Primena Bolcmanove statistike na atomske i molekulske gasove:

Molekuli ≡ jezgra + e^-

- Unutrašnje kretanje
  - Born-Openhajmerova aproksimacija
    - Elektronsko kretanje
    - Jezgarno kretanje
      - Ro-vib kretanje
        - Rotacija
        - Vibracija
      - Nukleonsko kretanje
- Kretanje centra mase

Idealni monoatomski gasovi:

$$Q = \frac{q^N}{N!}$$

$$\varepsilon = \varepsilon_{tr} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{el} + \varepsilon_{noc}$$

$$q = q_{tr}(V,T) \cdot q_{rot}(T) \cdot q_{vib}(T) \cdot q_{el}(T) \cdot q_{noc}(T)$$

Translaciona particiona f-ja:

$$\boxed{q_{tr} = V\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}}}$$

Rotaciona particiona f-ja:

Dvoatomski molekuli

$$E = \frac{J(J+1)\hbar^2}{2I} = \frac{J(J+1)\hbar^2}{2\mu r^2} = Bhc\,J(J+1)$$

$I = \mu r^2$

$J = 0, 1, 2, \ldots$

$$\boxed{B = \frac{\hbar^2}{2Ihc}}$$

↳ Rotaciona konstanta ($B \approx 1-10\ cm^{-1}$)

$$\boxed{\Theta_r = \frac{Bhc}{k}}$$

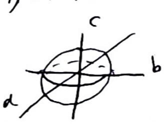
↳ Rotaciona temperatura

$$\boxed{q_{rot} = \frac{kT}{\sigma Bhc}}$$

σ → faktor simetrije

Višeatomski molekuli:

1) Sferne čigre:

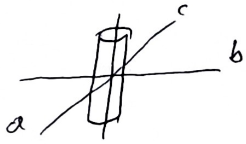


$I_a = I_b = I_c$

pr. CH_4

$$\boxed{q_{rot} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{kT}{Bhc}\right)^{\frac{3}{2}}}$$

2) Simetrične čigre:



$I_a = I_b \neq I_c$

pr. NH_3

$$\boxed{q_{rot} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{kT}{\underset{A''}{Bhc}}\right)\left(\frac{kT}{chc}\right)^{\frac{1}{2}}}$$

3) Asimetrične čigre:

$I_a \neq I_b \neq I_c$

pr. H_2O

$$\boxed{q_{rot} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{kT}{hc}\right)^{\frac{3}{2}} \cdot \frac{1}{(ABC)^{\frac{1}{2}}}}$$

→ VIBRACIONA PARTICIONA FUNKCIJA:

$f \equiv$ (BROJ NORMALNIH MODOVA) $\equiv$ (BROJ STEPENI SLOBODE)

$$f = \begin{cases} 3N-6 & \text{NELINEARAN MOLEKUL} \\ 3N-5 & \text{LINEARAN MOLEKUL} \end{cases}$$

$\boxed{\theta_{vib} = \frac{\omega\hbar}{k}}$ → KARAKTERISTIČNA VIB. E-JA

→ ZA VIŠEATOMSKI MOLEKUL:

$$\boxed{q_{vib} = \prod_{i=1}^{f} \frac{e^{-\frac{1}{2}\beta\omega_i\hbar}}{1-e^{-\beta\omega_i\hbar}}}$$

NULTA VIBRACIONA E-JA $\quad q^{0}_{vib} = \prod_{i=1}^{f} \frac{1}{1-e^{-\beta\omega_i\hbar}}$

→ ELEKTRONSKA PARTICIONA F-JA:

$$\boxed{q_{el} = \sum_i g_i \cdot e^{-\beta\varepsilon_i}}$$

$g_i = 2J+1$ ZA ATOMSKA STANJA $^{2S+1}L_J$

$$q_{el} = g_0 \cdot e^{-\beta\varepsilon_0} + g_1 e^{-\beta\varepsilon_1} + \ldots = g_0 \cdot e^{-\beta(-D_e)} + g_1 e^{-\beta(\varepsilon_1' - D_e)} + \ldots =$$

$$= \underbrace{e^{\beta D_e}}_{\text{KLASIČNA ENERGIJA DISOCIJACIJE}} (g_0 + g_1 \cdot e^{-\beta\underbrace{\varepsilon_1'}_{\text{ENERGIJA EKSCITACIJE}}} + \ldots) = e^{\beta D_e} q^{0}_{el}$$

$$q_{el} \cdot q_{vib} = q^{0}_{el} \cdot q^{0}_{vib} \cdot e^{\beta D_0}$$

→ PRAVA ENERGIJA DISOCIJACIJE $\quad D_0 = D_e - \sum_{i=1}^{f} \frac{1}{2}\omega_i\hbar$

→ ZADACI:

5.7 $T = 25°C = 298{,}15\,K$

$V = 10\,cm^3 = 10 \cdot 10^{-6}\,m^3 = 10^{-5}\,m^3$

$M(Na) = 22{,}98976\ g/mol$

$\frac{m}{M} = \frac{N}{N_A} \Rightarrow m = \frac{M}{N_A} = 3{,}82 \cdot 10^{-23}\,g = 3{,}82 \cdot 10^{-26}\,kg$

$h = 6{,}626 \cdot 10^{-34}\,Js$

$k = 1{,}38 \cdot 10^{-23}\,\frac{J}{K}$

$$q_{tr} = V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} = 1{,}06598 \cdot 10^{27}$$

5.8 $M(Ar) = 39{,}948\ \frac{g}{mol}$

$T = 25°C = 298{,}15\,K$

$p = 10^6\,Pa$

$S_{tr} = ?$

$$Q = \frac{q^N}{N!} \Rightarrow Q_{tr} = \frac{1}{N!}(q_{tr})^N = \frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}}$$

$$F = -kT\ln Q_{tr} = -kT\ln\left[\frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}}\right] = -kT\left(N\ln\left[V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] - N\ln N + N\right) =$$

$$= -kT\left(N\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] + N\right)$$

$Nk = nR$

$$f = \frac{F}{n} = -\frac{NkT}{n}\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] - \frac{NkT}{n} = -\frac{\cancel{n}RT}{\cancel{n}}\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] - \frac{\cancel{n}RT}{\cancel{n}}$$

$$f = -RT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] - RT$$

$$S_{tr} = -\left(\frac{\partial f}{\partial T}\right)_V = R\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] + RT\frac{1}{\cancel{\frac{V}{N}}\left(\cancel{\frac{2\pi mkT}{h^2}}\right)^{\frac{3}{2}}}\cdot\cancel{\frac{V}{N}\left(\frac{2\pi mk}{h^2}\right)^{\frac{3}{2}}}\cdot\frac{3}{2}T^{\frac{1}{2}} + R$$

$$= R\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] + R\cancel{T}\frac{3}{2}\frac{1}{\cancel{T}} + R$$

$$\boxed{S_{tr} = R\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] + \frac{5}{2}R} \Rightarrow S_{tr} = 135{,}7002569\ \frac{J}{mol\,K}$$

$$\left.\begin{matrix} pV = NkT \\ \text{ZA } N=1 \end{matrix}\right\} V = \frac{kT}{p}$$

5.9 $M(He) = 4{,}002602\ \frac{g}{mol}$ → TRANSACIONI DOPRINOS ZA $f, U, C_{v,m}, S$

$T = 25°C = 298{,}15K$

$p = 10^5 Pa$

$$f = -RT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] - RT$$

$$f = -33\,912{,}611\ \frac{J}{mol}$$

POKAZANO U PROŠLOM ZADATKU

$$S = R\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] + \frac{5}{2}R$$

$$S = 126{,}21516\ \frac{J}{mol\,K}$$

$$\langle E\rangle \equiv U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N} = +kT^2\frac{\partial}{\partial T}\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$$

$$\hookrightarrow \frac{\partial}{\partial\beta} = \frac{\partial}{\partial T}\cdot\frac{\partial T}{\partial \beta} = \frac{\partial}{\partial T}\cdot\frac{1}{\frac{\partial\beta}{\partial T}} = \frac{\partial}{\partial T}\cdot\frac{1}{\left(-\frac{1}{kT^2}\right)} = -kT^2\frac{\partial}{\partial T}$$

$$\hookrightarrow \ln Q = \ln\left[\frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}}\right] = N\ln\left[V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] - N\ln N + N =$$

$$= N\left(\ln\left[V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] - \ln N\right) + N = N\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] + N$$

$$U = kT^2\frac{\partial}{\partial T}\left[N\ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right) + N\right] = kT^2\cdot N\cdot\frac{1}{\cancel{\frac{V}{N}}\left(\cancel{\frac{2\pi mkT}{h^2}}\right)^{\frac{3}{2}}}\cdot\cancel{\frac{V}{N}\left(\frac{2\pi mk}{h^2}\right)^{\frac{3}{2}}}\cdot\frac{3}{2}\cdot T^{\frac{1}{2}} =$$

$$= kT^2N\cdot\frac{3}{2}\cdot T^{\frac{1}{2}-\frac{3}{2}} = kT^{\cancel{2}}N\frac{3}{2}\cdot\frac{1}{\cancel{T}} = \frac{3}{2}NkT \Rightarrow \boxed{U = \frac{3}{2}RT} \quad U = 3718{,}438846\ \frac{J}{mol}$$

$$C_{v,m} = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}R = 12{,}5\ \frac{J}{mol\,K}$$

(5.10) $g_0 = 2 \quad \tilde{\nu}_0 = 0$

$g_1 = 1 \quad \tilde{\nu}_1 = 500\,cm^{-1}$

$g_2 = 3 \quad \tilde{\nu}_2 = 2500\,cm^{-1}$

$T = 1000\,K$

$\langle E_{el} \rangle = ?$

$$E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu} = \omega\hbar$$

$$q_{el} = \sum_{i=0}^{2} g_i \cdot e^{-\beta \varepsilon_i} = g_0\, e^{-\beta\varepsilon_0} + g_1\, e^{-\beta\varepsilon_1} + g_2\, e^{-\beta\varepsilon_2}$$

$$q_{el} = g_0 \cdot e^{-\beta hc\tilde{\nu}_0 \to 0} + g_1 \cdot e^{-\beta hc\tilde{\nu}_1} + g_2 \cdot e^{-\beta hc\tilde{\nu}_2}$$

$$\boxed{q_{el} = g_0 + g_1 e^{-\beta hc\tilde{\nu}_1} + g_2 e^{-\beta hc\tilde{\nu}_2}}$$

$1\,cm^{-1} = 100\,m^{-1}$

$q_{el} = 2{,}57$

$$\langle E_{el} \rangle = -\left(\frac{\partial \ln q_{el}}{\partial \beta}\right) = -\frac{\partial}{\partial\beta}\left[\ln\left(g_0 + g_1 e^{-\beta hc\tilde{\nu}_1} + g_2 e^{-\beta hc\tilde{\nu}_2}\right)\right] =$$

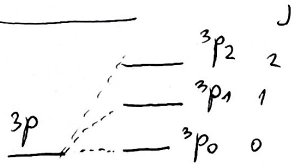
$$= -\frac{g_1 \cdot e^{-\beta hc\tilde{\nu}_1}(-hc\tilde{\nu}_1) + g_2 e^{-\beta hc\tilde{\nu}_2} \cdot (-hc\tilde{\nu}_2)}{g_0 + g_1 e^{-\beta hc\tilde{\nu}_1} + g_2 e^{-\beta hc\tilde{\nu}_2}} = \frac{hc\tilde{\nu}_1 g_1 e^{-\beta hc\tilde{\nu}_1} + hc\tilde{\nu}_2 g_2 e^{-\beta hc\tilde{\nu}_2}}{q_{el}}$$

$\langle E_{el} \rangle = 3{,}47186 \cdot 10^{-21}\,J = 174{,}777\,cm^{-1}$

(5.11) $g_0 = 5 \quad \tilde{\nu}_0 = 0 \quad {}^3P_2$

$g_1 = 3 \quad \tilde{\nu}_1 = 158{,}5\,cm^{-1} \quad {}^3P_1$

$g_2 = 1 \quad \tilde{\nu}_2 = 226{,}5\,cm^{-1} \quad {}^3P_0$



$g_0 = 2J + 1 = 5$

$g_1 = 3$

$g_2 = 1$

$T = 298{,}15\,K$

$P_i = \frac{\langle n_i \rangle}{\langle N \rangle} = ?$

$\varepsilon_i = hc\tilde{\nu}_i$

$$P_i = \frac{\langle n_i \rangle}{\langle N \rangle} = \frac{g_i \cdot e^{-\beta\varepsilon_i}}{q_{el}} = \frac{g_i\, e^{-\beta\varepsilon_i}}{g_0 + g_1 e^{-\beta\varepsilon_1} + g_2 e^{-\beta\varepsilon_2}}$$

$q_{el} = 6{,}73133$

$P_{J=0} = 0{,}74$

$P_{J=1} = 0{,}21$

$P_{J=2} = 0{,}05$

(5.12) $M(F) = 18{,}998403\,\frac{g}{mol} \quad T = 500\,K$

$g_0 = 4 \quad \tilde{\nu}_0 = 0$

$g_1 = 2 \quad \tilde{\nu}_1 = 404\,cm^{-1}$

→ ELEKTRONSKI DOPRINOS ZA $C_{v,m}$ i f

$$q_{el} = \sum_{i=0}^{1} g_i\, e^{-\beta\varepsilon_i} = g_0 + g_1\, e^{-\beta hc\tilde{\nu}_1}$$

$$f = -RT \ln q_{el} = -RT \ln\left[g_0 + g_1 e^{-\beta hc\tilde{\nu}_1}\right] \Rightarrow f = -6{,}4\,\frac{kJ}{mol}$$

$$\langle E\rangle = U = -\left(\frac{\partial \ln q_{el}}{\partial \beta}\right) = -\frac{\partial}{\partial \beta}\left[\ln\left(g_0 + g_1 e^{-\beta h c \tilde{\nu}_1}\right)\right] = -\frac{g_1 \cdot e^{-\beta h c \tilde{\nu}_1} \cdot (-hc\tilde{\nu}_1)}{g_0 + g_1 e^{-\beta h c \tilde{\nu}_1}} = \frac{hc\tilde{\nu}_1 g_1 e^{-\beta h c \tilde{\nu}_1}}{g_0 + g_1 e^{-\beta h c \tilde{\nu}_1}}$$

$$\langle E\rangle = U = \frac{hc\tilde{\nu}_1 g_1}{g_0 e^{\beta h c \tilde{\nu}_1} + g_1}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = -\frac{1}{kT^2}\frac{\partial}{\partial \beta}\left[\frac{hc\tilde{\nu}_1 g_1}{g_0 e^{\beta h c \tilde{\nu}_1} + g_1}\right]$$

$$\hookrightarrow \frac{\partial}{\partial T} = \frac{\partial}{\partial \beta}\cdot\frac{\partial \beta}{\partial T} = \left(-\frac{1}{kT^2}\right)\cdot\frac{\partial}{\partial \beta}$$

$$C_V = +\frac{1}{kT^2}\,\frac{hc\tilde{\nu}_1 g_1 \cdot g_0 \cdot e^{\beta h c \tilde{\nu}_1} \cdot hc\tilde{\nu}_1}{\left(g_0 e^{\beta h c \tilde{\nu}_1} + g_1\right)^2} = g_0 g_1 k \cdot \left(\frac{hc\tilde{\nu}_1}{kT}\right)^2 \cdot \frac{e^{\beta h c \tilde{\nu}_1}}{\left(g_1 + g_0 e^{\beta h c \tilde{\nu}_1}\right)^2}$$

$$C_{V,m} = g_0 g_1 R \left(\frac{hc\tilde{\nu}_1}{kT}\right)^2 \cdot \frac{e^{\beta h c \tilde{\nu}_1}}{\left(g_1 + g_0 e^{\beta h c \tilde{\nu}_1}\right)^2} \Rightarrow C_{V,m} = 1{,}3139\,\frac{J}{mol\,K} \approx 1{,}31\,\frac{J}{mol\,K}$$

↳ JAKO MALI DOPRINOS

5.13 Ako je $q_{el} \approx g_0$ IZRAČUNATI : U, F, μ, S, C_V

$$Q = \frac{q^N}{N!} = \frac{1}{N!}\left(q_{tr} \cdot q_{rot} \cdot q_{vib} \cdot q_{el} \cdot q_{nuc}\right)^N = Q' \cdot q_{el}^N = Q' \cdot g_0^N$$

$$\ln Q = \ln\left(Q' \cdot g_0^N\right) = \ln Q' + N \ln g_0$$

$$F = -kT\ln Q = -kT\ln Q' - NkT\ln g_0 = f(g_0)$$

$$U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N} = -\left(\frac{\partial \ln Q'}{\partial \beta}\right)_{V,N} \neq f(g_0)$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -kT\left(\frac{\partial \ln Q'}{\partial N}\right)_{V,T} - kT\ln g_0 = f(g_0)$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = -\frac{1}{kT^2}\left(\frac{\partial U}{\partial \beta}\right) = +\frac{1}{kT^2}\left(\frac{\partial^2 \ln Q'}{\partial \beta^2}\right)_{V,N} = k\beta^2\left(\frac{\partial^2 \ln Q'}{\partial \beta^2}\right)_{V,N} \neq f(g_0)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = kT\left(\frac{\partial \ln Q'}{\partial T}\right)_{V,N} + k\ln Q' + Nk\ln(g_0) = f(g_0)$$

5.14 $M(H) = 1{,}00794\,\frac{g}{mol}$

$M(H_2) = 2{,}01588\,\frac{g}{mol}$

$V = 100\,cm^3 = 100 \cdot 10^{-6}\,m^3$

$T = 25\,°C = 298{,}15\,K$

MOLEKUL H_2

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

$$q_{tr} = 2{,}7690 \cdot 10^{26}$$

5.15 O_2

$r = 120{,}75\ pm$

$T = 300K$

$M(O) = 15{,}999\ \frac{g}{mol}$

$q_{rot} = ?$

$\frac{m}{M} = \frac{N}{N_A}$

$$q_{rot} = \frac{kT}{\delta Bhc}$$

$\delta = 2$

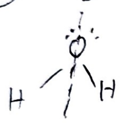
$$B = \frac{\hbar^2}{2Ihc} \Rightarrow Bhc = \frac{\hbar^2}{2I} = \frac{\hbar^2}{2\mu r^2}$$

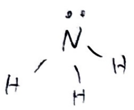
$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2} = \frac{m_0^2}{m_0 + m_0} = \frac{m_0}{2}$$

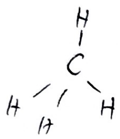
$$Bhc = \frac{2\hbar^2}{2m_0 r^2} = \frac{\hbar^2}{m_0 r^2}$$

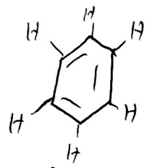
$$q_{rot} = \frac{kT}{\delta \cdot \frac{\hbar^2}{m_0 r^2}} = \frac{kT m_0 r^2}{\delta \hbar^2} = \frac{kT m_0 r^2}{\delta \left(\frac{h}{2\pi}\right)^2} = \frac{4\pi^2 kT m_0 r^2}{\delta h^2} \Rightarrow q_{rot} = 72{,}13$$

5.16 H_2O NH_3 CH_4 C_6H_6









$\delta = 2$ $\delta = 3$ $\delta = 12$ $\delta = 12$

5.17 HCl

$\delta = 1$

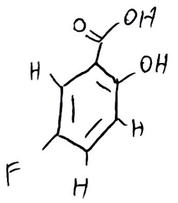
$T = 300k$

$B = 10{,}591\ cm^{-1}$

$$q_{rot} = \frac{kT}{\delta Bhc}$$

$q_{rot} = 19{,}66$

5.18 5-FLUOROSALICILNA KISELINA



$A = 0{,}061\ cm^{-1}$

$B = 0{,}030\ cm^{-1}$

$C = 0{,}020\ cm^{-1}$

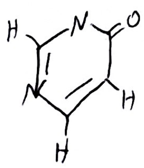
$T = 25°C = 298{,}15K$

$$q_{rot} = \frac{\sqrt{\pi}}{\delta}\left(\frac{kT}{hc}\right)^{\frac{3}{2}} \cdot \frac{1}{(ABC)^{\frac{1}{2}}}$$

$\delta = 1$

$q_{rot} = 8{,}7 \cdot 10^5$

5.19 PIRIMIDON



$A = 0{,}188\ cm^{-1}$

$B = 0{,}003\ cm^{-1}$

$C = 0{,}062\ cm^{-1}$

$T = 25°C = 298{,}15K$

$$q_{rot} = \frac{\sqrt{\pi}}{\delta}\left(\frac{kT}{hc}\right)^{\frac{3}{2}} \cdot \frac{1}{(ABC)^{\frac{1}{2}}}$$

$F = -kT \ln q_{rot}$

$$f = -RT \ln\left[\frac{\sqrt{\pi}}{\delta}\left(\frac{kT}{hc}\right)^{\frac{3}{2}} \cdot \frac{1}{\sqrt{ABC}}\right]$$

$f = 29{,}7\ \frac{kJ}{mol}$

5.20 → NAJZAUZETIJI ROTACIONI NIVO;

$$\frac{\langle n_j \rangle}{\langle N \rangle} = \frac{g_j \cdot e^{-\beta \overbrace{Bhc J(J+1)}^{\varepsilon}}}{q_{rot}} \qquad g_j = 2J+1$$

$$\frac{dN(J)}{dJ} = \frac{d}{dJ}\left[\frac{(2J+1)\, e^{-\beta Bhc J(J+1)}}{q_{rot}}\right] = 0 \quad \Rightarrow q_{rot} \neq 0 \quad e^{-\beta Bhc J(J+1)} > 1$$

$$\frac{dN(J)}{dJ} = 2 \cdot e^{-\beta Bhc J(J+1)} + (2J+1) e^{-\beta Bhc J(J+1)} (-\beta Bhc (2J+1)) = 0$$

$$(2 - (2J+1)^2 \beta Bhc) \underbrace{e^{-\beta Bhc J(J+1)}}_{\neq 0} = 0$$

$$2 - (2J+1)^2 \beta Bhc = 0$$

$$(2J+1)^2 = \frac{2}{\beta Bhc} = \frac{2kT}{Bhc} \Rightarrow 2J+1 = \sqrt{\frac{2kT}{Bhc}} \Rightarrow J_{nv} = \frac{1}{2}\sqrt{\frac{2kT}{Bhc}} - \frac{1}{2} \Rightarrow \boxed{J_{nv} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}}$$

5.21 H_2O

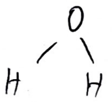
→ NORMALNI MOD JE OSCILUJUĆI SISTEM U KOME SVI DELOVI OSCILUJU ISTOM FREKVENCIJOM I FAZOM.

→ SVI DELOVI SISTEMA OSCILUJU TAKO DA DOLAZE U MINIMUM I MAKSIMUM U ISTO VREME.

$\tilde{\nu}_1 = 3755{,}8\ cm^{-1}$

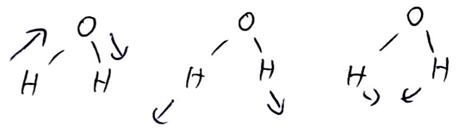
$\tilde{\nu}_2 = 3656{,}7\ cm^{-1}$

$\tilde{\nu}_3 = 1594{,}8\ cm^{-1}$



$$f = 3N - 6 = 3 \cdot 3 - 6 = 3 \Rightarrow \tilde{\nu}_1 \quad \tilde{\nu}_2 \quad \tilde{\nu}_3$$

ASIM. ISTEŽUĆA — SIM ISTEŽUĆA — SAVIJAJUĆA



$q_{vib} = ?$

$$q_{vib} = \prod_{i=1}^{3} \frac{e^{-\frac{1}{2}\beta \omega_i \hbar}}{1 - e^{-\beta \omega_i \hbar}} \qquad \boxed{\omega \hbar = hc\tilde{\nu}}$$

$$q_{vib} = \frac{e^{-\frac{1}{2}\beta hc\tilde{\nu}_1}}{1 - e^{-\beta hc\tilde{\nu}_1}} \cdot \frac{e^{-\frac{1}{2}\beta hc\tilde{\nu}_2}}{1 - e^{-\beta hc\tilde{\nu}_2}} \cdot \frac{e^{-\frac{1}{2}\beta hc\tilde{\nu}_3}}{1 - e^{-\beta hc\tilde{\nu}_3}}$$

⇒ BROJEVI U BROJIOCU SE ZANEMARUJU AKO SE OSNOVNI NIVO STAVI NA NULU

$$q_{vib} = \frac{1}{1 - e^{-\beta hc\tilde{\nu}_1}} \cdot \frac{1}{1 - e^{-\beta hc\tilde{\nu}_2}} \cdot \frac{1}{1 - e^{-\beta hc\tilde{\nu}_3}} \Rightarrow q_{vib} = 1{,}12$$

5.22 I_2

→ ROTACIONI I VIBRACIONI DOPRINOS f I $C_{V,m}$

$M(I) = 126{,}9044\ \frac{g}{mol}$

$T = 25°C = 298{,}15K$

$B = 0{,}037\ cm^{-1}$

$\tilde{\nu} = 214{,}6\ cm^{-1}$

$$Q = q_{rot} \cdot q_{vib} = \frac{kT}{\sigma Bhc} \cdot \frac{1}{1 - e^{-\beta hc\tilde{\nu}}} \qquad \boxed{\sigma = 2}$$

$$f = -RT \ln Q$$

$$f = -RT\left[\ln\left(\frac{kT}{\sigma Bhc}\right) - \ln\left(1 - e^{-\beta hc\tilde{\nu}}\right)\right] \qquad f = 20{,}7\ \frac{kJ}{mol}$$

$$S=-\left(\frac{\partial f}{\partial T}\right)_{\vartheta}=R\left[\ln\left(\frac{kT}{\delta Bhc}\right)-\ln\left(1-e^{-\beta hc\tilde{\nu}}\right)\right]+RT\left[\frac{1}{\frac{kT}{\delta Bhc}}\cdot\frac{k}{\delta Bhc}-\frac{1}{1-e^{-\beta hc\tilde{\nu}}}\cdot e^{-\beta hc\tilde{\nu}}\cdot\left(-\frac{hc\tilde{\nu}}{kT^2}\right)\right]$$

$$=R\left[\ln\left(\frac{kT}{\delta Bhc}\right)-\ln\left(1-e^{-\beta hc\tilde{\nu}}\right)\right]+RT\left[\frac{1}{T}+\frac{\frac{hc\tilde{\nu}}{kT^2}}{e^{\beta hc\tilde{\nu}}-1}\right]=$$

$$=R\left[\ln\left(\frac{kT}{\delta Bhc}\right)-\ln\left(1-e^{-\beta hc\tilde{\nu}}\right)\right]+R+\frac{\frac{Rhc\tilde{\nu}}{kT}}{e^{\beta hc\tilde{\nu}}-1}\implies S=1471{,}007\ \frac{J}{K\,mol}$$

$$\langle E\rangle\equiv U=-\left(\frac{\partial\ln Q}{\partial\beta}\right)=-\frac{\partial}{\partial\beta}\left[\ln\left(\frac{kT}{\delta Bhc}\right)-\ln\left(1-e^{-\beta hc\tilde{\nu}}\right)\right]_{V,N}=$$

$$=-\frac{\partial}{\partial\beta}\left[-\ln\left(\frac{\delta Bhc}{kT}\right)-\ln\left(1-e^{-\beta hc\tilde{\nu}}\right)\right]_{V,N}=$$

$$=\frac{\partial}{\partial\beta}\left[\ln(\beta B\delta hc)+\ln\left(1-e^{-\beta hc\tilde{\nu}}\right)\right]_{V,N}=\frac{\cancel{B\delta hc}}{\beta\cancel{B\delta hc}}+\frac{-e^{-\beta hc\tilde{\nu}}(-hc\tilde{\nu})}{1-e^{-\beta hc\tilde{\nu}}}$$

$$=\frac{1}{\beta}+\frac{hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}}-1}\implies\boxed{\langle E\rangle=kT+\frac{hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}}-1}}$$

$$\rightarrow\frac{\partial}{\partial T}=-\frac{1}{kT^2}\frac{\partial}{\partial\beta}=-k\beta^2\frac{\partial}{\partial\beta}$$

$$C_V=\left(\frac{\partial U}{\partial T}\right)_{V,N}=-\frac{1}{kT^2}\frac{\partial}{\partial\beta}\left[\frac{1}{\beta}+\frac{hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}}-1}\right]=-k\beta^2\left[-\frac{1}{\beta^2}-\frac{hc\tilde{\nu}\cdot e^{\beta hc\tilde{\nu}}\cdot hc\tilde{\nu}}{\left(e^{\beta hc\tilde{\nu}}-1\right)^2}\right]$$

$$=k\left[1+\left(\frac{hc\tilde{\nu}}{kT}\right)^2\frac{e^{\beta hc\tilde{\nu}}}{\left(e^{\beta hc\tilde{\nu}}-1\right)^2}\right]\implies\boxed{C_{V,m}=R\left[1+\left(\frac{hc\tilde{\nu}}{kT}\right)^2\frac{e^{\beta hc\tilde{\nu}}}{\left(e^{\beta hc\tilde{\nu}}-1\right)^2}\right]}$$

$$C_{V,m}=15{,}92\ \frac{J}{mol\,K}$$

5.23 H_2O $\quad M(O)=15{,}9994\ \frac{g}{mol}$

$T=100^\circ C=373{,}15\,K$ $\quad M(H)=1{,}00794\ g/mol$

$A=27{,}9\ cm^{-1}$ $\quad \tilde{\nu}_1=3755{,}8\ cm^{-1}$

$B=14{,}5\ cm^{-1}$ $\quad \tilde{\nu}_2=3656{,}7\ cm^{-1}$

$C=9{,}3\ cm^{-1}$ $\quad \tilde{\nu}_3=1594{,}8\ cm^{-1}$

→ NULTI VIBRACIONI NIVO JE NA NULI

→ ZANEMARENO JE ELEKTRONSKO KRETANJE

$C_{V,m}=?$ $\quad \delta=2$ $\quad f=3$

$$Q=\frac{1}{N!}\left(q_{tr}\cdot q_{rot}\cdot q_{vib}\right)^N=\frac{1}{N!}\left[V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\cdot\frac{\sqrt{\pi}}{\delta}\cdot\left(\frac{kT}{hc}\right)^{\frac{3}{2}}\cdot\frac{1}{(ABC)^{\frac{1}{2}}}\cdot\prod_{i=1}^{3}\frac{1}{1-e^{-\beta hc\tilde{\nu}_i}}\right]^N$$

$$-\ln\left(1-e^{-\beta hc\tilde{\nu}_3}\right)$$

$$\langle E\rangle=-\left(\frac{\partial\ln Q}{\partial\beta}\right)_{V,N}=\frac{\partial}{\partial\beta}\left[-N\ln N+N+\ln\left[V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right]+\ln\left(\frac{\sqrt{\pi}}{\delta}\left(\frac{kT}{hc}\right)^{\frac{3}{2}}\cdot\frac{1}{(ABC)^{\frac{1}{2}}}\right)-\ln\left(1-e^{-\beta hc\tilde{\nu}_1}\right)-\ln\left(1-e^{-\beta hc\tilde{\nu}_2}\right)\right.$$

$$\langle E\rangle = -\frac{\cancel{V}\left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}}\cdot\left(-\frac{3}{2}\right)\cdot\beta^{-\frac{5}{2}}}{\cancel{V}\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}}} - \frac{\frac{\sqrt{\pi}}{\cancel{\delta}}\left(\frac{1}{hc}\right)^{\frac{3}{2}}\cdot\frac{1}{(ABC)^{\frac{1}{2}}}\cdot\left(-\frac{3}{2}\right)\cdot\beta^{-\frac{5}{2}}}{\frac{\sqrt{\pi}}{\cancel{\delta}}\left(\frac{1}{hc\beta}\right)^{\frac{3}{2}}\frac{1}{(ABC)^{\frac{1}{2}}}} + \frac{1-e^{-\beta hc\tilde{\nu}_1}\cdot(-hc\tilde{\nu}_1)}{1-e^{-\beta hc\tilde{\nu}_1}} + \frac{hc\tilde{\nu}_2\, e^{-\beta hc\tilde{\nu}_2}}{1-e^{-\beta hc\tilde{\nu}_2}} +$$

$$+\frac{hc\tilde{\nu}_3\, e^{-\beta hc\tilde{\nu}_3}}{1-e^{-\beta hc\tilde{\nu}_3}} =$$

$$= \frac{3}{2}\beta^{-\frac{5}{2}+\frac{3}{2}} + \frac{3}{2}\beta^{-\frac{5}{2}+\frac{3}{2}} + \frac{hc\tilde{\nu}_1}{e^{\beta hc\tilde{\nu}_1}-1} + \frac{hc\tilde{\nu}_2}{e^{\beta hc\tilde{\nu}_2}-1} + \frac{hc\tilde{\nu}_3}{e^{\beta hc\tilde{\nu}_3}-1}$$

$$= \frac{3}{2}\cdot\frac{1}{\beta} + \frac{3}{2}\frac{1}{\beta} + \sum_{i=1}^{3}\left[\frac{hc\tilde{\nu}_i}{e^{\beta hc\tilde{\nu}_i}-1}\right] = \frac{3}{2}kT + \frac{3}{2}kT + \sum_{i=1}^{3}\left[\frac{hc\tilde{\nu}_i}{e^{\frac{hc\tilde{\nu}}{kT}}-1}\right]$$

$$C_{v,m} = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{V,N} = \frac{3}{2}R + \frac{3}{2}R + \sum_{i=1}^{3}\left[-\frac{hc\tilde{\nu}_i\cdot e^{\frac{hc\tilde{\nu}}{kT}}\cdot\left(-\frac{hc\tilde{\nu}_i}{kT^2}\right)}{\left(e^{\frac{hc\tilde{\nu}_i}{kT}}-1\right)^2}\right] \Rightarrow$$

$$\boxed{C_{v,m} = \underbrace{\frac{3}{2}R}_{\text{TRANSLACIJA}} + \underbrace{\frac{3}{2}R}_{\text{ROTACIJA}} + \underbrace{\sum_{i=1}^{3}\left[k\left(\frac{hc\tilde{\nu}_i}{kT}\right)^2\cdot\frac{e^{\beta hc\tilde{\nu}_i}}{(e^{\beta hc\tilde{\nu}_i}-1)^2}\right]}_{\text{VIBRACIJA}}}$$

↳ DA LI OVO TREBA STVARNO RAČUNATI?

IZRAČUNATI KARAKTERISTIČNE TEMPERATURE:

→ ROTACIJA: $\theta_{rot} = \frac{Bhc}{k}$

$\theta_1^{rot} = 40{,}14\,K$

$\theta_2^{rot} = 20{,}86\,K$

$\theta_3^{rot} = 13{,}38\,K$

} DOSTA MANJE OD 373,15 K PA VAŽI VISOKOTEMPERATURSKA APROKSIMACIJA, TJ. SVAKI STEPEN SLOBODE DOPRINOSI $C_{v,m}$ SA $\frac{1}{2}R$

→ VIBRACIJA: $\theta_{vib} = \frac{hc\tilde{\nu}}{k}$

$\theta_1^{vib} = 5403{,}97\,K$

$\theta_2^{vib} = 5261{,}38\,K$

$\theta_3^{vib} = 2294{,}65\,K$

} DOSTA VIŠE OD 373,15 K PA OVI MODOVI NISU POBUĐENI I NE DOPRINOSE ZNAČAJNO $C_{v,m}$

$$C_{v,m} \approx \frac{3}{2}R + \frac{3}{2}R = 3R = 24{,}9\ \frac{J}{mol\,K}$$

5.24 D_2

$m(D) \equiv m(^2H) = 2{,}013553\, D_a$

↳ DALTON: $1 D_a = 1{,}66054 \cdot 10^{-27}\, kg$

$T = 298\, K$

$p = 10^5\, P_a$

$B = 29{,}9\, cm^{-1}$

$\tilde{\nu} = 3054\, cm^{-1}$

$S = ?$

→ ZANEMARITI DOPRINOS ELEKTRONSKOG KRETANJA

→ NULTI VIBRACIONI NIVO JE NA NULI

$$Q = \frac{1}{N!}\left(q_{tr} \cdot q_{rot} \cdot q_{vib}\right)^N = \frac{1}{N!}\left(V\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}} \cdot \frac{kT}{\delta B h c} \cdot \frac{1}{1 - e^{-\beta h c \tilde{\nu}}}\right)^N$$

$$F = -kT \ln Q$$

$$F = -NkT\left[\ln\left(V\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}}\right) + \ln\left(\frac{kT}{\delta B h c}\right) - \ln\left(1 - e^{-\beta h c \tilde{\nu}}\right) - \ln N + 1\right]$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk\left[\ln\left(\frac{V}{N}\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}}\right) + \ln\left(\frac{kT}{\delta B h c}\right) - \ln\left(1 - e^{-\beta h c \tilde{\nu}}\right)\right] +$$

$$+ NkT\left[\frac{\cancel{V}\left(\cancel{\frac{2\pi m k}{h^2}}\right)^{\frac{3}{2}} \cdot \frac{3}{2} T^{+\frac{1}{2}}}{\cancel{V}\left(\cancel{\frac{2\pi m k T}{h^2}}\right)^{\frac{3}{2}}} + \frac{\frac{k}{\cancel{\delta B h c}}}{\frac{kT}{\cancel{\delta B h c}}} - \frac{-e^{-\beta h c \tilde{\nu}} \cdot \left(+\frac{h c \tilde{\nu}}{k T^2}\right)}{1 - e^{-\beta h c \tilde{\nu}}}\right] =$$

$$S = \frac{3}{2} R\cancel{T} \cdot \frac{1}{\cancel{T}} + R\cancel{T} \cdot \frac{1}{\cancel{T}} + R\frac{\frac{h c \tilde{\nu}}{kT}}{e^{\beta h c \tilde{\nu}} - 1} + R\left[\ln\left(\frac{kT}{p}\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}}\right) + \ln\left(\frac{kT}{\delta B h c}\right) - \ln\left(1 - e^{-\beta h c \tilde{\nu}}\right)\right]$$

$$\boxed{S = \frac{3}{2} R + R + R\frac{\frac{h c \tilde{\nu}}{kT}}{e^{\beta h c \tilde{\nu}} - 1} + R\left[\ln\left(\frac{kT}{p}\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}}\right) + \ln\left(\frac{kT}{\delta B h c}\right) - \ln\left(1 - e^{-\beta h c \tilde{\nu}}\right)\right]}$$

$$S = 127{,}90\, \frac{J}{mol\, K}$$

5.25 NO

$T = 600\, K$

$g_0 = 2 \quad \varepsilon_0 = 0$

$g_1 = 2 \quad \varepsilon_1 = 121{,}1\, cm^{-1}$

$S_{el} = ?$

→ ELEKTRONSKI DOPRINOS MOLARNOJ ENTROPIJI

$$q_{el} = \sum_{i=0}^{1} g_i \cdot e^{-\beta \varepsilon_i} = g_0 \cdot e^{-\beta \varepsilon_0 \to 0} + g_1 e^{-\beta \varepsilon_1}$$

$$q_{el} = g_0 + g_1 e^{-\beta \varepsilon_1}$$

$$F = -kT \ln q_{el} = -kT \ln\left(g_0 + g_1 e^{-\beta \varepsilon_1}\right)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = k\cancel{T} \cdot \frac{g_1 e^{-\beta \varepsilon_1} \cdot \left(+\frac{\varepsilon_1}{k T^2}\right)}{g_0 + g_1 e^{-\beta \varepsilon_1}} + k \ln\left(g_0 + g_1 e^{-\beta \varepsilon_1}\right)$$

$$S = \frac{R \cdot \frac{\varepsilon_1}{kT}}{\frac{g_0}{g_1} e^{\beta \varepsilon_1} + 1} + R \ln\left(g_0 + g_1 e^{-\beta \varepsilon_1}\right)$$

↓ MOLARNA ENTROPIJA

$$S = 11{,}44\, \frac{J}{mol\, K}$$

5.26 $C_{v,m}$ i $C_{p,m}$ NA VISOKIM TEMPERATURAMA

$$\begin{pmatrix}\text{STEPENI}\\ \text{SLOBODE}\end{pmatrix} = \begin{pmatrix}\text{TRANSLACIONO}\\ \text{KRETANJE}\end{pmatrix} + \begin{pmatrix}\text{ROTACIONO}\\ \text{KRETANJE}\end{pmatrix} + \begin{pmatrix}\text{VIBRACIONO}\\ \text{KRETANJE}\end{pmatrix}$$

$C_{v,m}$

- Translaciono kretanje: $= \frac{3}{2}R$
- Rotaciono kretanje:
  - LINEARNI MOLEKULI $= \frac{2}{2}R$
  - NELINEARNI MOLEKULI $= \frac{3}{2}R$
- Vibraciono kretanje:
  - LINEARNI $(3N-5)R$
  - NELINEARNI $(3N-6)R$

$$\boxed{C_{p,m} - C_{v,m} = R}$$ → MAJEROVA RELACIJA $\Rightarrow C_{p,m} = C_{v,m} + R$

	$C_{v,m}$	$C_{p,m}$
Ar	$\frac{3}{2}R$	$\frac{5}{2}R$
O_2	$\frac{7}{2}R$	$\frac{9}{2}R$
H_2O	$6R$	$7R$
CO_2	$\frac{13}{2}R$	$\frac{15}{2}R$
CH_4	$12R$	$13R$

$Ar \Rightarrow C_{v,m} = \frac{3}{2}R \qquad C_{p,m} = \frac{3}{2}R + R = \frac{5}{2}R$

$O_2 \Rightarrow C_{v,m} = \frac{3}{2}R + \frac{2}{2}R + (3\cdot 2 - 5)R = \frac{7}{2}R \qquad C_{p,m} = \frac{7}{2}R + R = \frac{9}{2}R$

$H_2O \Rightarrow C_{v,m} = \frac{3}{2}R + \frac{3}{2}R + (3\cdot 3 - 6)R = 6R \qquad C_{p,m} = 7R$

$CO_2 \Rightarrow C_{v,m} = \frac{3}{2}R + \frac{2}{2}R + (3\cdot 3 - 5)R = \frac{13R}{2} \qquad C_{p,m} = \frac{15}{2}R$

$CH_4 \Rightarrow C_{v,m} = \frac{3}{2}R + \frac{3}{2}R + (3\cdot 5 - 6)R = 12R \qquad C_{p,m} = 13R$

→ KONSTANTA RAVNOTEŽE HEMIJSKE REAKCIJE IDEALNIH GASOVA:

→ OPŠTA HEM. R-JA: $\alpha_1 A_1 + \alpha_2 A_2 + \ldots \rightleftarrows \beta_1 B_1 + \beta_2 B_2 + \ldots$

→ TREBA DA NAĐEMO USLOV TD RAVNOTEŽE ⇒ KORISTIĆEMO FORMALIZAM KANONSKOG ANSAMBLA

↳ TREBA DA MINIMIZUJEMO HEMHOLCOVU SLOBODNU ENERGIJU

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

→ SADA MOŽEMO DA ISKORISTIMO NEKI REDUKOVANI BROJ ČESTICA:

$$\frac{dN_{A_1}}{\nu_{\alpha_1}} = \frac{dN_{A_2}}{\nu_{\alpha_2}} = \ldots = \frac{dN_{B_1}}{\nu_{\beta_1}} = \frac{dN_{B_2}}{\nu_{\beta_2}} = \ldots = d\tilde{N} \Rightarrow \boxed{dN_i = \nu_i\, d\tilde{N}}$$

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

$$\boxed{\left(\frac{\partial F}{\partial \tilde{N}}\right)_{T,V} = \sum_i \mu_i \nu_i = 0}$$ → USLOV TERMODINAMIČKE RAVNOTEŽE

$$Q = \frac{q_{A_1}^{N_{A_1}}}{N_{A_1}!} \cdot \frac{q_{A_2}^{N_{A_2}}}{N_{A_2}!} \cdot \ldots \cdot \frac{q_{B_1}^{N_{B_1}}}{N_{B_1}!} \cdot \frac{q_{B_2}^{N_{B_2}}}{N_{B_2}!} \cdot \ldots = \prod_i \frac{q_i^{N_i}}{N_i!}$$

$$\ln Q = \sum_i \ln\left(\frac{q_i^{N_i}}{N_i!}\right) = \sum_i \left(N_i \ln q_i - N_i \ln N_i + N_i\right) = \sum_i \left(N_i \ln \frac{q_i}{N_i} + N_i\right)$$

$$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{V,T,N_{j\neq i}} = \frac{\partial}{\partial N_i}\left[-kT\ln Q\right]_{V,T,N_{j\neq i}} = -kT\left[\ln\frac{q_i}{N_i} + \cancel{N_i} \cdot \frac{-\cancel{\frac{q_i}{N_i^2}}}{\cancel{\frac{q_i}{N_i}}} + 1\right]$$

$$\mu_i = -kT\ln\frac{q_i}{N_i}$$

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

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

$$\prod_i \left(\frac{q_i}{N_i}\right)^{\nu_i} = 1 \Rightarrow \boxed{K_N = \prod_i N_i^{\nu_i} = \prod_i q_i^{\nu_i}}$$ → KONSTANTA RAVNOTEŽE HEMIJSKE REAKCIJE

→ POŠTO IZUČAVAMO IDEALNE GASOVE, ČESTO ĆEMO TRAŽITI K_p UMESTO K_N

PARCIJALNI PRITISAK PRODUKTA B_1

$$K_p = \frac{\left(\frac{p_{B_1}}{p^\ominus}\right)^{\beta_1} \cdot \left(\frac{p_{B_2}}{p^\ominus}\right)^{\beta_2} \cdot \ldots}{\left(\frac{p_{A_1}}{p^\ominus}\right)^{\alpha_1} \cdot \left(\frac{p_{A_2}}{p^\ominus}\right)^{\alpha_2} \cdot \ldots} = \left(\frac{1}{p^\ominus}\right)^{\sum_i \nu_i} \prod_i p_i^{\nu_i}$$

STANDARDNI PRITISAK

$$K_p = \left(\frac{1}{p^0}\right)^{\sum_i \nu_i} \prod_i p_i^{\nu_i}$$ IDEALAN GAS: $p_i = \frac{N_i kT}{V}$

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

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

$$q_{el} \cdot q_{VIB} = \left(\sum_i g_i e^{-\beta \varepsilon_i}\right)\left(\prod_{i=1}^{f} \frac{e^{-\frac{1}{2}\beta \omega_i \hbar}}{1-e^{-\beta \omega_i \hbar}}\right) = e^{\beta D_0}(g_0 + g_1 e^{-\beta \varepsilon_1} + \ldots) \prod_{i=1}^{f} \frac{1}{1-e^{-\beta \omega_i \hbar}} =$$

$$= q_{el}^0 \, q_{VIB}^0 \, e^{\beta D_0}$$ D_0 → PRAVA ENERGIJA DISOCIJACIJE

$$q = q_{tr} \cdot q_{rot} \cdot q_{VIB} \cdot q_{EL} \cdot q_{NOC} = q_{tr} \cdot q_{rot} \cdot q_{VIB} \cdot q_{el}^0 \cdot e^{\beta D_0} q_{NOC} = q^0 e^{\beta D_0}$$

$$\boxed{K_N = \prod_i q_i^{\nu_i} = \left(\prod_i q_i^{0\,\nu_i}\right) e^{\beta \sum_i \nu_i D_{0,i}}}$$

$\left(\prod_i q_i^{0\,\nu_i}\right)$ → ENTROPIJSKI ČLAN

$e^{\beta \sum_i \nu_i D_{0,i}}$ → ENERGIJSKI ČLAN

→ REFERENTNI ENERGETSKI NIVOI BI TREBALO DA BUDU ISTI ZA SVE HEMIJSKE VRSTE.

→ ZADACI:

5.27 $T = 1000\,K$ $M(Br) = 79{,}904\,\frac{g}{mol}$ $p^0 = 10^5\,Pa$

$\tilde{\nu}_{Br_2} = 322\,cm^{-1}$

$B_{Br_2} = 0{,}081\,cm^{-1}$

$D_{0,Br_2} = 1{,}97\,eV$

$g_{0,Br} = 4$

$g_{0,Br_2} = 1$

$K_p = ?$

$$Br_{2(g)} \rightleftarrows 2Br_{(g)}$$

$$q_{Br} = q_{tr} \cdot q_{el} \cdot q_{noc}^{\,\,"1"} \qquad q_{Br_2} = q_{tr} \cdot q_{rot} \cdot q_{vib} \cdot q_{el} \cdot q_{not}^{\,\,"1"}$$

$$K_p = \left(\frac{kT}{p^0 V}\right)^{\sum_i \nu_i} \prod_i q_i^{\nu_i} = \left(\frac{kT}{p^0 V}\right)^{2-1} \cdot \frac{q_{Br}^2}{q_{Br_2}}$$

$$K_p(T) = \frac{kT}{p^0 V}\,\frac{\left[V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \cdot g_{0,Br}\right]^2 \cdot q_{noc}^{2} \overset{\approx}{\ } 1}{V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \cdot \frac{kT}{\underset{\overset{\shortparallel}{2}}{\sigma} B_{Br_2} hc} \cdot \frac{1}{1-e^{-\beta hc \tilde{\nu}_{Br_2}}} \cdot g_{0,Br_2}\, e^{\beta D_{0,Br_2}} \cdot \underset{\approx 1}{q_{noc}}}$$

5.28 $T = 1000\,K$ $\quad M(K) = 39{,}0983\,\frac{g}{mol}$ $\quad p^0 = 10^5\,Pa$

$\tilde{\nu}_{K_2} = 92{,}3\,cm^{-1}$

$B_{K_2} = 0{,}561\,cm^{-1}$ $\qquad K_{2(g)} \rightleftarrows 2K_{(g)}$

$D_0 = 0{,}51\,eV$

$g_{0,K} = 2$ $\qquad q_K = q_{tr} \cdot q_{el} \cdot \underset{\approx 1}{q_{noc}}$ $\qquad q_{K_2} = q_{tr} \cdot q_{rot} \cdot q_{vib} \cdot q_{el} \cdot \underset{\approx 1}{q_{noc}}$

$g_{0,K_2} = 1$ $\qquad \rightarrow$ ISTA FORMULA KAO U PROŠLOM ZADATKU

$K_p = ?$

5.29 $T = 298\,K$ $\quad \rightarrow$ IZOTOPSKA IZMENA:

$g_{0,I_2} = 1$

$$2\,{}^{125}I\,{}^{127}I_{(g)} \rightleftarrows {}^{125}I\,{}^{125}I_{(g)} + {}^{127}I\,{}^{127}I_{(g)}$$

$K_p = ?$

$$q_{I_2} = q_{tr}\, q_{rot}\, q_{vib}\, q_{el}\, q_{noc}$$

$$K_p = \underbrace{\left(\frac{kT}{p^0 V}\right)^{\sum_i \nu_i}}_{=1} \prod_i q_i^{\nu_i} = q_{125-125} \cdot q_{127-127} \cdot q_{125-127}^{-2}$$

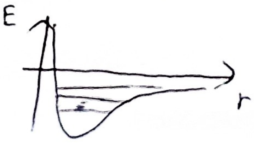
$$K_p = \left[V\left(\frac{2\pi m_{125-125} kT}{h^2}\right)^{\frac{3}{2}} \cdot \frac{kT}{\sigma_{125-125} B_{125-125} hc} \cdot \frac{1}{1-e^{-\beta hc \tilde{\nu}_{125-125}}} \cdot g_{0,125-125} \cdot e^{\beta D_{0,125-125}} \cdot g^{noc}_{0,125-125}\right] \cdot$$

$$\cdot \left[V\left(\frac{2\pi m_{127-127} kT}{h^2}\right)^{\frac{3}{2}} \cdot \frac{kT}{\sigma_{127-127} B_{127-127} hc} \cdot \frac{1}{1-e^{-\beta hc \tilde{\nu}_{127-127}}} \cdot g_{0,127-127}\, e^{\beta D_{0,127-127}} \cdot g^{noc}_{0,127-127}\right] \cdot$$

$$\cdot \left[V\left(\frac{2\pi m_{125-127} kT}{h^2}\right)^{\frac{3}{2}} \cdot \frac{kT}{\sigma_{125-127} B_{125-127} hc} \cdot \frac{1}{1-e^{-\beta hc \tilde{\nu}_{125-127}}} \cdot g_{0,125-127}\, e^{\beta D_{0,125-127}} \cdot g^{noc}_{0,125-127}\right]^{-2}$$

$$\left.\begin{aligned} &B_{125-125} \approx B_{127-127} \approx B_{125-127} \\ &\tilde{\nu}_{125-125} \approx \tilde{\nu}_{127-127} \approx \tilde{\nu}_{125-127} \\ &D_{0,125-125} \approx D_{0,127-127} \approx D_{0,125-127} \end{aligned}\right\}$$

– SLIČNE POTENCIJALNE KRIVE



MASA JE VRLO SLIČNA

$$K_p = \underbrace{m_{125-125}^{\frac{3}{2}} \cdot m_{127-127}^{\frac{3}{2}} \cdot m_{125-127}^{3}}_{\approx 1} \cdot \underbrace{\underset{\overset{\|}{2}}{\sigma_{125-125}^{-1}} \cdot \underset{\overset{\|}{2}}{\sigma_{127-127}^{-1}} \cdot \underset{\overset{\|}{1^2=1}}{\sigma_{125-127}^{2}}}_{\frac{1}{4}} \cdot \underbrace{q_{0,125-125}^{noc} \cdot q_{0,127-127}^{noc} \cdot \left(q_{0,125-127}^{noc}\right)^{-2}}_{\overset{\|}{1}}$$

JAKO SLIČNE MASE

$$K_p \approx \frac{1}{4} = 0{,}25$$

5.30 $T = 298\,K$ $\quad M(H) = 1{,}008\ \frac{g}{mol}$ $\quad M(O) = 15{,}999\ \frac{g}{mol}$ $\quad M(Cl) = 35{,}45\ \frac{g}{mol}$ $\quad M(D) = 2{,}014\ \frac{g}{mol}$

$\tilde{\nu}_{H_2O}^{1} = 3\,656{,}7\ cm^{-1}$ $\quad \tilde{\nu}_{HDO}^{1} = 2\,726{,}7\ cm^{-1}$ $\quad \tilde{\nu}_{HCl} = 2\,991\ cm^{-1}$

$\tilde{\nu}_{H_2O}^{2} = 1\,594{,}8\ cm^{-1}$ $\quad \tilde{\nu}_{HDO}^{2} = 1\,402{,}2\ cm^{-1}$ $\quad \tilde{\nu}_{DCl} = 2\,145\ cm^{-1}$

$\tilde{\nu}_{H_2O}^{3} = 3\,755{,}8\ cm^{-1}$ $\quad \tilde{\nu}_{HDO}^{3} = 3\,707{,}5\ cm^{-1}$

$A_{H_2O} = 27{,}88\ cm^{-1}$ $\quad A_{HDO} = 23{,}38\ cm^{-1}$ $\quad B_{HCl} = 10{,}59\ cm^{-1}$

$B_{H_2O} = 14{,}51\ cm^{-1}$ $\quad B_{HDO} = 9{,}102\ cm^{-1}$ $\quad B_{DCl} = 5{,}449\ cm^{-1}$

$C_{H_2O} = 9{,}29\ cm^{-1}$ $\quad C_{HDO} = 6{,}417\ cm^{-1}$

→ IZOTOPSKA IZMENA:

$$H_2O_{(g)} + DCl_{(g)} \rightleftharpoons HCl_{(g)} + HDO_{(g)}$$

$$q_{H_2O} = q_{tr}^{H_2O} \cdot q_{rot}^{H_2O} \cdot q_{vib}^{H_2O} \cdot q_{el}^{H_2O} \cdot q_{noc}^{H_2O}$$

⋮

→ $q_{el}\, q_{noc}$ SLIČNO IZMEĐU H_2O i HDO, ODNOSNO HCl i DCl JER SU IM SLIČNE POTENCIJALNE POVRŠI

→ $q_{vib} \approx 1$ ZA SVE MOLEKULE i SVE NORMALNE MODOVE S OBZIROM DA JE 298K NEDOVOLJNO DA SE POBUDE VIŠA VIBRACIONA STANJA

$$\Theta_{vib}^{\tilde{\nu}_{HDO}^{2}} = \frac{hc\tilde{\nu}_{HDO}^{2}}{k} = 2017{,}5K >> 298K$$

→ SAMO DOPRINOS TRANSLACIJE i ROTACIJE:

$$K_p = K_N = \frac{\cancel{V}\left(\frac{2\pi m_{HCl} \cancel{kT}}{\cancel{h^2}}\right)^{\frac{3}{2}} \cdot \frac{\cancel{kT}}{\sigma_{HCl} \cdot B_{HCl}\cancel{hc}} \cdot \cancel{V}\left(\frac{2\pi m_{HDO}\, kT}{\cancel{h^2}}\right)^{\frac{3}{2}} \frac{\sqrt{\pi}}{\sigma_{HDO}} \left(\frac{kT}{\cancel{hc}}\right)^{\frac{3}{2}} \cdot \frac{1}{\left(A_{HDO} \cdot B_{HDO} \cdot C_{HDO}\right)^{\frac{1}{2}}}}{\cancel{V}\left(\frac{2\pi m_{DCl} \cancel{kT}}{\cancel{h^2}}\right)^{\frac{3}{2}} \cdot \frac{\cancel{kT}}{\sigma_{DCl} B_{DCl}\cancel{hc}} \cdot \cancel{V}\left(\frac{2\pi m_{H_2O} \cancel{kT}}{\cancel{h^2}}\right)^{\frac{3}{2}} \frac{\sqrt{\pi}}{\sigma_{H_2O}} \left(\frac{kT}{\cancel{hc}}\right)^{\frac{3}{2}} \cdot \frac{1}{\left(A_{H_2O} \cdot B_{H_2O} \cdot C_{H_2O}\right)^{\frac{1}{2}}}}$$

$$K_p = \left(\frac{m_{HCl}\, m_{HDO}}{m_{DCl}\, m_{H_2O}}\right)^{\frac{3}{2}} \cdot \frac{\sigma_{DCl}\, \sigma_{H_2O}}{\sigma_{HCl}\, \sigma_{HDO}} \left(\frac{B_{DCl}^2 \cdot A_{H_2O}\, B_{H_2O}\, C_{H_2O}}{B_{HCl}^2 \cdot A_{HDO}\, B_{HDO}\, C_{HDO}}\right)^{\frac{1}{2}} =$$

$$= 1{,}041517718 \cdot 2 \cdot 0{,}35359518 \quad \Rightarrow K_p = 1{,}778069$$