Konstanta ravnoteže hemijske reakcije idealnih gasova

$$g_{tr} = V\left(\frac{2\pi m kT}{h^2}\right)^{\frac{3}{2}}$$

$$g_{rot} = \frac{kT}{\sigma B hc} \quad \text{или} \quad g_{rot} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{kT}{hc}\right)^{\frac{3}{2}}\frac{1}{\sqrt{ABC}}$$

$$g_{vib} = \prod_{i=1}^{f}\frac{e^{-\frac{1}{2}\beta\omega_i\hbar}}{1-e^{-\beta\omega_i\hbar}} = e^{-\beta\sum_{i=1}^{f}\frac{1}{2}\omega_i\hbar}\prod_{i=1}^{f}\frac{1}{1-e^{-\beta\omega_i\hbar}} = g_{vib}^{0}\, e^{-\beta\sum_{i=1}^{f}\frac{1}{2}\omega_i\hbar}$$

$$g_{el} = \sum_i g_i e^{-\beta\varepsilon_i} = e^{\beta D_e}\left(g_0 + g_1 e^{-\beta\varepsilon_1'} + \dots\right) = g_{el}^{0} e^{\beta D_e}$$

$$g_{el} g_{vib} = g_{el}^{0} g_{vib}^{0} e^{\beta D_0}$$

$$D_0 = D_e - \sum_{i=1}^{f}\frac{1}{2}\omega_i\hbar$$

$$\alpha_1 A_1 + \alpha_2 A_2 + \dots \rightleftharpoons \beta_1 B_1 + \beta_2 B_2 + \dots$$

$$F = U - TS + \mu N = -kT\ln Q \qquad dF = -SdT - PdV + \sum_i \mu_i dN_i$$

$$\frac{dN_{A_1}}{\nu_{\alpha_1}} = \frac{dN_{A_2}}{\nu_{\alpha_2}} = \dots = \frac{dN_{B_1}}{\nu_{\beta_1}} = \dots = d\tilde{N} \Rightarrow dN_i = \nu_i \cdot d\tilde{N}$$

$$dF = -SdT - PdV + \sum_i \mu_i \nu_i d\tilde{N}$$

$$\left(\frac{\delta F}{\delta \tilde{N}}\right)_{T,V} = \sum_i \mu_i \nu_i = 0$$ Uslov termodinamičke ravnoteže

$$Q = \frac{g_{A_1}^{N_{A_1}}}{N_{A_1}!}\cdot\frac{g_{A_2}^{N_{A_2}}}{N_{A_2}!}\cdot\ldots = \prod_i \frac{g_i^{N_i}}{N_i!}$$

$$\ln Q = \sum_i\left(N_i \ln\frac{g_i}{N_i} + N_i\right)$$

$$\mu_i = \left(\frac{\delta F}{\delta N_i}\right)_{T,V,N_{j\neq i}} = -kT\left(\frac{\delta \ln Q}{\delta N_i}\right)_{T,V,N_{j\neq i}} \Rightarrow \mu_i = -kT\ln\frac{g_i}{N_i}$$

$$\sum_i \mu_i \nu_i = 0 \qquad \sum_i\left(-kT\ln\frac{g_i}{N_i}\right)\nu_i = 0 \quad / : (-kT)$$

$$\sum_i \ln\left(\frac{g_i}{N_i}\right)^{\nu_i} = 0$$

$$\prod_i\left(\frac{g_i}{N_i}\right)^{\nu_i} = 1 \qquad \boxed{\prod_i g_i^{\nu_i} = \prod_i N_i^{\nu_i} = K_N} \qquad \boxed{K_p = \left(\frac{kT}{p^0 V}\right)^{\sum_i \nu_i} K_N}$$

$$K_p = \frac{\left(\frac{p_{B_1}}{p^0}\right)^{\beta_1}\left(\frac{p_{B_2}}{p^0}\right)^{\beta_2}\cdot\ldots}{\left(\frac{p_{A_1}}{p^0}\right)^{\alpha_1}\cdot\ldots} = \left(\frac{1}{p^0}\right)^{\sum_i \nu_i}\prod_i p_i^{\nu_i}$$

$$2\,{}^{125}I\,{}^{127}I \rightleftharpoons {}^{125}I\,{}^{125}I + {}^{127}I\,{}^{127}I$$ Primer reakcije izotopske izmene

$\sigma = 1$; $\sigma = 2$; $\sigma = 2$

$$K_p \approx \frac{1}{4}$$

Primer reakcije disocijacije azota

$$N_{2(g)} \rightleftharpoons 2N_{(g)}$$

$$1s^2 2s^2 2p^3 \rightarrow {}^4S_{\frac{3}{2}} \qquad g_J = \frac{3}{2}\cdot 2 + 1 = 4$$

$g_0^{N_2} = 1 \qquad g_0^{N} = 4 \qquad T = 400\,K$

$r_{eq}^{N_2} = 1{,}097685\,\text{Å}$ ($10^{-10}\,m$) $\qquad p^0 = 1\,bar$

$D_e = 735{,}88\ \frac{kJ}{mol}$

$\tilde{\nu} = 2358{,}57\ cm^{-1}$

$$K_p = \left(\frac{kT}{p^0 V}\right)^{2-1}\frac{g_N^2}{g_{N_2}^1}$$

$g_N = g_{tr,N}\, g_{el,N}$

$g_{N_2} = g_{tr,N_2}\, g_{rot,N_2}\, g_{vib,N_2}\, g_{el,N_2}$

$$K_p = \frac{kT}{p^0 V}\,\frac{\left[V\left(\frac{2\pi m_N kT}{h^2}\right)^{\frac{3}{2}} g_0^N\cdot e^{-\beta\varepsilon_0^N}\right]^2}{V\left(\frac{2\pi m_{N_2} kT}{h^2}\right)^{\frac{3}{2}}\cdot\frac{kT}{\sigma_{N_2}B_{N_2}hc}\cdot\frac{e^{-\frac{1}{2}\beta hc\tilde{\nu}_{N_2}}}{1-e^{-\beta hc\tilde{\nu}_{N_2}}}\, g_0^{N_2} e^{-\beta\varepsilon_0^{N_2}}}$$

$$B = \frac{\hbar^2}{2Ihc} = \frac{\hbar^2}{2\mu r^2 hc}$$

$$\mu_{N_2} = \frac{m_N\cdot m_N}{m_N + m_N} = \frac{m_N}{2}$$

$$B_{N_2}hc = \frac{\hbar^2}{m_N r_{N_2}^2}$$

$$K_p = \frac{kT}{p^0}\left(\frac{2\pi kT}{h^2}\right)^{\frac{3}{2}}\frac{m_N^3}{m_{N_2}^{\frac{3}{2}}}\;\frac{\hbar^2\sigma_{N_2}}{m_N r_{N_2}^2 kT}\;\frac{1-e^{-\beta hc\tilde{\nu}_{N_2}}}{e^{-\frac{1}{2}\beta hc\tilde{\nu}_{N_2}}}\;\frac{(g_0^N)^2}{g_0^{N_2}}\,e^{-\beta\left(\varepsilon_0^{N_2}-2\varepsilon_0^{N}\right)}$$

($\sigma_{N_2} = 2$; $\varepsilon_0^{N_2}-2\varepsilon_0^{N}$: D_e)

$$K_p = \frac{kT}{p^0}K_{tr}\,K_{rot}\,K_{vib}\cdot K_{el}$$

$$\left(1-e^{-\beta hc\tilde{\nu}_{N_2}}\right)\frac{(g_0^N)^2}{g_0^{N_2}}\,e^{-\beta\left(\varepsilon_0^{N_2}+\frac{1}{2}hc\tilde{\nu}_{N_2}-2\varepsilon_0^{N}\right)}$$

$$D_e + \frac{1}{2}hc\tilde{\nu}_{N_2} = D_0$$

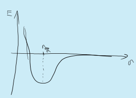
Primer reakcije izotopske izmene

$$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)} \qquad P = 5\,bar \qquad T = 1000^\circ C$$

$\sigma = 2$; $\sigma = 2$; $\sigma = 1$

$\tilde{\nu}_{H_2} = 4342\ cm^{-1}$

$m_D \approx 2m_H$



Сличне пот. криве $\Rightarrow$

$\Rightarrow\ r_{H_2} \approx r_{D_2} \approx r_{HD}$

$D_e^{H_2} \approx D_e^{D_2} \approx D_e^{HD}$

$g_0^{H_2} \approx g_0^{D_2} \approx g_0^{HD}$

$k_{HD} \approx k_{H_2} \approx k_{D_2}$

Хармонијске виб. $\Rightarrow$

$\Rightarrow\ \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

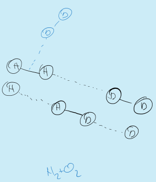
$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \sim \frac{1}{\sqrt{\mu}}$

$$K_p = \left(\frac{kT}{p^0 V}\right)^{2-1-1}\cdot\frac{g_{HD}^2}{g_{H_2}\cdot g_{D_2}} = K_N$$

($\left(\frac{kT}{p^0 V}\right)^{2-1-1} = 1$)

$$K = \frac{\left[V\left(\frac{2\pi m_{HD}kT}{h^2}\right)^{\frac{3}{2}}\frac{kT}{\sigma_{HD}B_{HD}hc}\,\frac{e^{-\frac{1}{2}\beta hc\tilde{\nu}_{HD}}}{1-e^{-\beta hc\tilde{\nu}_{HD}}}\,g_{el}^{HD}\right]^2}{V\left(\frac{2\pi m_{H_2}kT}{h^2}\right)^{\frac{3}{2}}\frac{kT}{B_{H_2}hc\cdot\sigma_{H_2}}\cdot\frac{e^{-\frac{1}{2}\beta hc\tilde{\nu}_{H_2}}}{1-e^{-\beta hc\tilde{\nu}_{H_2}}}\cdot g_{el}^{H_2}\cdot V\left(\frac{2\pi m_{D_2}kT}{h^2}\right)^{\frac{3}{2}}\frac{kT}{\sigma_{D_2}B_{D_2}hc}\,\frac{e^{-\frac{1}{2}\beta hc\tilde{\nu}_{D_2}}}{1-e^{-\beta hc\tilde{\nu}_{D_2}}}\cdot g_{el}^{D_2}} =$$

$$= \underbrace{\frac{m_{HD}^3}{m_{H_2}^{\frac{3}{2}}\cdot m_{D_2}^{\frac{3}{2}}}}_{K_{tr}}\;\underbrace{\frac{\sigma_{H_2}B_{H_2}\sigma_{D_2}B_{D_2}}{(\sigma_{HD}B_{HD})^2}}_{K_{rot}}\;\underbrace{\frac{\left(1-e^{-\beta hc\tilde{\nu}_{H_2}}\right)\left(1-e^{-\beta hc\tilde{\nu}_{D_2}}\right)}{\left(1-e^{-\beta hc\tilde{\nu}_{HD}}\right)^2}}_{K_{vib,1}}\cdot\underbrace{\frac{\left(e^{-\frac{1}{2}\beta hc\tilde{\nu}_{HD}}\right)^2}{e^{-\frac{1}{2}\beta hc\tilde{\nu}_{H_2}}\cdot e^{-\frac{1}{2}\beta hc\tilde{\nu}_{D_2}}}}_{K_{vib,2}}\cdot\underbrace{\frac{\left(g_{el}^{HD}\right)^2}{g_{el}^{H_2}\,g_{el}^{D_2}}}_{K_{el}}$$



$$K_{tr} = \frac{9}{2^{\frac{3}{2}}}$$

K_{rot}

$$B = \frac{\hbar^2}{2Ihc} = \frac{\hbar^2}{2\mu r^2 hc} \sim \frac{1}{\mu} \qquad r_{HD} \approx r_{H_2} \approx r_{D_2}$$

$$K_{rot} = \frac{\sigma_{H_2}\sigma_{D_2}}{\sigma_{HD}}\cdot\frac{\mu_{HD}^2}{\mu_{H_2}\mu_{D_2}} = \frac{32}{9}$$

($\sigma_{H_2} = 2$, $\sigma_{D_2} = 2$, $\sigma_{HD} = 1$)

K_{vib}:

$$\tilde{\nu} \sim \frac{1}{\sqrt{\mu}} \qquad k_{H_2} \approx k_{D_2} \approx k_{HD}$$

$$\tilde{\nu}_{H_2} = \tilde{\nu}_{H_2} \sim \frac{1}{\sqrt{\mu_{H_2}}} = \frac{1}{\sqrt{\frac{m_H}{2}}}$$

$$\tilde{\nu}_{D_2} \sim \frac{1}{\sqrt{\mu_{D_2}}} = \frac{1}{\sqrt{\frac{m_D}{2}}} = \frac{1}{\sqrt{\frac{2m_H}{2}}} = \frac{1}{\sqrt{2}\cdot\sqrt{\frac{m_H}{2}}} \Rightarrow \tilde{\nu}_{D_2} = \frac{1}{\sqrt{2}}\tilde{\nu}_{H_2}$$

$$\tilde{\nu}_{HD} \sim \frac{1}{\sqrt{\mu_{HD}}} \Rightarrow \tilde{\nu}_{HD} = \frac{\sqrt{3}}{2}\tilde{\nu}_{H_2}$$

$K_{el} \approx 1$

$K_{vib,1} = 0{,}98489865 \approx 1$ $\qquad K_{vib,2} = 0{,}9250404858 \approx 1$

$$K = \underbrace{K_{tr}K_{rot}\cdot K_{vib,1}}_{\text{Ентропијски члан}}\,\underbrace{K_{vib,2}\cdot K_{el}}_{\text{Енергијски члан}} = 4{,}220997\cdot 0{,}92504$$

(↓ контролише)

$$\boxed{K = 3{,}9046}$$