2 T_\mathrm{k}^2}{p_\mathrm{k}} \quad \Omega_a=0{,}45724 \quad b=\frac{\Omega_b R T_\mathrm{k}}{p_\mathrm{k}} \quad \Omega_b=0{,}07780$$

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

**vodik :** $\alpha=1{,}202\exp\left(-0{,}30288T_\mathrm{r}\right)$

$$(a\alpha)_\mathrm{M}=\sum y_i y_j (a\alpha)_{ij} \quad b_\mathrm{M}=\sum y_i b_i$$

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

$$A_\mathrm{M}=\frac{(a\alpha)_\mathrm{M} p}{R^2T^2} \quad B_\mathrm{M}=\frac{b_\mathrm{M} p}{RT}$$

$$z^3-(1-B_\mathrm{M})z^2+\left(A_\mathrm{M}-3B_\mathrm{M}^2-2B_\mathrm{M}\right)z-\left(A_\mathrm{M}B_\mathrm{M}-B_\mathrm{M}^2-B_\mathrm{M}^3\right)=0$$

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

Peng - Robinson

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

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: $\mathrm{CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)}$.

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

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

C = A – B , dvije neovisne reakcije

### 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 |

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

### 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 |

### Stand. Gibbsove reakcijske energije i konstante ravnoteže

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

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

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

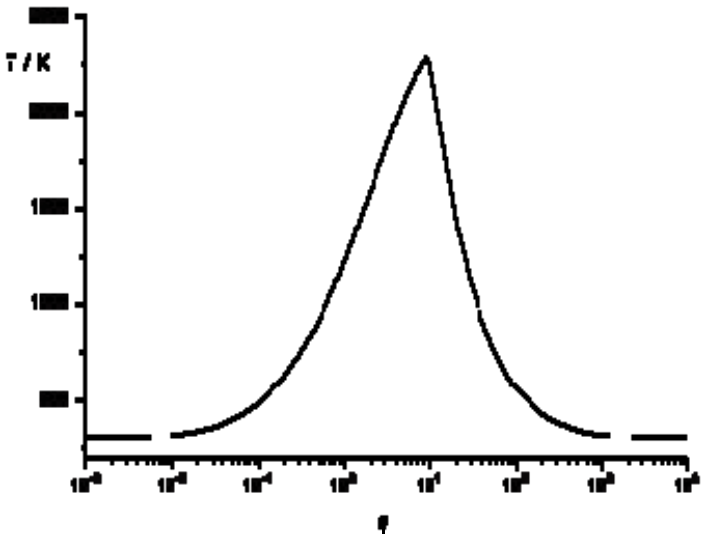
# Homogena kemijska ravnoteža

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

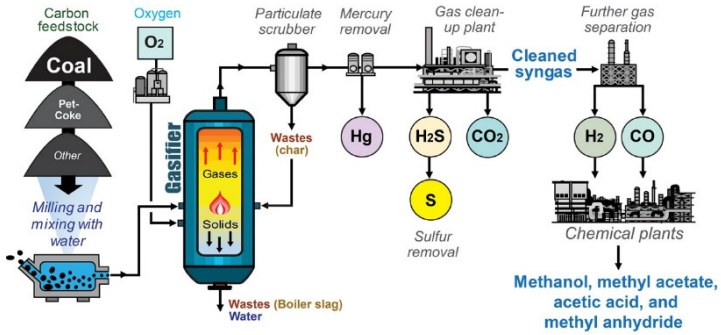
| reakcija | $CH_4$ | $H_2O$ | CO | $CO_2$ | $H_2$ | C |
|---|---|---|---|---|---|---|
| $B-2\times(A-E)$ | 0 | -2 | 0 | 1 | 2 | -1 |
| $C-(A-E)$ | 0 | -1 | 1 | 0 | 1 | -1 |
| $D-2\times E$ | 1 | 0 | 0 | 0 | -2 | -1 |

# Homogena kemijska ravnoteža

Više kemijskih reakcija – 1. primjer

## Termodinamički podaci

| | $CH_4$ | $H_2O$ | $CO$ | $CO_2$ | $H_2$ | C |
|---|---|---|---|---|---|---|
| $\Delta g_f^\circ$ / J mol$^{-1}$ | 19720 | -192420 | -200240 | -395790 | 0 | 0 |
| $n_0$ / mol | 0 | 1 | 0 | 0 | 0 | $\infty$ |




Water gas

## 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 | $\xi_{r3}$ | $\xi_{r3}/(1+\xi_{r1}+\xi_{r2}-\xi_{r3})$ |
| $H_2O$ | 1 | $1-2\xi_{r1}-\xi_{r2}$ | $(1-2\xi_{r1}-\xi_{r2})/(1+\xi_{r1}+\xi_{r2}-\xi_{r3})$ |
| CO | 0 | $\xi_{r2}$ | $\xi_{r2}/(1+\xi_{r1}+\xi_{r2}-\xi_{r3})$ |
| $CO_2$ | 0 | $\xi_{r1}$ | $\xi_{r1}/(1+\xi_{r1}+\xi_{r2}-\xi_{r3})$ |
| $H_2$ | 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

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

Idealni plin

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

Tlak jednak standardnom

# Homogena kemijska ravnoteža

Više kemijskih reakcija – 1. primjer

## Ravnotežne jednadžbe

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

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

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

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

## Fizikalno smislena rješenja

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

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

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

## Rješenja

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

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

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

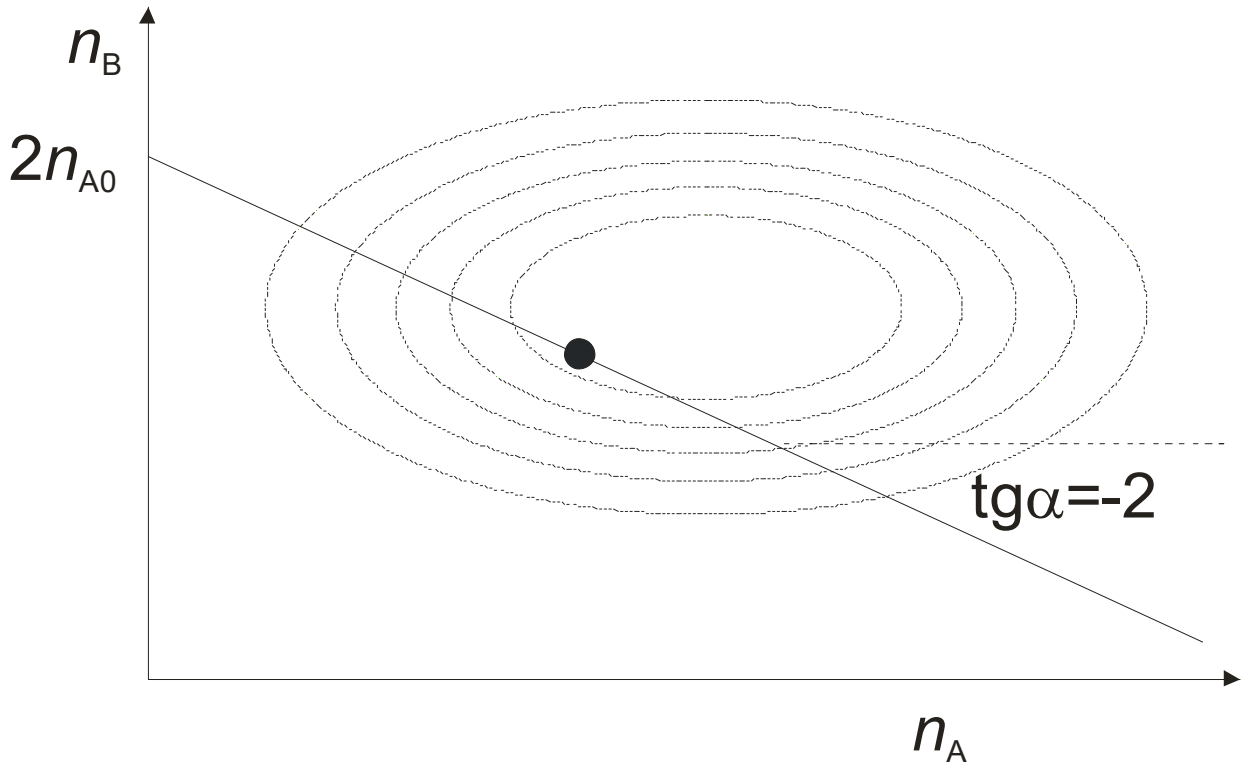
$$y_{CO} = \frac{\xi_{r2}}{(1 + \xi_{r1} + \xi_{r2} - \xi_{r3})} = 0,363869$$

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

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

# 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

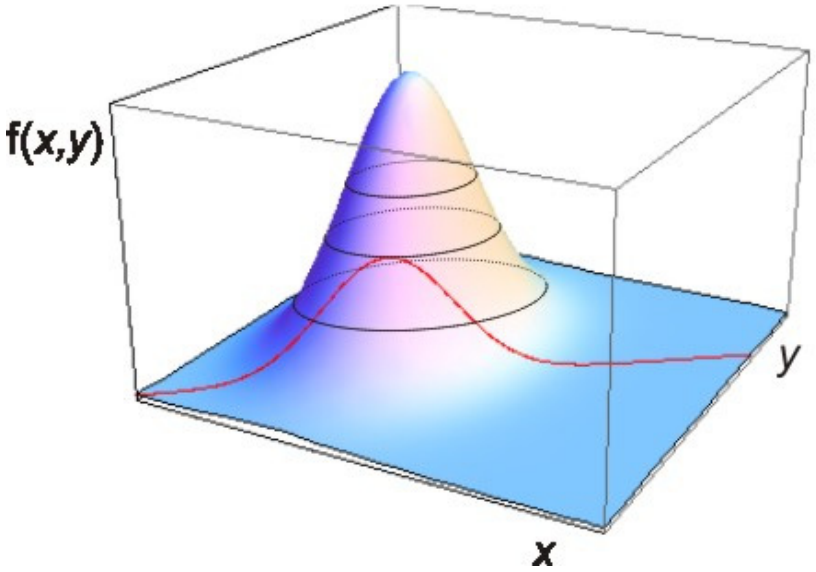
$\mathrm{A} \rightarrow 2\mathrm{B}$

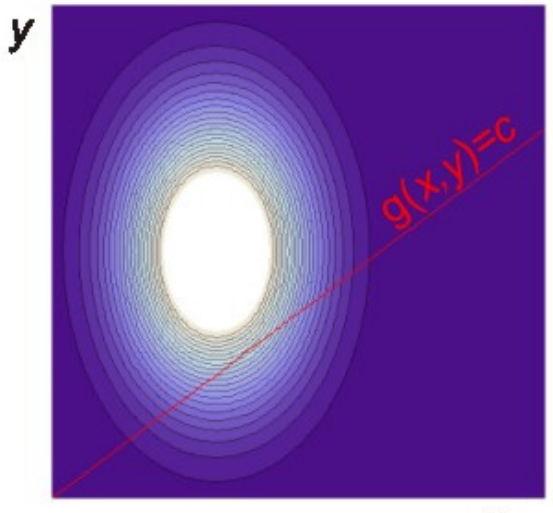
$n_{A0} = n_A + n_B/2$

# Minimiziranje Gibbsove energije

Metoda neodređenih Lagrangeovih množitelja

Traženje ekstrema funkcija uz ograničenja  iznosa varijabli




$f(x,y)=d$ Izvorna jednadžba

$g(x,y)=c$ Izvorno ograničenje

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

Nova jednadžba

Novi sustav jednadžbi

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

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

Izvorno ograničenje

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

# 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)

Water gas



Termodinamički podaci

| | $CH_4$ | $H_2O$ | CO | $CO_2$ | $H_2$ |
|---|---|---|---|---|---|
| $\Delta g_f^\circ$ / Jmol$^{-1}$ | 19720 | -192420 | -200240 | -395790 | 0 |
| $n_0$ / mol | 2 | 3 | 0 | 0 | 0 |
| $\beta_C$ | 1 | 0 | 1 | 1 | 0 |
| $\beta_O$ | 0 | 1 | 1 | 2 | 0 |
| $\beta_H$ | 4 | 2 | 0 | 0 | 2 |

Izvorno ograničenje
Ukupna množina 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

$$G=G\left(n_1,n_2,n_3,\ldots,n_{nk}\right)_{p,T}\rightarrow \min$$ 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 $\frac{\partial \mathrm{F}}{\partial x}=\frac{\partial \mathrm{f}}{\partial x}+\lambda\frac{\partial \mathrm{g}}{\partial x}=0$ $\frac{\partial \mathrm{F}}{\partial y}=\frac{\partial \mathrm{f}}{\partial y}+\lambda\frac{\partial \mathrm{g}}{\partial y}=0$ $\frac{\partial \mathrm{F}}{\partial \lambda}=\mathrm{g}(x,y)-c=0$

Diferenciranje po nepoznanicama – množinama 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

$$\left(\frac{\partial F}{\partial \lambda_{\mathrm{j}}}\right)_{p,T,n_{\mathrm{i}}}=\sum_{\mathrm{i}=1}^{\mathrm{nk}}n_{\mathrm{i}}\beta_{\mathrm{ji}}-b_{\mathrm{j}}=0$$

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

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

Za idealne plinove

$$19720 + 8{,}314 \cdot 1000 \cdot \ln\left(\frac{1}{1} \cdot \frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_C \cdot 1 + \lambda_O \cdot 0 + \lambda_H \cdot 4 = 0$$

$$-192420 + 8{,}314 \cdot 1000 \cdot \ln\left(\frac{1}{1} \cdot \frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_C \cdot 0 + \lambda_O \cdot 1 + \lambda_H \cdot 2 = 0$$

$$-200240 + 8{,}314 \cdot 1000 \cdot \ln\left(\frac{1}{1} \cdot \frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_C \cdot 1 + \lambda_O \cdot 1 + \lambda_H \cdot 0 = 0$$

$$-395790 + 8{,}314 \cdot 1000 \cdot \ln\left(\frac{1}{1} \cdot \frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_C \cdot 1 + \lambda_O \cdot 2 + \lambda_H \cdot 0 = 0$$

$$0 + 8{,}314 \cdot 1000 \cdot \ln\left(\frac{1}{1} \cdot \frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_C \cdot 0 + \lambda_O \cdot 0 + \lambda_H \cdot 2 = 0$$

$$19720 + 8314 \cdot \ln\left(\frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_C + 4 \cdot \lambda_H = 0$$

$$-192420 + 8314 \cdot \ln\left(\frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_O + 2 \cdot \lambda_H = 0$$

$$-200240 + 8314 \cdot \ln\left(\frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_C + \lambda_O = 0$$

$$-395790 + 8314 \cdot \ln\left(\frac{n_1}{n_1+n_2+n_3+n_4+n_5}\right) + \lambda_C + 2 \cdot \lambda_O = 0$$

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

# 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

$$n_1 \rightarrow 0{,}169605$$
$$n_2 \rightarrow 0{,}848531$$
$$n_3 \rightarrow 1{,}50932$$
$$n_4 \rightarrow 0{,}321074$$
$$n_5 \rightarrow 5{,}81226$$
$$\lambda_C \rightarrow 6347{,}83$$
$$\lambda_O \rightarrow 208418$$
$$\lambda_H \rightarrow 1657{,}96$$

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 amonijeva 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,
$k_H(N_2)$=9,224·10$^7$ kPa,
$k_H(H_2)$=7,158·10$^7$ 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 $n^{\mathrm{V}}_{\mathrm{H_2}}$ $n^{\mathrm{V}}_{\mathrm{N_2}}$ $n^{\mathrm{V}}_{\mathrm{NH_3}}$ $n^{\mathrm{V}}_{\mathrm{H_2O}}$ $n^{\mathrm{L}}_{\mathrm{H_2}}$ $n^{\mathrm{L}}_{\mathrm{N_2}}$ $n^{\mathrm{L}}_{\mathrm{NH_3}}$ $n^{\mathrm{L}}_{\mathrm{H_2O}}$

Kemijska ravnoteža u parnoj fazi

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

Lijeva strana

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

Desna strana

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

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

Idealna para

# 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

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

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

Sniženje ravnotežne konstante uslijed niskog tlaka

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

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

# 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

$$n^{\mathrm{V}}_{\mathrm{H_2O}} + n^{\mathrm{L}}_{\mathrm{H_2O}} = 5\ \mathrm{mol}$$

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

$$2\left(n^{\mathrm{V}}_{\mathrm{N_2}} + n^{\mathrm{L}}_{\mathrm{N_2}}\right) + \left(n^{\mathrm{V}}_{\mathrm{NH_3}} + n^{\mathrm{L}}_{\mathrm{NH_3}}\right) = 2\ \mathrm{mol}$$

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

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

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

Rezultati

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