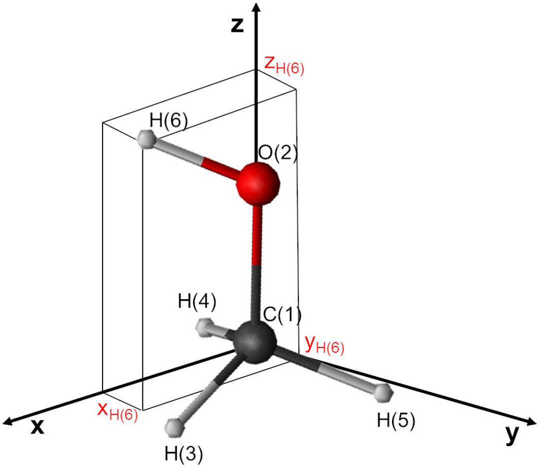
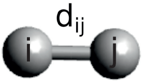
x

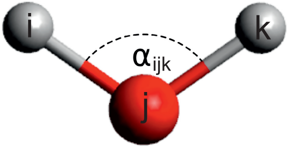
y

z

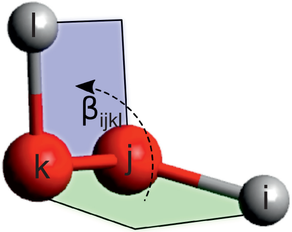

z
$z_{H(6)}$
H(6)
O(2)
H(4)
C(1)
$y_{H(6)}$
$x_{H(6)}$
x
H(5)
y
H(3)



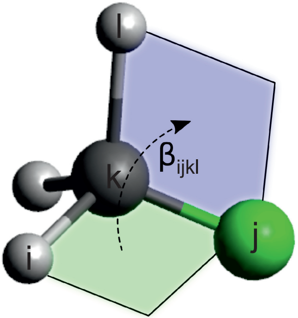
długość wiązania d_{ij}



kąt walencyjny α_{ijk}



właściwy kąt torsyjny β_{ijkl}



niewłaściwy kąt torsyjny β_{ijkl}

$\mathring{A}$

10^{-10}

$180°$

j

k

l

360°

$-180°$

$0°$

$\pm 180°$

$ijkl$

$$\beta = 180^\circ$$

$$\beta = -180^\circ$$

$$d_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$$

x_i

y_i

z_i

x_j

y_j

z_j

$$\cos \alpha_{ijk} = \frac{(x_i - x_j)(x_k - x_j) + (y_i - y_j)(y_k - y_j) + (z_i - z_j)(z_k - z_j)}{d_{ij} d_{jk}}$$

$$\cos \alpha_{ijk} = \frac{\overrightarrow{ji} \circ \overrightarrow{jk}}{|\overrightarrow{ji}||\overrightarrow{jk}|} = \frac{\overrightarrow{ji} \circ \overrightarrow{jk}}{d_{ij} d_{jk}}$$

$$|\overrightarrow{ji}|$$

$$|\overrightarrow{jk}|$$

○

a

b

$$\mathbf{a} \circ \mathbf{b} = a_x b_x + a_y b_y + a_z b_z$$

$$j - k$$

$$\overrightarrow{ji}$$

$$\overrightarrow{kl}$$

$$\cos \beta_{ijkl} = \frac{\frac{\overrightarrow{ji} \circ \overrightarrow{kl}}{d_{ij} d_{kl}} + \cos \alpha_{ijk} \cos \alpha_{jkl}}{\sin \alpha_{ijk} \sin \alpha_{jkl}}$$

$$\sin\beta_{ijkl} = \frac{(\overrightarrow{ji} \times \overrightarrow{kl}) \circ \overrightarrow{jk}}{d_{ij} d_{jk} d_{kl} \sin\alpha_{ijk} \sin\alpha_{jkl}}$$

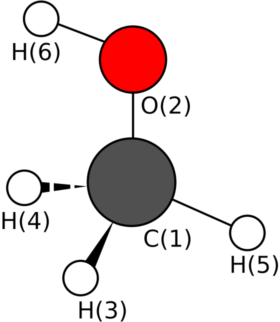
$$\mathbf{a} \times \mathbf{b} = \begin{pmatrix} a_y b_z - a_z b_y \\ -a_x b_z + a_z b_x \\ a_x b_y - a_y b_x \end{pmatrix}$$

$$\cos\beta_{ijkl} = \frac{\frac{\overrightarrow{ki}\circ\overrightarrow{kl}}{d_{kl}d_{ki}} - \cos\alpha_{ikj}\cos\alpha_{lkj}}{\sin\alpha_{ikj}\sin\alpha_{lkj}} = \frac{\cos\alpha_{ikl} - \cos\alpha_{ikj}\cos\alpha_{lkj}}{\sin\alpha_{ikj}\sin\alpha_{lkj}}$$

$$\sin \beta_{ijkl} = \frac{(\overrightarrow{ki} \times \overrightarrow{kl}) \circ \overrightarrow{jk}}{d_{ki} d_{kj} d_{kl} \sin \alpha_{ikj} \sin \alpha_{lkj}} = -\frac{(\overrightarrow{ki} \times \overrightarrow{kl}) \circ \overrightarrow{kj}}{d_{ki} d_{kj} d_{kl} \sin \alpha_{ikj} \sin \alpha_{lkj}}$$

$$xy$$

xz


H(6)
O(2)
H(4)
C(1)
H(5)
H(3)

d_{ij}

α_{ijk}

β_{ijkl}

$1,4$

$$i = 2$$

$$j = 1$$

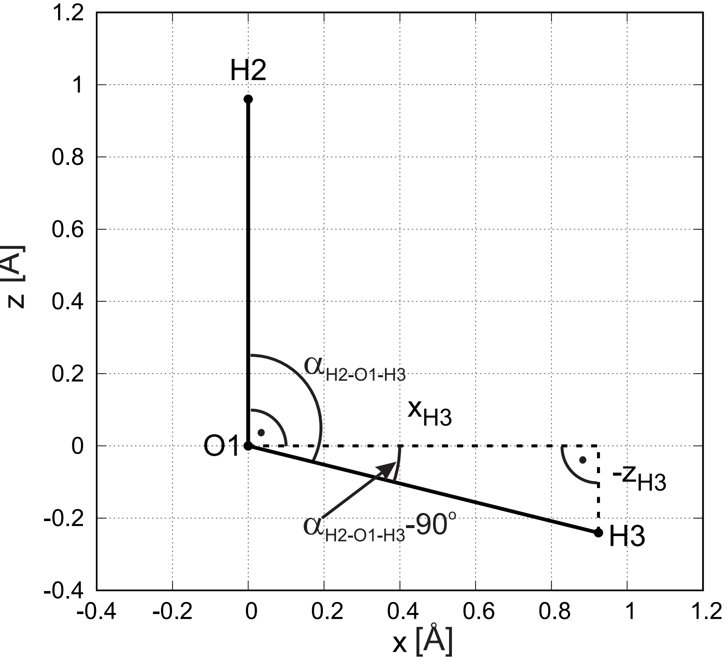
$$109,47^\circ$$

$$k = 2$$

• • •

$120, 0^{\circ}$

$$l = 3$$



H2
O1
H3
$\alpha_{H2\text{-}O1\text{-}H3}$
x_{H3}
$-z_{H3}$
$\alpha_{H2\text{-}O1\text{-}H3}$-90°
z [Å]
x [Å]
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1
1.2

$$d_{O1H2} = z_{H2} = 0,96 \text{ Å}$$

$$d_{O1H3} = \sqrt{x_{H3}^2 + (-z_{H3})^2} = \sqrt{0,924220^2 + 0,240365^2} = 0,955 \text{ Å}$$

$$d_{O1H3} = \sqrt{(x_{H3} - x_{O1})^2 + (y_{H3} - y_{O1})^2 + (z_{H3} - z_{O1})^2} =$$

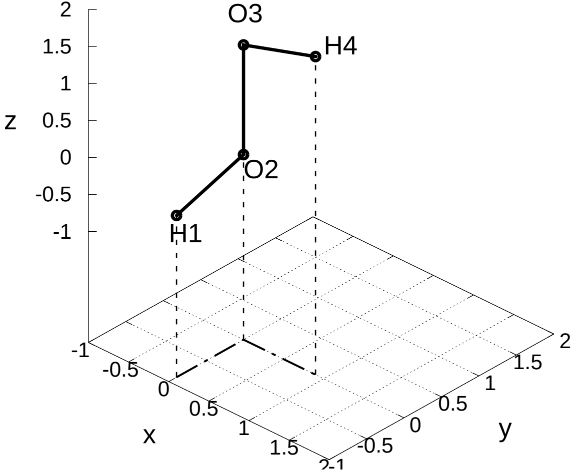
$$\sqrt{(0,92422-0)^2+(0-0)^2+(-0,240365-0)^2}=0,955\ \mathring{A}$$

$$\cos(\alpha_{H2O1H3} - 90^\circ) = \frac{x_{H3}}{d_{O1H3}} = \frac{0,924225}{0,955} = 0,9677749$$

$$\alpha_{H2O1H3} - 90^\circ = 14,58517 \;\Rightarrow\; \alpha_{H2O1H3} = 104,58^\circ$$

$$\cos\alpha_{H2O1H3} = \frac{(x_{H2}-x_{O1})(x_{H3}-x_{O1})+(y_{H2}-y_{O1})(y_{H3}-y_{O1})+(z_{H2}-z_{O1})(z_{H3}-z_{O1})}{d_{H2O1}d_{O1H3}} =$$

$$\frac{(0-0)(0,924220-0)+(0-0)(0-0)+(0,96-0)(-0,240365-0)}{0,96\times 0,955}=-0,2517\Rightarrow \alpha=104,5^{\circ}$$



O3
H4
O2
H1
z
x
y

$$d_{O2O3} = 1,48$$

$$d_{H1O2} = \sqrt{(0-0)^2 + (-0,895669-0)^2 + (-0,316667-0)^2} = 0,95\ \AA$$

$$d_{O2O3} = \sqrt{(0-0)^2 + (0-0)^2 + (1,48-0)^2} = 1,48\ \mathring{A}$$

$$d_{O3H4} = \sqrt{(0 - 0,895669)^2 + (0 - 0)^2 + (1,796667 - 1,48)^2} = 0,95\ \mathring{A}$$

$$\cos \alpha_{H1O2O3} = \frac{(0-0)(0-0)+(-0,895669-0)(0-0)+(-0,316667-0)(1,48-0)}{0,95 \times 1,48} =$$

$$-0,333334$$

$$\alpha_{H1O2O3} = 109,47^\circ$$

$$\cos\alpha_{H4O3O2} = \frac{(0,895669-0)(0-0)+(0-0)(0-0)+(1,796667-1,48)(0-1,48)}{0,95\times 1,48} =$$

$$\alpha_{H4O3O2} = 109,47^\circ$$

yz

90°

$$\cos\beta_{H1O2O3H4} = \frac{\frac{(x_{H1}-x_{O2})(x_{H4}-x_{O3})+(y_{H1}-y_{O2})(y_{H4}-y_{O3})+(z_{H1}-z_{O2})(z_{H4}-z_{O3})}{d_{H1O2}d_{O3H4}} - \cos\alpha_{H1O2O3}\cos\alpha_{O2O3H4}}{\sin\alpha_{H1O2O3}\sin\alpha_{O2O3H4}} =$$

$$\frac{\frac{0{,}895669\times 0+(-0{,}895669-0)\times 0+(-0{,}316667-0)(1{,}796667-1{,}48)}{0{,}95\times 0{,}95}+(-0,333334)(-0,333334)}{0,942809\times 0,942809}=0$$

$$\sin \alpha_{H1O2O3} = \sin \alpha_{O2O3H4} = \sqrt{1 - (-0,333334)^2} = 0,942809$$

$$\overrightarrow{O2H1} \times \overrightarrow{O3H4} = \begin{pmatrix} (y_{H1} - y_{O2})(z_{H4} - z_{O3}) - (z_{H1} - z_{O2})(y_{H4} - y_{O3}) \\ -(x_{H1} - x_{O2})(z_{H4} - z_{O3}) + (z_{H1} - z_{O2})(x_{H4} - x_{O3}) \\ (x_{H1} - x_{O2})(y_{H4} - y_{O3}) - (y_{H1} - y_{O2})(x_{H4} - x_{O3}) \end{pmatrix} =$$

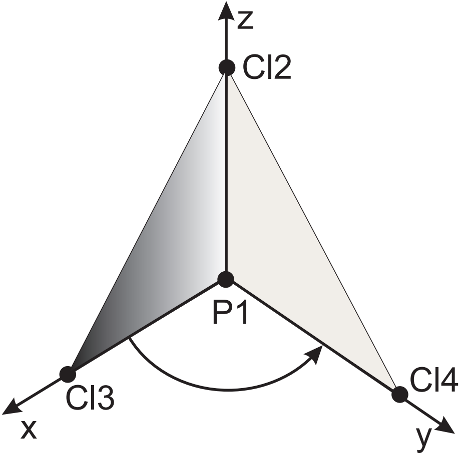
$$\begin{pmatrix} (-0,895669-0)(1,796667-1,48)-(-0,316667-0)(0-0) \\ -(0-0)(1,796667-1,48)+(-0,316667-0)(0,895669-0) \\ (0-0)(0-0)-(-0,895669-0)(0,895669-0) \end{pmatrix} = \begin{pmatrix} -0,283630 \\ -0,283630 \\ 0,802223 \end{pmatrix}$$

$$\sin\beta_{H1O2O3O4} = \frac{(\overrightarrow{O2H1} \times \overrightarrow{O3H4}) \circ \overrightarrow{O2O3}}{d_{H1O2}d_{O3O3}d_{O3H4}\sin\alpha_{H1O2O3}\sin\alpha_{O2O3O3}} =$$

$$\frac{(-0,283630 \times 0 - 0,283630 \times 0 + 0,802223 \times 1,48)}{0,95 \times 0,95 \times 1,48 \times 0,942809 \times 0,942809} = 1$$

$$\beta_{H1H2O3O4} = 90^\circ$$

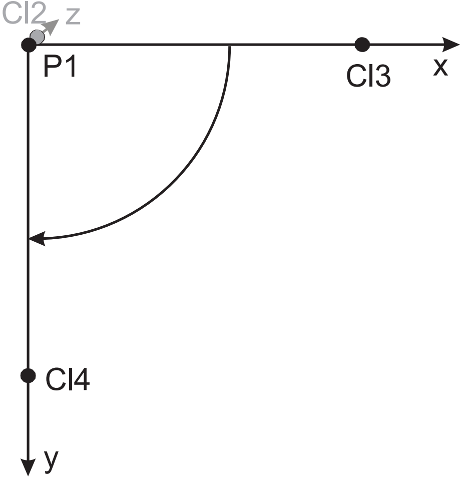
$$(\overrightarrow{O2H1} \times \overrightarrow{O3H4}) \circ \overrightarrow{O2O3}$$


z
Cl2
P1
Cl3
Cl4
x
y

$$d_{P1Cl2} = d_{P1Cl3} = d_{P1Cl4} = 2,02\ \mathring{A}$$

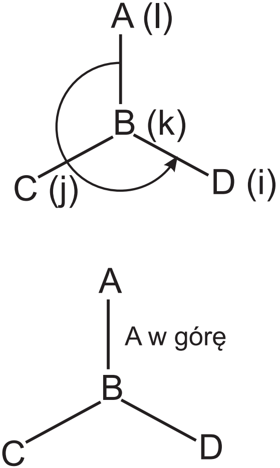
$$\alpha_{Cl2P1Cl3} = \alpha_{Cl2P1Cl4} = \alpha_{Cl3P1Cl4} = 90^\circ$$

$$\beta_{Cl4P1Cl3Cl2} = -90^\circ$$

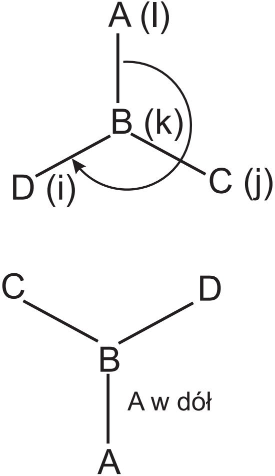

Cl2
z
P1
Cl3
x
Cl4
y

→

$\beta_{Cl4P1Cl2Cl3}$



$\beta_{ABCD}<0$
chiralność S
(A>C>D)



$\beta_{ABCD}>0$
chiralność R
(A>C>D)

$$\cos \alpha = 0$$

$$\sin \alpha = 1$$

$$\cos\beta_{Cl4P1Cl2Cl3} = \frac{\frac{2{,}02\times 0+0\times 2{,}02+0\times 0}{2{,}02\times 2{,}02} - 0\times 0}{1\times 1} = 0$$

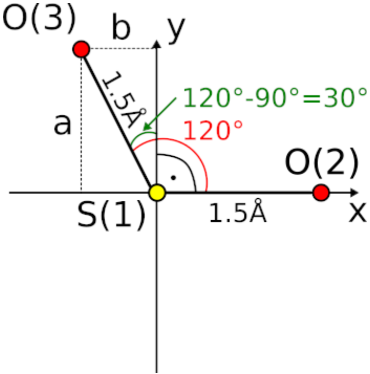
$$\overrightarrow{P1Cl3} \times \overrightarrow{P1Cl4} = \begin{pmatrix} 0 \times 0 - 2,02 \times 0 \\ -2,02 \times 0 + 0 \times 0 \\ 2,02 \times 2,02 - 0 \times 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 4,0804 \end{pmatrix}$$

$$(\overrightarrow{P1Cl3} \times \overrightarrow{P1Cl4}) \circ \overrightarrow{Cl2P1} = 0 \times 0 + 0 \times 0 + 4,0804 \times (-2,02) = -8,242408 < 0$$

$$\beta_{Cl2P1Cl3Cl4} = -90^\circ$$

$$2v$$

120°

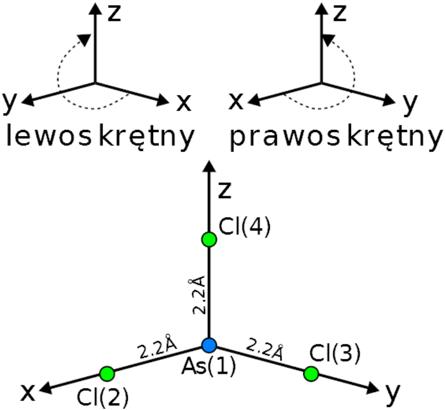

O(3)
b
y
1.5Å
120°-90°=30°
120°
a
O(2)
S(1)
1.5Å
x

2

$$-x_{O(3)} = b = 1,5 \sin 30^\circ = 1,5/2 = 0,75 \text{ Å}$$

$$y_{O(3)} = a = 1,5\cos 30^\circ = 1,5\sqrt{3}/2 = 1,299\ \text{Å}$$

$3v$


z
y
x
lewoskrętny
z
x
y
prawoskrętny
z
Cl(4)
2.2Å
2.2Å
2.2Å
Cl(3)
As(1)
x
Cl(2)
y

$$d_{H1N2} = 1,031$$

$$d_{N2N3} = 1,245$$

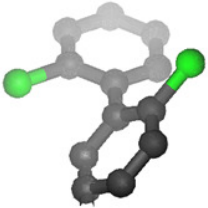
$$d_{N3Cl4} = 1,728$$

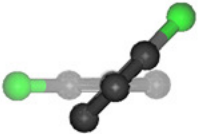
$$\alpha_{H1N2N3} = 120,8^{\circ}$$

$$\alpha_{N2N3Cl4} = 120,7°$$

$$\beta_{H1N2N3Cl4} = 0°$$

$2, 2'$



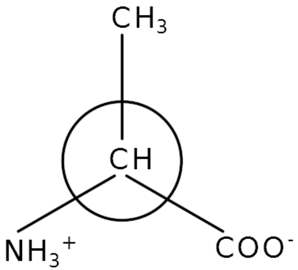


-135°

$3) \cdots$

3

$-120°$



$$\frac{+}{3} \cdots$$

—

2

$$x_{O2} = 1,3$$

$$x_{O3} = x_{O4} = -0,65$$

$$y_{O3} = -y_{O4} = 1,1258$$

$$f'(x) = \frac{\mathbf{d}f}{\mathbf{d}x} = \lim_{h \to 0} \frac{f(x+h) - f(x)}{h} = \lim_{\Delta x \to 0} \frac{\Delta f}{\Delta x}$$

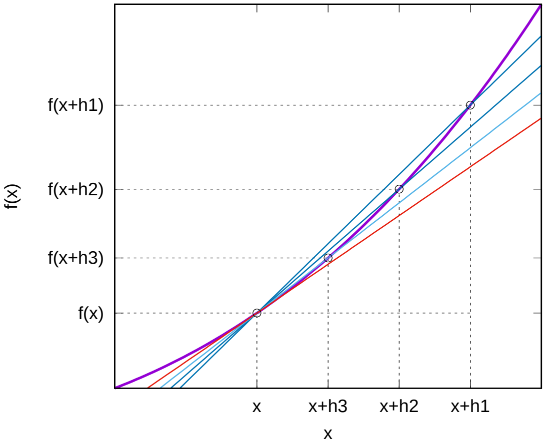
$$(x, f(x))$$

$$(x+h, f(x+h))$$

h

$$\overline{(x, x+h)}$$

$$\overline{(f(x), f(x+h))}$$


f(x+h1)
f(x+h2)
f(x+h3)
f(x)
f(x)
x
x+h3
x+h2
x+h1
x

$$[x]$$

$x > 0$

$$x = 0$$

$x < 0$

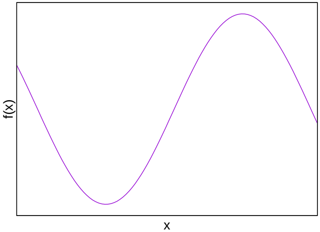
$$f(x) = |x|$$

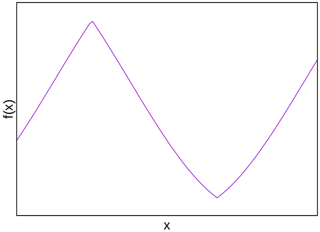
C^1

$$f(x+h) = f(x) + f'(x)h + \frac{1}{2}f''(x)h^2 + \frac{1}{3!}f'''(x)h^3 + \ldots + \frac{1}{n!}f^{(n)}(x)h^n + \ldots$$

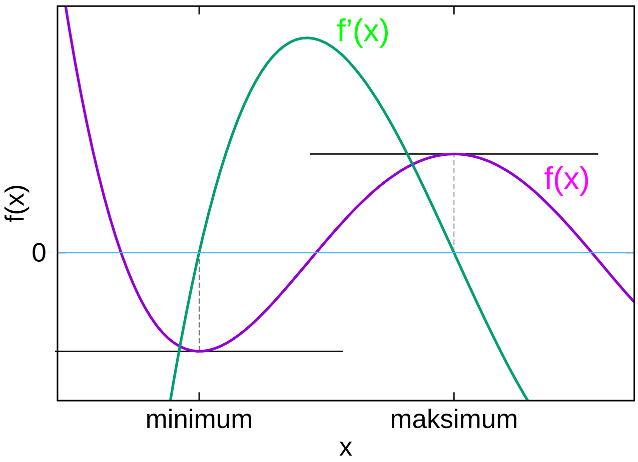
$$= \sum_{n=0}^{\infty} \frac{1}{n!} f^{(n)}(x) h^n$$

$$f^{(0)}(x)$$


f(x)
x


f(x)
x

$$f'(x) = 0$$


f'(x)
f(x)
f(x)
0
minimum
maksimum
x

$$x^*$$

$$f'(x^*) = 0$$

$$f(x) \approx f(x^*) + \frac{1}{2} f''(x^*)(x - x^*)^2$$

$$f''(x^*) > 0$$

$$f''(x^*) < 0$$

$$f'(x) = 0, \quad f''(x) > 0 : \quad \text{minimum}$$

$$f'(x) = 0, \quad f''(x) < 0 : \quad \text{maksimum}$$

$$f''(x^*) = 0$$

$f(x, y)$

$$(x, y, z)$$

$$f'$$

$$\frac{\mathrm{d}f}{\mathrm{d}x}$$

$$\frac{\mathrm{d}f}{\mathrm{d}y}$$

$$\frac{\partial f}{\partial x}$$

$$\frac{\partial f}{\partial y}$$

$$f(x, y) = x^2 + y - y^2$$

$$\frac{\partial f}{\partial x} = 2x$$

$$\frac{\partial f}{\partial y} = 1 - 2y$$

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right)$$

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)$$

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)$$

$$\frac{\partial^2 f}{\partial y^2} = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial y}\right)$$

$$\frac{\partial^2 f}{\partial y \partial x}$$

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

$$\nabla f$$

$$\mathbf{grad}\, f$$

n

$$x_1, x_2, \dots x_n$$

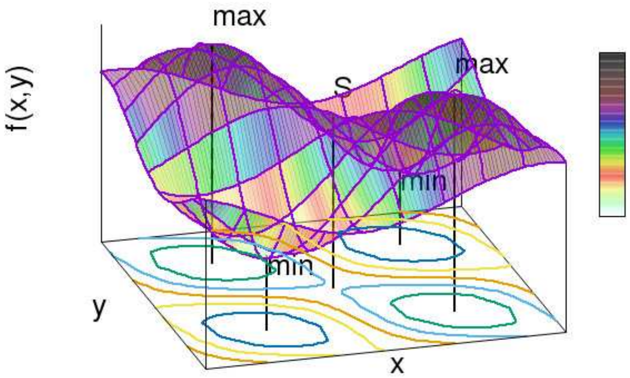
$$\nabla f = \mathbf{grad} f = \begin{pmatrix} \frac{\partial f}{\partial x_1} \\ \frac{\partial f}{\partial x_2} \\ \vdots \\ \frac{\partial f}{\partial x_n} \end{pmatrix}$$

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 f}{\partial x_1^2} & \frac{\partial^2 f}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_1 \partial x_n} \\ \frac{\partial^2 f}{\partial x_2 \partial x_1} & \frac{\partial^2 f}{\partial x_2^2} & \cdots & \frac{\partial^2 f}{\partial x_2 \partial x_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 f}{\partial x_n \partial x_1} & \frac{\partial^2 f}{\partial x_n \partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_n^2} \end{pmatrix}$$

m

$$1 \leq m < n$$

$$n - m$$



max
max
S
min
min
f(x,y)
y
x

$$\frac{\partial f(x_1^*, x_2^*, \ldots x_n^*)}{\partial x_1} = 0, \ \ \frac{\partial f(x_1^*, x_2^*, \ldots x_n^*)}{\partial x_2} = 0, \ldots, \frac{\partial f(x_1^*, x_2^*, \ldots x_n^*)}{\partial x_n} = 0$$

$$(x^*, y^*)$$

$$f(x,y) \approx f(x^*,y^*) + \frac{1}{2}\left[\frac{\partial f(x^*,y^*)}{\partial x^2}(x-x^*)^2 + 2\frac{\partial f(x^*,y^*)}{\partial x \partial y}(x-x^*)(y-y^*)+\right.$$

$$\frac{\partial f(x^*, y^*)}{\partial y^2}(y - y^*)^2\Bigg] = f(x,^*, y^*) + \frac{1}{2}(x - x^*, y - y^*)\mathbf{H}\begin{pmatrix} x - x^* \\ y - y^* \end{pmatrix}$$

$$\mathbf{z}^T \mathbf{H} \mathbf{z}$$

Z

H

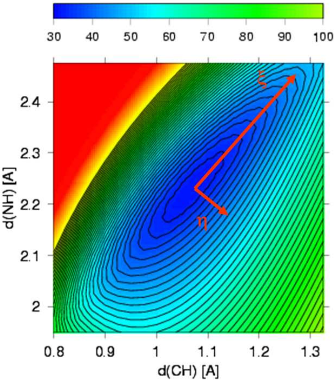
ξ

η

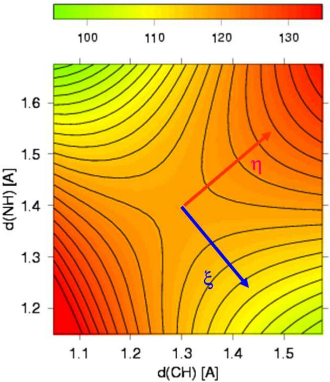
$$f(\xi, \eta) = f(0,0) + \frac{1}{2}\left[\frac{\partial^2 f(0,0)}{\partial \xi^2}\xi^2 + \frac{\partial^2 f(0,0)}{\partial \eta^2}\eta^2\right]$$

ξ, η

Energia [kcal/mol]



Okolice minimum odpowiadającego cząsteczce HCN



Okolice stanu przejściowego

$$\mathbf{V}^T\mathbf{H}\mathbf{V} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$$

V

$$\mathbf{v_1} \circ \mathbf{v_1} = v_{11}^2 + v_{21}^2 = 1$$

$$\mathbf{v_1} \circ \mathbf{v_2} = v_{11}v_{12} + v_{21}v_{22} = 0$$

$$\mathbf{v_2} \circ \mathbf{v_2} = v_{12}^2 + v_{22}^2 = 1$$

$$\mathbf{V} = \begin{pmatrix} \xi_x & \eta_x \\ \xi_y & \eta_y \end{pmatrix}$$

$$\lambda_1 = \frac{\partial^2 f}{\partial \xi^2}, \ \ \lambda_2 = \frac{\partial^2 f}{\partial \eta^2}$$

$$\det(\mathbf{H}-\lambda\mathbf{I}) = \begin{vmatrix} \frac{\partial^2 f}{\partial x_1^2}-\lambda & \frac{\partial^2 f}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_1 \partial x_n} \\ \frac{\partial^2 f}{\partial x_2 \partial x_1} & \frac{\partial^2 f}{\partial x_2^2}-\lambda & \cdots & \frac{\partial^2 f}{\partial x_2 \partial x_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 f}{\partial x_n \partial x_1} & \frac{\partial^2 f}{\partial x_n \partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_n^2}-\lambda \end{vmatrix} = 0$$

I

$$\mathbf{I} = \begin{pmatrix} 1 & 0 & \ldots & 0 \\ 0 & 1 & \ldots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \ldots & 1 \end{pmatrix}$$

$$\lambda_1 > 0, \lambda_2 > 0, \ldots \lambda_n > 0$$

$$\lambda_1 < 0, \lambda_2 > 0, \dots \lambda_n > 0$$

$m > 1$

$$\lambda_1 < 0, \lambda_2 < 0, \ldots \lambda_m < 0$$

$$\lambda_{m+1} > 0 \ldots \lambda_n > 0$$

$$\lambda_1 < 0, \lambda_2 < 0, \ldots \lambda_n < 0$$

$n > 1$

$n = 1$

d

$$E(d) = 815(d - 1,09\ \text{Å})^2$$

$$E'(d) = (815d^2 - 2 \times 815 \times 1,09d - 815 \times 1,09^2)'$$

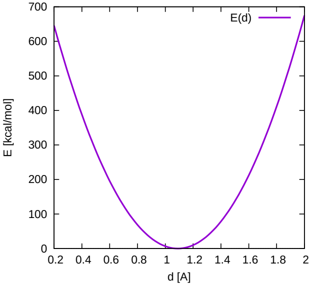
$$= 2 \times 815d - 2 \times 815 \times 1,09 = 2 \times 815(d - 1,09)$$

$$E(g(d)) = 815g(d)^2, g(d) = d - 1,09$$

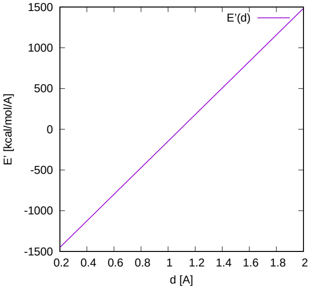
$$E'(g(d)) = E'(g)g'(d) = 2 \times 815(g(d)) \times 1 = 2 \times 815(d - 1,09)$$

$$E'(d^*) = 2 \times 815(d^* - 1,09) = 0 \Rightarrow d^* = 1,09$$

$$E''(d^*) = (2 \times 815(d^* - 1,09))' = 2 \times 815 > 0$$



E(d)
E [kcal/mol]
d [A]
700
600
500
400
300
200
100
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2



E'(d)
E' [kcal/mol/A]
d [A]
1500
1000
500
0
-500
-1000
-1500
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2

$$A - H \cdots A \rightleftharpoons A \cdots H - A$$

$$E(x) = a(x^2 - b^2)^2 - c$$

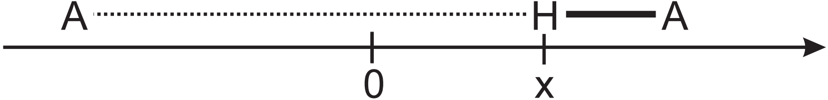
a

b

c

$$a > 0$$

$b \geq 0$


A
H
A
0
x

$$E'(x) = 2a(x^2 - b^2) \times 2x = 0$$

$$x^2 - b^2 = 0 \text{ lub } x = 0$$

$$x_1 = -b,\ x_2 = 0,\ x_3 = b$$

x_1

x_2

x_3

$$E''(x) = 2a \times 2x \times 2x + 2a(x^2 - b^2) \times 2 = 4a(3x^2 - b^2)$$

$$E''(-b) = 4a(3(-b)^2 - b^2) = 8ab^2 > 0 \ (a > 0)$$

$$E''(0) = 4a(0 - b^2) = -4ab^2 < 0$$

$$E''(b) = 4a(3b^2 - b^2) = 8ab^2 > 0$$

$$E(x_1) = E(x_3) = -c$$

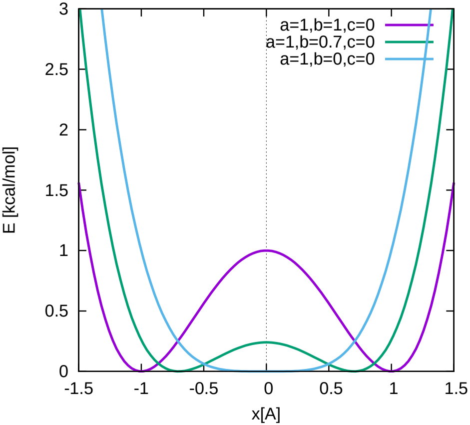
$$E(x_2) = ab^4 - c$$

$$\Delta E^* = E(x_2) - E(x_1) = E(x_3) - E(x_1) = ab^4$$

$$b = 0$$

$$a = 1$$

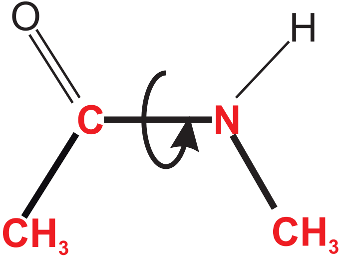
$$c = 0$$



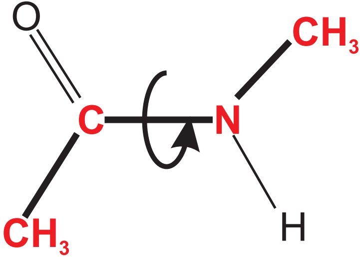
a=1,b=1,c=0
a=1,b=0.7,c=0
a=1,b=0,c=0
E [kcal/mol]
x[A]
3
2.5
2
1.5
1
0.5
0
-1.5
-1
-0.5
0
0.5
1
1.5

ω

$$[-\pi, \pi]$$



$\omega=0$



$\omega=\pi\ (180^\circ)$

$$E(\omega) = 1,2[1 + \cos\omega] + 10[1 - \cos(2\omega)]$$

$$E'(\omega) = -1,2 \sin \omega + 2 \times 10 \sin(2\omega)$$

$$= -1,2\sin\omega + 20\sin(2\omega) = \sin\omega(40\cos\omega - 1,2)$$

$$\sin(2\omega) = 2\sin\omega\cos\omega$$

$$\sin \omega = 0$$

$$\cos\omega = 1,2/40 = 0,03$$

$[-180°, 180°]$

$\omega_1 = -\pi\ (-180^\circ),\ \omega_2 = -1,5408\ (-88,28^\circ), \omega_3 = 0,\ \omega_4 = 1,5408\ (88,28^\circ),\ \omega_5 = \pi\ (180^\circ)$

$$E''(\omega) = -1{,}2\cos\omega + 2 \times 20\cos(2\omega)$$

$$= -1,2\cos\omega + 40(2\cos^2\omega - 1)$$

$$\cos(2\omega) = 2\cos^2\omega - 1$$

$$E''(-\pi) = E''(\pi) = -1,2(-1) + 40(2 \times (-1)^2 - 1) = 41,2 \;\Rightarrow\; \text{minimum}$$

$$E''(-1,5408) = E''(1,5408) = -1,2 \times 0,03 + 40(2 \times 0,03^2 - 1) =$$

$$-39,964 < 0 \ \Rightarrow \ \text{maksimum}$$

$$E''(0) = -1,2 + 40(2-1) = 38,8 > 0 \;\Rightarrow\; \text{minimum}$$

$$\cos \omega_2 = \cos \omega_4 = 0,03$$

$$\omega = 0$$

$$\omega = \pi \ (180^\circ)$$

$$\Delta E = E(0) - E(\pi) = 2,4$$

$$\Delta E^* = E(1,5408) - E(0) = 20,018$$

$$\cos(2\omega)$$

$\omega[^\circ]$

-180

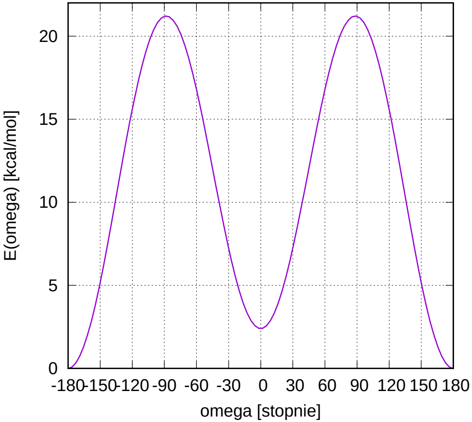
$-88, 28$

88, 28

$$E(\omega)$$

$20,018$

$2, 4$


E(omega) [kcal/mol]
0
5
10
15
20
-180
-150
-120
-90
-60
-30
0
30
60
90
120
150
180
omega [stopnie]

A

B

$$x = d_{\mathrm{A}\cdots\mathrm{H}}$$

$$y = d_{\mathrm{B} \cdots \mathrm{H}}$$

$$E(x, y) = 2(x - y)^2 - (x + y - 3)^2$$

$$\frac{\partial E}{\partial x} = 2 \times 2(x - y) - 2(x + y - 3) = 2x - 6y + 6$$

$$\frac{\partial E}{\partial y} = -2 \times 2(x-y) - 2(x+y-3) = -6x + 2y + 6$$

$$2x - 6y = -6$$

$$-6x + 2y = -6$$

$$x^* = 1,5$$

$$y^* = 1,5$$

$$\frac{\partial^2 E}{\partial x^2} = \frac{\partial(2x - 6y + 6)}{\partial x} = 2$$

$$\frac{\partial^2 E}{\partial y \partial x} = \frac{\partial(2x - 6y + 6)}{\partial y} = -6$$

$$\frac{\partial^2 E}{\partial x \partial y} = \frac{\partial(-6x + 2y + 6)}{\partial x} = -6$$

$$\frac{\partial^2 E}{\partial y^2} = \frac{\partial(-6x + 2y + 6)}{\partial y} = 2$$

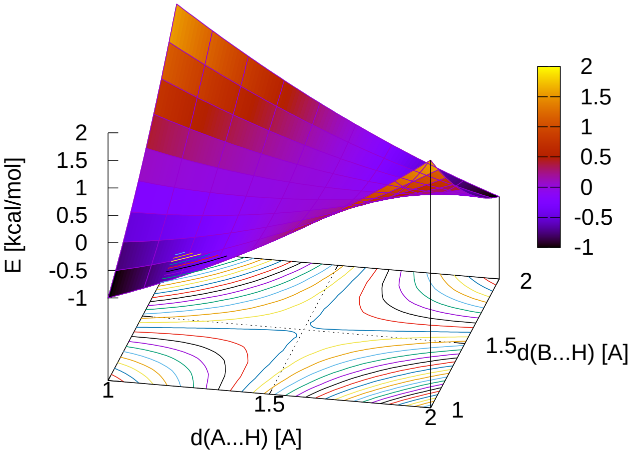
$$\det(\mathbf{H} - \lambda\mathbf{I}) = \begin{vmatrix} 2-\lambda & 6 \\ 6 & 2-\lambda \end{vmatrix} = 0$$

λ

$$(2-\lambda)^2 - 36 = 0 \;\Rightarrow\; 2-\lambda = \pm 6$$

$$\lambda_1 = -4$$

$$\lambda_2 = 8$$



E [kcal/mol]
2
1.5
1
0.5
0
-0.5
-1
d(A...H) [A]
1
1.5
2
d(B...H) [A]
1
1.5
2
2
1.5
1
0.5
0
-0.5
-1

*

τ_1

τ_2

$$E(\tau_1, \tau_2) = \cos(\tau_1 + \tau_2) - \cos(\tau_1 - \tau_2)$$

$$\frac{\partial E}{\partial \tau_1} = -\sin(\tau_1 + \tau_2) + \sin(\tau_1 - \tau_2) = 0$$

$$\frac{\partial E}{\partial \tau_2} = -\sin(\tau_1 + \tau_2) - \sin(\tau_1 - \tau_2) = 0$$

$$-2\sin(\tau_1+\tau_2)=0 \ \Rightarrow\ \tau_1+\tau_2=k\pi, k\in C$$

$$2\sin(\tau_1 - \tau_2) = 0 \ \Rightarrow \ \tau_1 - \tau_2 = m\pi, m \in C$$

$$\tau_1 = \frac{k+m}{2}$$

$$\tau_2 = \frac{k - m}{2}$$

$\pi\ (180^\circ)$

$\pi/2\ (90^\circ)$

$$\tau_1 = \pi$$

$$\tau_2 = \pi/2$$

$(\pi/2, \pi/2)$

$$(\pi/2, -\pi/2)$$

$$(0, 0)$$

$-\pi$

$-\pi/2$

$\pi/2$

π

$$\frac{\partial^2 E}{\partial \tau_1^2} = -\cos(\tau_1 + \tau_2) + \cos(\tau_1 - \tau_2) \qquad \frac{\partial^2 E}{\partial \tau_2 \partial \tau_1} = -\cos(\tau_1 + \tau_2) - \cos(\tau_1 - \tau_2)$$

$$\frac{\partial^2 E}{\partial \tau_1 \partial \tau_2} = -\cos(\tau_1 + \tau_2) - \cos(\tau_1 - \tau_2) \qquad \frac{\partial^2 E}{\partial \tau_2^2} = -\cos(\tau_1 + \tau_2) + \cos(\tau_1 - \tau_2)$$

$$\tau_1 = \pi/2$$

$$\mathbf{H} = \begin{pmatrix} -\cos\pi + \cos 0 & -\cos\pi - \cos 0 \\ -\cos\pi - \cos 0 & -\cos\pi + \cos 0 \end{pmatrix} = \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$$

$(-\pi/2, \pi/2)$

$$\tau_2 = -\pi/2$$

$$\mathbf{H} = \begin{pmatrix} -\cos 0 + \cos \pi & -\cos 0 - \cos \pi \\ -\cos 0 - \cos \pi & -\cos 0 + \cos \pi \end{pmatrix} = \begin{pmatrix} -2 & 0 \\ 0 & -2 \end{pmatrix}$$

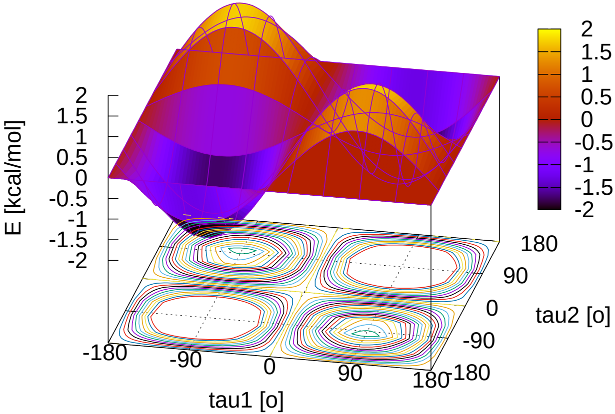
$(-\pi, \pi)$

$$\tau_1 = 0$$

$$\tau_2 = 0$$

$$\mathbf{H} = \begin{pmatrix} -\cos 0 + \cos 0 & -\cos 0 - \cos 0 \\ -\cos 0 - \cos 0 & -\cos 0 + \cos 0 \end{pmatrix} = \begin{pmatrix} 0 & -2 \\ -2 & 0 \end{pmatrix}$$

$$\det(\mathbf{H} - \lambda\mathbf{I}) = \begin{vmatrix} -\lambda & -2 \\ -2 & -\lambda \end{vmatrix} \;\Rightarrow\; \lambda^2 = 4,\; \lambda_1 = -2,\; \lambda_2 = 2$$



E [kcal/mol]
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
tau1 [o]
-180
-90
0
90
180
tau2 [o]
-180
-90
0
90
180
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2

λ_1

λ_2

λ_3

$$\Delta E = E_2 - E_1 = -260 - (-210) = -50$$

$$\Delta E^* = -200 - (-210) = 10$$

α

$$E(\alpha) = 47(\alpha - 104,5)^2$$

$$\alpha^* = 104,5^\circ$$

r^*

$$E(r) = 0,02 \left[\left(\frac{2,3}{r} \right)^{12} - 2 \left(\frac{2,3}{r} \right)^{6} \right]$$

$$r^* = 2, 3$$

$$E^* = -0.02$$

C

D

$$E(r) = \frac{C}{r^{12}} - \frac{D}{r^{10}}$$

$$r^* = \sqrt{\frac{12C}{10D}}$$

*

$n > m$

r°

$$E(r) = \epsilon \left[\left(\frac{r^\circ}{r} \right)^n - k \left(\frac{r^\circ}{r} \right)^m \right]$$

$$k = n/m$$

$$E^* = -\epsilon$$

$\mathcal{T}$

$$E(\tau) = 3,5[1 + \cos(2\tau)]$$

$$\tau = \pm\pi/2$$

$$\tau = -\pi, 0, \pi$$

$$\Delta E^* = 7$$

$$E(\tau) = 1,3[1 + \cos(3\tau)]$$

$$\tau = -\pi, -\pi/3, \pi/3, \pi$$

$\tau = -2\pi/3, 0, 2\pi/3$

$$A \cdots H$$

$$B \cdots H$$

$$E(x, y) = 2(x - y)^2 + (x + y - 3)^2$$

$$(x^* = 1,5; y^* = 1,5)$$

(θ)

$$(\tau)$$

$$E(\theta, \tau) = 50(\theta - 120^\circ)^2 + 2,5[1 + \cos(2\tau)]$$

θ

$$[0^\circ, 180^\circ]$$

$$(\theta = 120^\circ, \tau = \pm 90^\circ)$$

$$(\theta = 120^\circ, \tau = -180^\circ, 0^\circ, 180^\circ)$$

E

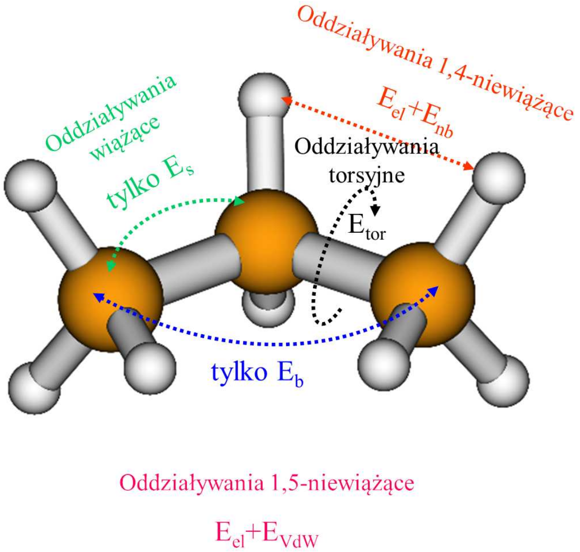
$\times$

$$E = 0, \lambda_1 = 10, \lambda_2 = 20, \lambda_3 = 30$$

$$E = 15, \lambda_1 = -5, \lambda_2 = -4, \lambda_3 = -4$$

$$E = 5, \lambda_1 = -5, \lambda_2 = 5, \lambda_3 = 10$$

$$E = -8, \lambda_1 = 10, \lambda_2 = 10, \lambda_3 = 20.$$



Oddziaływania 1,4-niewiążące
$E_{el}+E_{nb}$
Oddziaływania wiążące
tylko E_s
Oddziaływania torsyjne
E_{tor}
tylko E_b
Oddziaływania 1,5-niewiążące
$E_{el}+E_{VdW}$

$$E = E_s + E_b + E_{tor} + E_{el} + E_{nb}$$

E_s

E_b

E_{tor}

E_{el}

nb

3

$$E_s = \sum_{\text{wiązania}} \frac{1}{2} k_i^d (d_i - d_i^\circ)^2$$

d_i

$$d_i^\circ$$

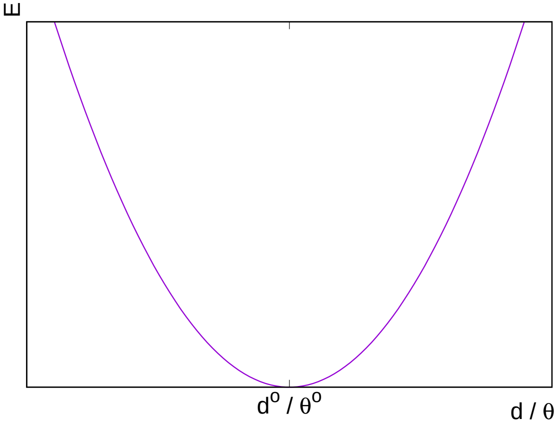
k_i^d

$$E_b = \sum_{\substack{\text{kąty}\\ \text{walencyjne}}} \frac{1}{2} k_i^{\theta} (\theta_i - \theta_i^{\circ})^2$$

θ_i

$$\theta_i^\circ$$

$$k_i^{\theta}$$


E
d° / θ°
d / θ

$$E_{tor} = \sum_{\substack{\text{kąty} \\ \text{torsyjne}}} \frac{V_i}{2}[1 \pm \cos(n_i \tau_i)]$$

τ_i

n_i

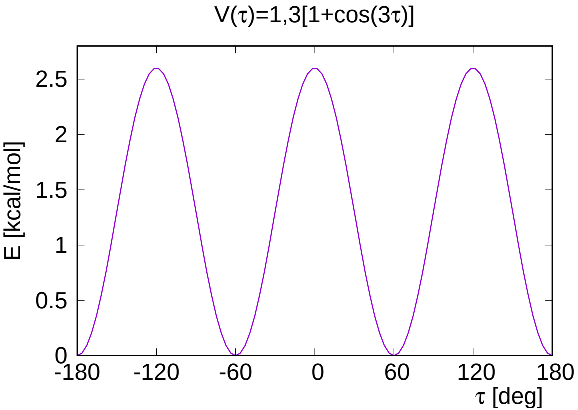
V_i

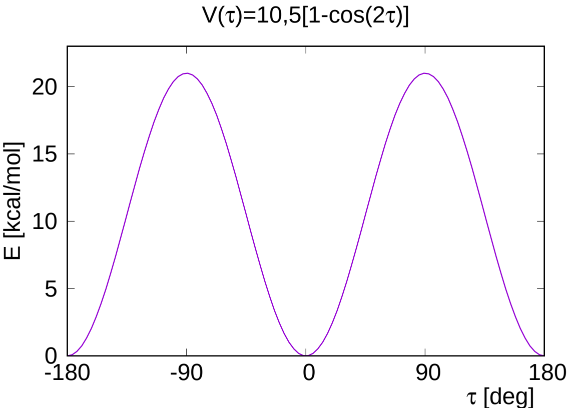
$$\tau = 0$$

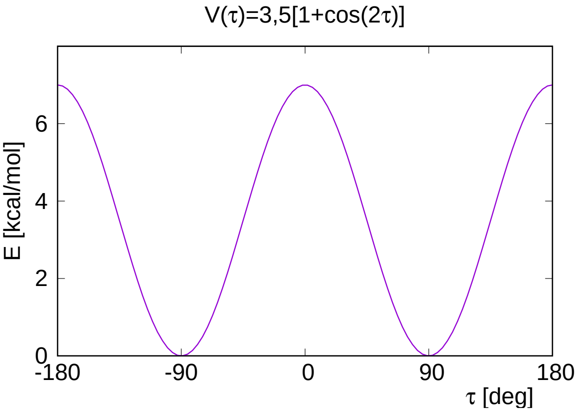
$n = 2$

$$\tau = \pm 90^\circ$$

$\tau = 0^\circ$


V(τ)=1,3[1+cos(3τ)]
E [kcal/mol]
2.5
2
1.5
1
0.5
0
-180
-120
-60
0
60
120
180
τ [deg]


V(τ)=10,5[1-cos(2τ)]
E [kcal/mol]
0
5
10
15
20
-180
-90
0
90
180
τ [deg]

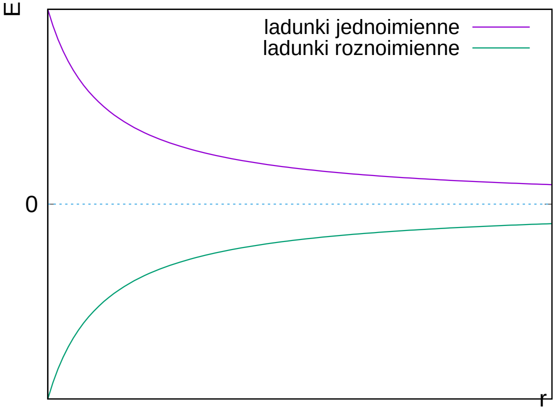

V(τ)=3,5[1+cos(2τ)]
E [kcal/mol]
0
2
4
6
-180
-90
0
90
180
τ [deg]

$$E_{el} = \sum_{i} \sum_{\substack{j<i \\ j \text{ nie(sąsiednio)związany z } i}} 332 \frac{q_i q_j}{D r_{ij}}$$

q_i

q_j

$$r_{ij}$$


E
ladunki jednoimienne
ladunki roznoimienne
0
r

$$E_{el} = \frac{q_1 q_2}{4\pi\epsilon_\circ D r}$$

$$\epsilon_{\circ} = 8,85419 \times 10^{-12}$$

$$e = 1,6022 \times 10^{-19}$$

$$6,022 \times 10^{23} \frac{(1,6022 \times 10^{-19}\ \mathrm{C})^2}{4 \times 3,14159 \times 8,85419 \times 10^{-12} \times \mathrm{F} \times \mathrm{m}^{-1} \times 10^{-10}\ \mathrm{m}} = 1,3894 \times 10^6\ \mathrm{J}$$

$$331,9 \approx 332$$

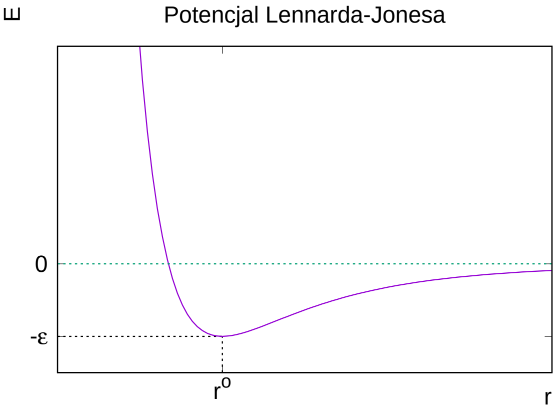
$$E_{nb} = \sum_{i} \sum_{\substack{j<i \\ j \text{ nie(sąsiednio)związany z } i}} \varepsilon_{ij} \left[\left(\frac{r_{ij}^{\circ}}{r_{ij}} \right)^{12} - 2 \left(\frac{r_{ij}^{\circ}}{r_{ij}} \right)^{6} \right]$$

$$r_{ij}^{\circ}$$

ε_{ij}

$$r_{ij}^{\circ} = r_i^{\circ} + r_j^{\circ}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$$



Potencjal Lennarda-Jonesa
E
0
-ε
r^o
r

$\mathcal{E}$

$$E_{nb}$$

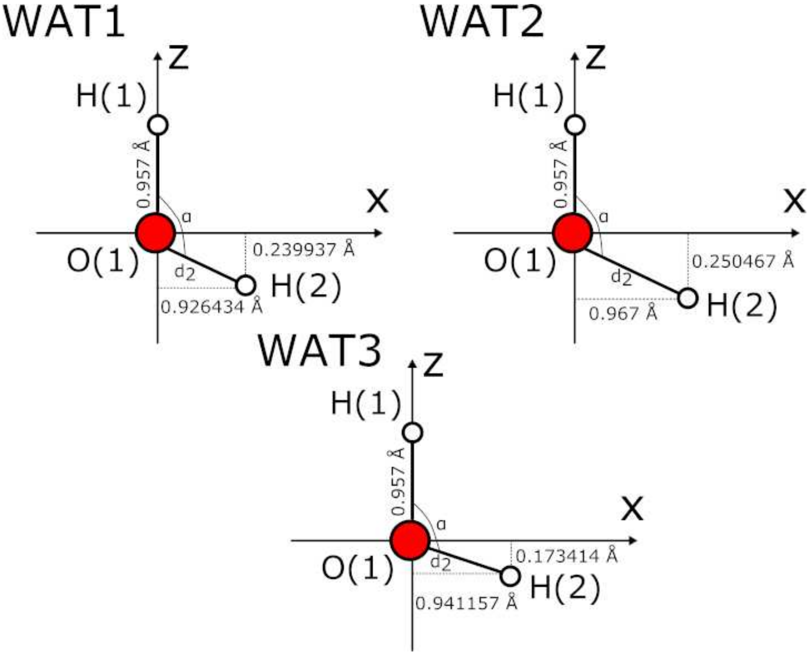
$$d^{\circ}_{OH} = 0,957$$

$$\theta^{\circ}_{H-O-H} = 104,52^{\circ}$$

$$k^d = 1106$$

$$k^{\theta} = 94$$

2



WAT1
Z
H(1)
0.957 Å
α
X
O(1)
0.239937 Å
d2
H(2)
0.926434 Å
WAT2
Z
H(1)
0.957 Å
α
X
O(1)
0.250467 Å
d2
H(2)
0.967 Å
WAT3
Z
H(1)
0.957 Å
α
X
O(1)
0.173414 Å
d2
H(2)
0.941157 Å

d_1

d_2

$$d_2 = \sqrt{0,926434^2 + 0,239937^2} = 0,957 \text{ Å}$$

$\cos \alpha$

$$\sin(\alpha - 90^\circ) = \frac{0,239937}{0,997} \quad \Rightarrow \quad \alpha = 104,52^\circ$$

$$k = 94\frac{\text{kcal}}{\text{mol} \times \text{rad}^2} = \frac{94}{\left(\frac{180}{\pi}\right)^2}\ \frac{\text{kcal}}{\text{mol} \times \text{deg}^2} = 0,02864\ \frac{\text{kcal}}{\text{mol} \times \text{deg}^2}$$

$$E_s = \frac{1106}{2}(0,957 - 0,957)^2 + \frac{1106}{2}(0,957 - 0,957)^2 = 0 \ \frac{\text{kcal}}{\text{mol}}$$

$$E_b = \frac{0,02864}{2}(104,52 - 104,52)^2 = 0 \ \frac{\text{kcal}}{\text{mol}}$$

$$E_{WAT1} = E_s + E_b = 0 \ \frac{\text{kcal}}{\text{mol}}$$

$$d_1 = 0,975$$

d_2

$$d_2 = \sqrt{0,967^2 + 0,250467^2} = 0,9989 \text{ Å}$$

$$\cos\alpha = \frac{(x_{H1}-x_{O1})(x_{H2}-x_{O1})+(y_{H1}-y_{O1})(y_{H2}-y_{O1})+(z_{H1}-z_{O1})(z_{H2}-z_{O1})}{d_1 d_2} =$$

$$\frac{(0-1)(0,967092-0)+(0-0)(0-0)+(-0,250467-1)(0,957-0)}{0,975\times 0,9989}=$$

$$-0,25074 \ \Rightarrow \ \alpha = 104,52^\circ$$

$$E_s = 553(0,957 - 0,957)^2 + 553(0,9989 - 0,957)^2 = 0,97 \ \frac{\mathrm{kcal}}{\mathrm{mol}}$$

$$E_b = 0,01432(104,52 - 104,52)^2 = 0 \ \frac{\text{kcal}}{\text{mol}}$$

$$E_{WAT2} = E_s + E_b = 0,97\ \frac{\mathrm{kcal}}{\mathrm{mol}}$$

$$d_1 = d_2 = 0,975$$

$$\alpha = 100,44^\circ$$

$$E_s = 553(0,957 - 0,957)^2 + 553(0,957 - 0,957)^2 = 0 \ \frac{\text{kcal}}{\text{mol}}$$

$$E_b = 0,01432(100,44 - 104,52)^2 = 0,24 \ \frac{\text{kcal}}{\text{mol}}$$

$$E_{WAT3} = E_s + E_b = 0,24\ \frac{\mathrm{kcal}}{\mathrm{mol}}$$

$r = 3$

$$q_H = 0,5$$

$$q_{Cl} = -0,5$$

$$k_d = 705$$

$$\Delta E_{A\cdots B} = E_{A\cdots B} - (E_A + E_B)$$

$$r^{\circ}_{HCl} = r^{\circ}_{H} + r^{\circ}_{Cl} = 2,5 + 0,6 = 3,1 \text{ Å}$$

$$\varepsilon_{HCl} = \sqrt{\varepsilon_H \varepsilon_{Cl}} = \sqrt{0,01 \times 0,1} = 0,032 \ \frac{\text{kcal}}{\text{mol}}$$

$$r^{\circ}_{HH} = 2r^{\circ}_{H} = 2 \times 0,6 = 1,2\ \text{Å}$$

$$\varepsilon_{HH} = \varepsilon_H = 0,01 \ \frac{\text{kcal}}{\text{mol}}$$

$$r^{\circ}_{ClCl} = 2r^{\circ}_{Cl} = 2 \times 2,5 = 5,0 \text{ Å}$$

$$\varepsilon_{ClCl} = \varepsilon_{Cl} = 0,1 \ \frac{\mathrm{kcal}}{\mathrm{mol}}$$

$$E_A + E_B = 0$$

$$\Delta E = E_{nb}(H1 \cdots H2) + E_{el}(H1 \cdots H2) + E_{nb}(H1 \cdots Cl2) + E_{el}(H1 \cdots Cl2)$$

$$+E_{nb}(Cl1\cdots H2)+E_{el}(Cl1\cdots H2)+E_{nb}(Cl1\cdots Cl2)+E_{el}(Cl1\cdots Cl2)$$

$$r_{H1H2} = 1,3 + 3 = 4,3$$

$$r_{H1Cl2} = 1,3 + 3 + 1,3 = 5,6$$

$$r_{Cl1H2} = 3$$

$$r_{Cl1Cl2} = 3 + 1,3 = 4,3$$

$$E_{nb}(H1 \cdots H2) = 0,01 \left[\left(\frac{1,2}{4,3} \right)^{12} - 2 \left(\frac{1,2}{4,3} \right)^{6} \right] = -0,0000 \ \frac{\mathrm{kcal}}{\mathrm{mol}}$$

$$E_{nb}(H1 \cdots Cl2) = 0,032 \left[\left(\frac{3,1}{5,6} \right)^{12} - 2 \left(\frac{3,1}{5,6} \right)^{6} \right] = -0,0018 \ \frac{\text{kcal}}{\text{mol}}$$

$$E_{nb}(Cl1 \cdots H2) = 0,032 \left[\left(\frac{3,1}{3} \right)^{12} - 2 \left(\frac{3,1}{3} \right)^{6} \right] = -0,0305 \ \frac{\mathrm{kcal}}{\mathrm{mol}}$$

$$E_{nb}(Cl1 \cdots Cl2) = 0,1 \left[\left(\frac{5}{4,3} \right)^{12} - 2 \left(\frac{5}{4,3} \right)^{6} \right] = 0,1166 \ \frac{\text{kcal}}{\text{mol}}$$

$$E_{el}(H1 \cdots H2) = 332 \frac{0,5 \times 0,5}{4,3} = 19,3023 \ \frac{\text{kcal}}{\text{mol}}$$

$$E_{el}(H1 \cdots Cl2) = 332\frac{0,5 \times (-0,5)}{5,6} = -14,8214 \ \frac{\text{kcal}}{\text{mol}}$$

$$E_{el}(Cl1 \cdots H2) = 332 \frac{(-0,5) \times 0,5}{3} = -27,6667 \ \frac{\text{kcal}}{\text{mol}}$$

$$E_{el}(Cl1 \cdots Cl2) = 332\frac{(-0,5) \times (-0,5)}{4,3} = 19,3023\ \frac{\mathrm{kcal}}{\mathrm{mol}}$$

$$\Delta E = -3,79$$

$$\Delta E = E_s(Cl1 - H2) +$$

$$E_{nb}(H1 \cdots H2) + E_{el}(H1 \cdots H2) + E_{nb}(H1 \cdots Cl2) + E_{el}(H1 \cdots Cl2)$$

$$d_{Cl1-H1} = 1,35$$

$$r_{H1H2} = 1,35 + 3 = 4,35$$

$$r_{H1Cl2} = 1,35 + 3 + 1,3 = 5,65$$

r

$$E_s(Cl1 - H2) = \frac{705}{2}(1,35 - 1,30)^2 = 0,8813 \ \frac{\text{kcal}}{\text{mol}}$$

$$E_{nb}(H1 \cdots H2) = 0,01 \left[\left(\frac{1,2}{4,35} \right)^{12} - 2 \left(\frac{1,2}{4,35} \right)^{6} \right] = -0,0000 \ \frac{\text{kcal}}{\text{mol}}$$

$$E_{nb}(H1 \cdots Cl2) = 0,032 \left[\left(\frac{3,1}{5,65} \right)^{12} - 2 \left(\frac{3,1}{5,65} \right)^{6} \right] = -0,0017 \ \frac{\mathrm{kcal}}{\mathrm{mol}}$$

$$E_{nb}(Cl1 \cdots Cl2) = 0,1 \left[\left(\frac{5}{4,35} \right)^{12} - 2 \left(\frac{5}{4,35} \right)^{6} \right] = 0,07060 \ \frac{\text{kcal}}{\text{mol}}$$

$$E_{el}(H1 \cdots H2) = 332\frac{0,5 \times 0,5}{4,35} = 19,0805\ \frac{\text{kcal}}{\text{mol}}$$

$$E_{el}(H1 \cdots Cl2) = 332\frac{0,5 \times (-0,5)}{5,65} = -14,6903 \ \frac{\text{kcal}}{\text{mol}}$$

$$E_{el}(Cl1 \cdots Cl2) = 332 \frac{(-0,5) \times (-0,5)}{4,35} = 19,0805 \ \frac{\text{kcal}}{\text{mol}}$$

$$\Delta E = -3,2153$$

$$M_{Cl} = 35,5$$

$$M_{Na} = 23$$

$$\rho_{NaCl} = 2,16$$

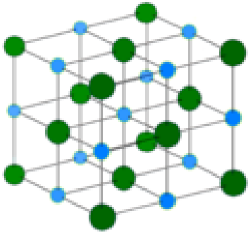
3

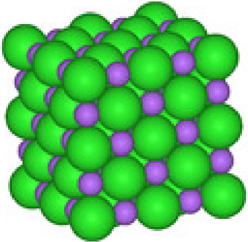
$$Cl^{-} = -1$$

$$Na^{+} = +1$$

+

—





N_{jon}

n_{jon}

$$N_{jon} = 2N_{NaCl} = n_{jon}^3 \;\Rightarrow\; n_{jon} = (2N_{NaCl})^{\frac{1}{3}}$$

$$r = \frac{d}{n_{jon} - 1} = \frac{d}{(2N_{NaCl})^{\frac{1}{3}} - 1}$$

$$d = 1\ \text{cm}$$

$$N_{NaCl} = \frac{N_A \times \rho}{M_{NaCl}} = \frac{6,022 \times 10^{23} \times 2,16}{23 + 35,5} = 4,4470 \times 10^{22}$$

$$n_{jon} = (4,4470 \times 10^{22})^{\frac{1}{3}} = 3,5429 \times 10^{7}$$

$$r = \frac{1 \text{ cm}}{5,5429 \times 10^{7} - 1} = 2,8226 \times 10^{-8} \text{ cm } = 2,8226 \text{ Å}$$

$$\Delta E = 6(E_{nb} + E_{el}) =$$

$$6\left\{\varepsilon_{NaCl}\left[\left(\frac{r^{\circ}_{NaCl}}{r}\right)^{12}-2\left(\frac{r^{\circ}_{NaCl}}{r}\right)^{6}\right]-\frac{332}{r}\right\}=$$

$$6\left\{0,01732\left[\left(\frac{4,4}{2,8226}\right)^{12}-2\left(\frac{4,4}{2,8226}\right)^{6}\right]-\frac{332}{2,8226}\right\}=$$

$$6(3,0690 - 117,6221) = -687,32\ \frac{\text{kcal}}{\text{mol}}$$

$$d_{CO}^{\circ} = 1,25$$

$$k_{CO}^{d} = 1312$$

$$\theta^{\circ}_{OCO} = 120^{\circ}$$

$$k_{OCO}^{\theta} = 160$$

$$E = 6,24$$

$$E_s = 4,92$$

$$E_b = 1,32$$

$$\varepsilon = 0,0203$$

$$r^{\circ}_{\mathrm{He}\cdots\mathrm{He}} = 2,28$$

$$E = -0,0014$$

三

$$k^d$$

d°

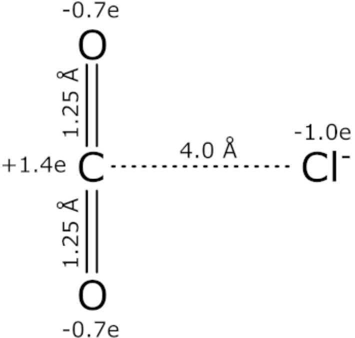
$$\Delta E = -0,38$$

$$D = 80$$

2

$$d^{\circ} = 1,16$$

$$k^d = 1608$$


-0.7e
O
1.25 Å
-1.0e
4.0 Å
+1.4e
C
Cl-
1.25 Å
O
-0.7e

$$E = 12,65$$

$$E_s = 13,02$$

$$E_{el} = -0,07$$

$$E_{nb} = -0,30$$

$$D = 2,24$$

$$D = 24,5$$

$r = 3, 30$

$$d_{OH} = 1,0$$

$$\varepsilon_{Ca^{2+}} = 0,10$$

$$r^{\circ}_{Ca^{2+}} = 1,7$$

$$\varepsilon_O = 0,20$$

$$r_O^{\circ} = 1,6$$

$$\varepsilon_H = 0,02$$

$$r_H^\circ = 1,0$$

$$q_O = -1, 1$$

$$q_H = 0,1$$

$$d^{\circ}_{OH} = 0,964$$

$$k_{OH} = 1010$$

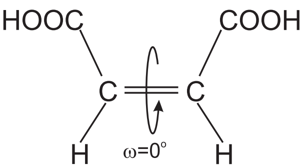
$$\Delta E = -7,90$$

$$\Delta E_s = 0,65$$

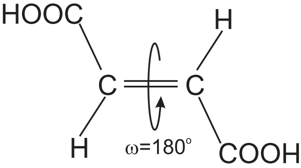
$$\Delta E_{el} = -8,40$$

$$\Delta E_{nb} = -0,15$$

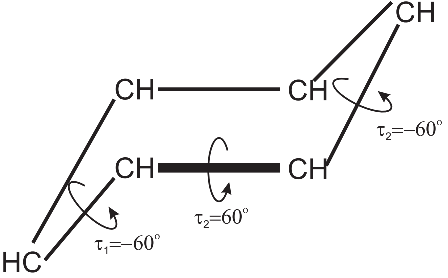
$$r^* \approx 2,57$$



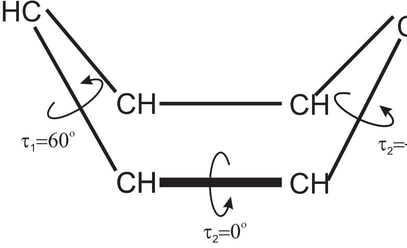
kwas maleinowy



kwas fumarowy



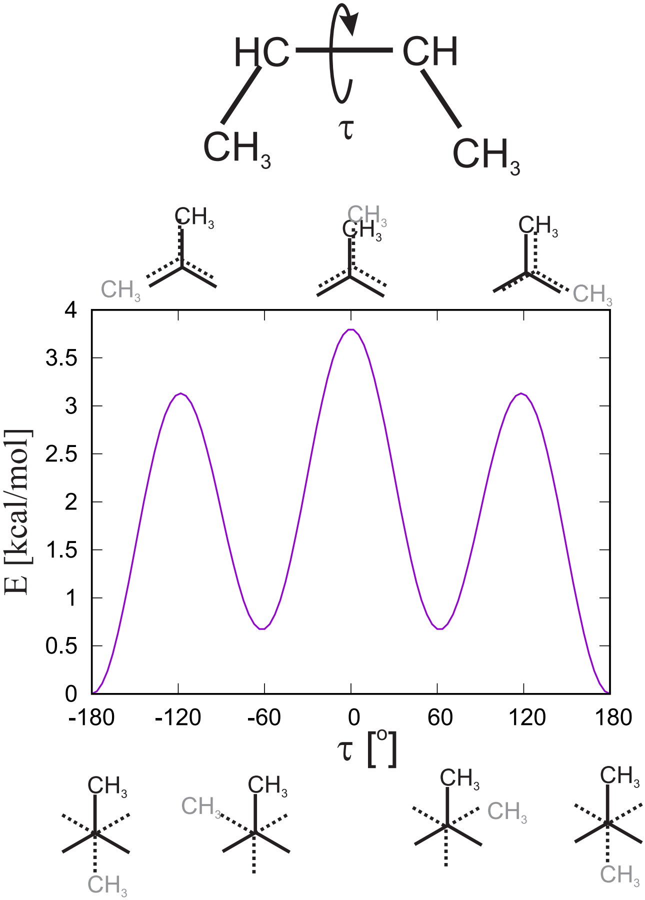
konformacja krzesłowa



konformacja łódkowa

ϕ

ψ



HC
CH
τ
CH_3
CH_3
E [kcal/mol]
τ [°]
-180
-120
-60
0
60
120
180
0
0.5
1
1.5
2
2.5
3
3.5
4

$$W = Fs$$

W

F

s

mgh

g

$$W = -\Delta E_p = Fs \ \Rightarrow \ F = -\frac{\Delta E_p}{s}$$

$$s = \Delta x$$

$$\Delta x \to 0$$

$$F_x = \lim_{\Delta x \to 0} -\frac{\Delta E_p}{\Delta x} = -\frac{\partial E_p}{\partial x}$$

F

$$\mathbf{F} = \begin{pmatrix} F_x \\ F_y \\ F_z \end{pmatrix} = - \begin{pmatrix} \frac{\partial E_p}{\partial x} \\ \frac{\partial E_p}{\partial y} \\ \frac{\partial E_p}{\partial z} \end{pmatrix} = -\nabla E_p$$

$$x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_n, y_n, z_n$$

$$\mathbf{F}_i = -\begin{pmatrix} \frac{\partial E_p}{\partial x_i} \\ \frac{\partial E_p}{\partial y_i} \\ \frac{\partial E_p}{\partial z_i} \end{pmatrix}$$

$$E = \sum_{i=2}^{n} \sum_{j=1}^{i-1} e_{ij}(r_{ij})$$

$$F_{x_i} = -\frac{\partial E}{\partial x_i} = -\sum_{\substack{j=1 \\ j \neq i}}^{n} e'(r_{ij}) \frac{\partial r_{ij}}{\partial x_i}$$

$$r_{ij} = \sqrt{(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2}$$

$$\frac{\partial r_{ij}}{\partial x_i} = \frac{2(x_j - x_i)(-1)}{2\sqrt{(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2}} = \frac{x_i - x_j}{r_{ij}} = \hat{x}_{ji}$$

$$\nabla_i r_{ij} = \begin{pmatrix} \hat{x}_{ji} \\ \hat{y}_{ji} \\ \hat{z}_{ji} \end{pmatrix} = \hat{\mathbf{r}}_{ji}$$

$$\mathbf{F}_i = -\sum_{\substack{j=1 \\ j\neq i}}^{n} e'(r_{ij})\hat{\mathbf{r}}_{ji} = \sum_{\substack{j=1 \\ j\neq i}}^{n} \mathbf{f}_{j\to i}$$

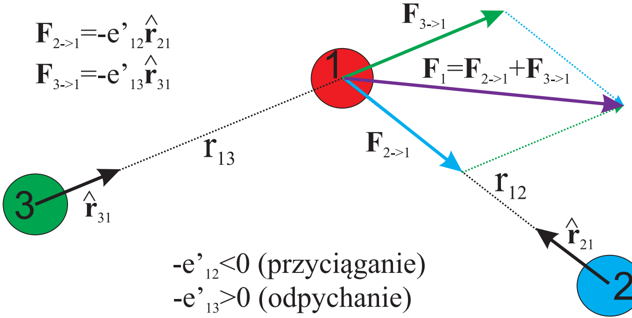
$$\mathbf{f}_{j\to i} = -e'(r_{ij})\hat{\mathbf{r}}_{ji}$$

$$\mathbf{f}_{j \to i}$$

$\mathbf{f}_{i \to j}$

$$\hat{\mathbf{r}}_{ij}$$

$$\hat{\mathbf{r}}_{ji}$$



$\mathbf{F}_{2->1}=-e'_{12}\hat{\mathbf{r}}_{21}$
$\mathbf{F}_{3->1}=-e'_{13}\hat{\mathbf{r}}_{31}$
$\mathbf{F}_{3->1}$
1
$\mathbf{F}_1=\mathbf{F}_{2->1}+\mathbf{F}_{3->1}$
$\mathbf{r}_{13}$
$\mathbf{F}_{2->1}$
$\mathbf{r}_{12}$
3
$\hat{\mathbf{r}}_{31}$
$\hat{\mathbf{r}}_{21}$
$-e'_{12}<0$ (przyciąganie)
$-e'_{13}>0$ (odpychanie)
2

$$1 \ \frac{\mathrm{kcal}}{\mathrm{mol}\times}\mathrm{\AA}= \frac{4186\mathrm{J}}{6{,}022\times 10^{23}\times 10^{-10}\mathrm{m}} = 6,95\times 10^{-11}\ \mathrm{N}$$

$\tau = 180°$

$$\varepsilon_C = 0,11$$

$$r_C^{\circ} = 1,8$$

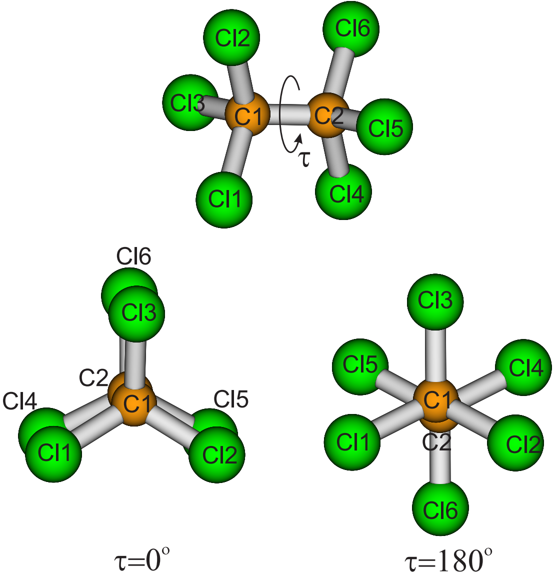
$$\varepsilon_{Cl} = 0,53$$

$$r^{\circ}_{Cl} = 1,735$$

$$q_C = 0,18$$

$$q_{Cl} = -0,06$$

$$V_3/2 = 1,6$$


Cl2
Cl6
Cl3
C1
C2
Cl5
τ
Cl1
Cl4
Cl6
Cl3
C2
Cl4
C1
Cl5
Cl1
Cl2
Cl3
Cl5
Cl4
C1
Cl1
C2
Cl2
Cl6
τ=0°
τ=180°

$$E = E_{nb} + E_{el} + E_{tor} = \sum_{i=1}^{3}\sum_{j=4}^{6} \varepsilon_{ClCl} \left[\left(\frac{r^{\circ}_{ClCl}}{r_{Cl_iCl_j}} \right)^{12} - 2 \left(\frac{r^{\circ}_{ClCl}}{r_{Cl_iCl_j}} \right)^{6} \right]$$

$$+\sum_{i=1}^{3}\sum_{j=4}^{6}332\frac{q_{Cl}^{2}}{r_{Cl_iCl_j}}+\frac{V_3}{2}\left[1+\cos(3\tau)\right]$$

$$r_{Cl1Cl4} = r_{Cl2Cl5} = r_{Cl3Cl6}$$

$$r_{Cl1Cl5} = r_{Cl1Cl6} = r_{Cl2Cl4} = r_{Cl2Cl6} = r_{Cl3Cl4} = r_{Cl3Cl5}$$

$1 \cdots$

4

$2\cdots$

5

r_{Cl1Cl4}

r_{Cl2Cl5}

$$r_{Cl1Cl4} = 2,102667 - (-0,642667) = 2,7453 \text{ Å}$$

$$r_{Cl1Cl5} = \sqrt{(-0,82460 - 1,649206)^2 + 1,428254^2 + (2,102667 - (-0,642667))^2}$$

$$= 3,9619 \ \mathring{A}$$

$$\varepsilon_{ClCl} = \sqrt{\varepsilon_{Cl}\varepsilon_{Cl}} = 0,53 \text{ kcal/mol}$$

$$r^{\circ}_{ClCl} = r^{\circ}_{Cl} + r^{\circ}_{Cl} = 2 \times 1,735 = 3,47\ \mathring{A}$$

$$E_{nb} = 3 \times E_{nb}(Cl1 \cdots Cl4) + 6 \times E_{nb}(Cl1 \cdots Cl5) =$$

$$3 \times 0,53 \left[\left(\frac{3,47}{2,7453} \right)^{12} - 2 \left(\frac{3,47}{2,7453} \right)^{6} \right] +$$

$$6 \times 0,53 \left[\left(\frac{3,47}{3,9619} \right)^{12} - 2 \left(\frac{3,47}{3,9619} \right)^{6} \right] = 3 \times 4,4900 + 6(-0,3705)$$

$$= 11,2470 \text{ kcal/mol}$$

$$E_{el} = 3 \times E_{el}(Cl1 \cdots Cl4) + 6 \times E_{el}(C1 \cdots Cl5) =$$

$$3 \times 332 \frac{(-0,06)^2}{2,7453} + 6 \times 332 \frac{(-0,06)^2}{3,9619} =$$

$$3 \times 0,4354 + 6 \times 0,3017 = 3,1164 \text{ kcal/mol}$$

$$E_{tor} = 1,6[1 + \cos(3 \times 0)] = 3,2 \text{ kcal/mol}$$

$$E_I = 11,2470 + 3,1164 + 3,2 = 17,5634$$

$$r_{Cl1Cl4} = 4,29143$$

$$r_{Cl2Cl5} = 3,2026$$

$$E_{nb} = 3(-0,2549) + 6(-0.3276) = -2,7276$$

$$E_{el} = 3 \times 0,2785 + 6 \times 0,3732 = 3,0747$$

$$E_{tor} = 1,6[1 + \cos(-3\pi)] = 0$$

$$E_{II} = 0,3471$$

$$\Delta E = E_I - E_{II} = 17,5634 - 0,3471 = 17,2163$$

$$\Delta E^* = 10,8$$

=

$$E(d) = 804(d - 1,16\text{Å})^2$$

$$d_{O1=C2} = x$$

$$d_{C2=O3} = 2,32 - x$$

$$E(x) = E_{O1=C2} + E_{C2=O3} = 804(x - 1,16)^2 + 804(2,32 - x - 1,16)^2$$

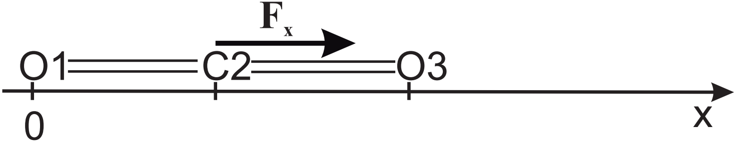
$$= 1608(x - 1,16)^2$$

$$F_x = -\frac{\partial E}{\partial x} = -2 \times 1608(x - 1,16)$$

$$x = 0,96$$

$$F_x(1,16) = -3216(-0,2) = 643,2$$

$$643,2 \times 6,95 \times 10^{-11} = 4,47 \times 10^{-8}$$



F x
O1
C2
O3
0
x

$$\mathbf{F}_{C2} = \mathbf{F}_{O1\to C2} + \mathbf{F}_{O3\to C2} = -e'_{C2O1}(d_{C2O2}) \times 1 - e'_{C2O3}(d_{C2O3}) \times (-1) =$$

$$-[804(d_{C2O1}-1,16)^2]' + [804(d_{C2O3}-1,16)^2]' =$$

$$-1608[(d_{C2O1}-1,16)-(d_{C2O3}-1,16)]=-1608(-0,2-0,2)$$

$$= 643,2 \text{ kcal/mol/Å}$$

$$\overrightarrow{O1C2}$$

$\overrightarrow{O3C2}$

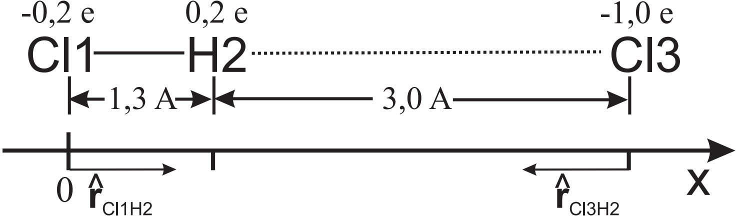
$$\varepsilon_H = 0,01$$

$$r_H^\circ = 0,6$$

$$\varepsilon_{Cl} = 0,10$$

$$r^{\circ}_{Cl} = 2,5$$

$$d^{\circ}_{HCl} = 1,3$$



-0,2 e
0,2 e
-1,0 e
Cl1
H2
Cl3
1,3 A
3,0 A
0
r̂Cl1H2
r̂Cl3H2
x

$$\mathbf{F}_{H2} = \mathbf{F}_{Cl1\to H2} + \mathbf{F}_{Cl3\to H2} = -e'_{H2Cl1}(r_{H2Cl1}) \times 1 - e'_{H2Cl3}(r_{H2Cl3}) \times (-1) = e'_{H2Cl3}$$

$$-e'_{H2Cl1} = 0$$

$$\hat{\mathbf{r}}_{Cl1H2}$$

$$\hat{\mathbf{r}}_{Cl3H2}$$

$$\varepsilon_{HCl} = \sqrt{0,1 \times 0,01} = 0,0316$$

$$r_{HCl}^{\circ} = 0,6 + 2,5 = 3,1$$

$$r = r_{H2Cl3}$$

$$e_{H2Cl3} = e_{nb} + e_{el} = 0,0316 \left[\left(\frac{3,1}{r} \right)^{12} - 2 \left(\frac{3,1}{r} \right)^{6} \right] + 332 \frac{0,2 \times (-1,0)}{r}$$

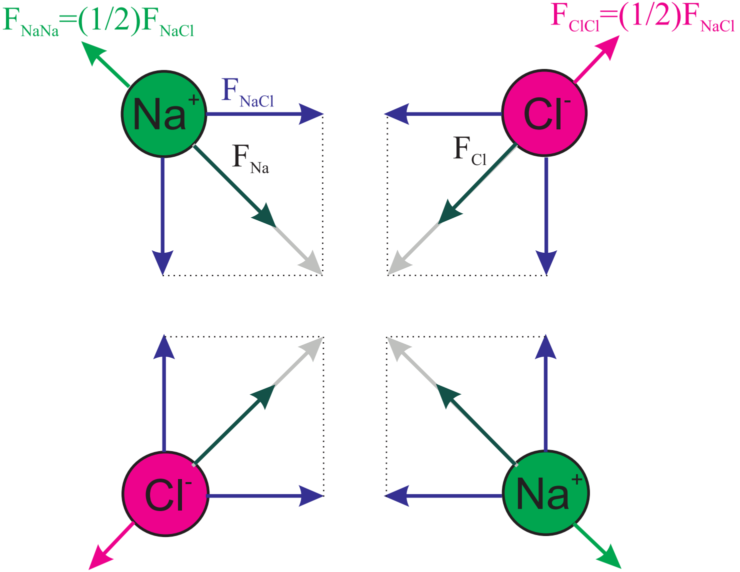
$$r_{H2Cl3} = r$$

$$F_{H2} = -\frac{12 \times 0,0316}{r}\left[\left(\frac{3,1}{r}\right)^{12} - \left(\frac{3,1}{r}\right)^{6}\right] + 332\frac{0,2}{r^2}$$

$$r = 3,0$$

$$F_{H2} = 7,34$$

$$1,63 \times 10^{-10}$$



$F_{NaNa}=(1/2)F_{NaCl}$
$F_{ClCl}=(1/2)F_{NaCl}$
F_{NaCl}
F_{Na}
F_{Cl}
Na^+
Cl^-
Cl^-
Na^+

$$F_{NaCl}$$

$$\sqrt{2}F_{NaCl}$$

$$F_{el} \sim \frac{1}{r^2},\ r_{NaNa} = r_{ClCl} = \sqrt{2} r_{NaCl}$$

$$F_{Na} = F_{Cl} = (\sqrt{2} - \tfrac{1}{2})F_{NaCl}$$

$$\tau = 90^\circ$$

$$E_{tor} = \frac{3,35}{2}[1 + \cos \tau] + \frac{3,27}{2}[1 + \cos(2\tau)]$$

$$q_N = -0.3$$

$$q_H = 0.3$$

$$\varepsilon_H = 0,016$$

$$r_O^\circ = 1,9$$

$$E_{II} - E_I = 6,90$$

$$d^{\circ} = 1,13$$

$$d = 1,23$$

$$k_{CO} = 1870$$

$$1,87 \times 10^{-8}$$

$$d^{\circ}_{CO} = 1,16$$

$$k_{CO} = 1595$$

$$d^{\circ}_{C=S} = 1,56$$

$$k_{SC} = 753$$

$$F_O = 7,975 \times 10^{-9}$$

$$F_C = -4,45 \times 10^{-10}$$

$$F_S = -7,53 \times 10^{-9}$$

$$k = 1385$$

$$d^\circ = 0,92$$

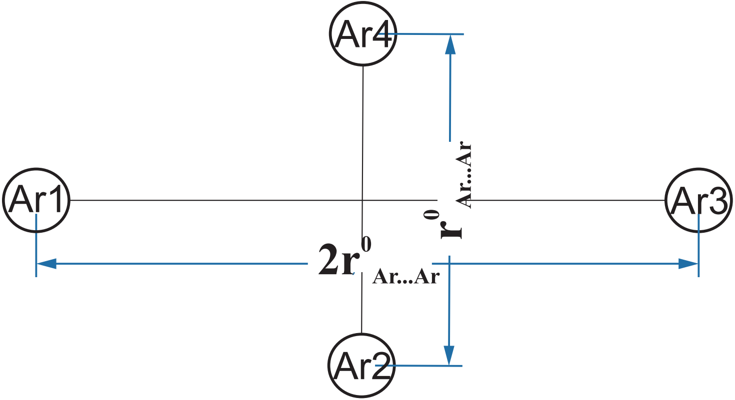
$$\varepsilon_H = 0,015$$

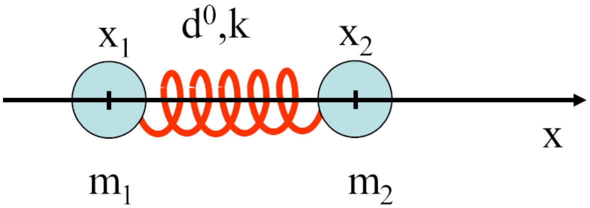
$$r_H^\circ = 0,60$$

$$\varepsilon_F = 0,30$$

$$r_F^\circ = 1,90$$

$$8,67 \times 10^{-10}$$


Ar4
Ar1
Ar3
Ar2
$2r^0_{Ar...Ar}$
$r^0_{Ar...Ar}$



x1
d0,k
x2
x
m1
m2

$$E(x_1, x_2) = \frac{1}{2}k[(x_2 - x_1) - d^\circ]^2$$

$$E = 0$$

$$k = \frac{\partial^2 E}{\partial {x_1}^2} = \frac{\partial^2 E}{\partial {x_2}^2}$$

$$F_1 = -\frac{\partial E}{\partial x_1} = k(x_2 - x_1 - d^\circ)$$

$$F_2 = -\frac{\partial E}{\partial x_2} = -k(x_2 - x_1 - d^\circ) = -F_1$$

$$m_1 a_1 = m_1 \frac{\mathrm{d}^2 x_1}{\mathrm{d}t^2} = F_1 = k(x_2 - x_1 - d^\circ)$$

$$m_2 a_2 = m_2 \frac{\mathrm{d}^2 x_2}{\mathrm{d}t^2} = F_2 = -k(x_2 - x_1 - d^\circ)$$

$$m_1 \frac{\mathrm{d}^2 x_1}{\mathrm{d}t^2} + m_2 \frac{\mathrm{d}^2 x_2}{\mathrm{d}t^2} = 0$$

$$x_{CM} = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

$$\frac{\mathrm{d}^2 x_{CM}}{\mathrm{d}t^2} = 0$$

m_1

m_2

$$\frac{\mathrm{d}^2 x_2}{\mathrm{d}t^2} - \frac{\mathrm{d}^2 x_1}{\mathrm{d}t^2} = -k\left(\frac{1}{m_1} + \frac{1}{m_2}\right)(x_2 - x_1 - d^\circ)$$

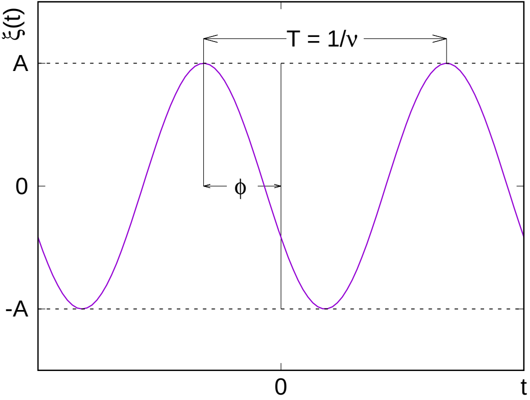
$$\xi = x_2 - x_1 - d^{\circ}$$

$$\frac{\mathrm{d}^2\xi}{\mathrm{d}t^2} = -\frac{k}{\mu}\xi$$

$$\mu = \left(\frac{1}{m_1} + \frac{1}{m_2}\right)^{-1} = \frac{m_1 m_2}{m_1 + m_2}$$

$$\xi(t) = A\cos\left(\omega t + \phi\right)$$

$$\omega = \sqrt{\frac{k}{\mu}}$$



ξ(t)
T = 1/ν
A
0
-A
ϕ
0
t

T

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

$$\lambda = \frac{c}{\nu}$$

$$\overline{\nu} = \frac{1}{\lambda} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$-1$$

$$\sqrt{2}$$

$3n$

$$\mathbf{W} = \begin{pmatrix} \frac{k_{11}}{m_1} & \frac{k_{12}}{\sqrt{m_1 m_2}} & \cdots & \frac{k_{1,3n}}{\sqrt{m_1 m_{3n}}} \\ \frac{k_{21}}{\sqrt{m_2 m_1}} & \frac{k_{22}}{m_2} & \cdots & \frac{k_{2,3n}}{\sqrt{m_2 m_{3n}}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{k_{3n,1}}{\sqrt{m_{3n} m_1}} & \frac{k_{3n,2}}{\sqrt{m_{3n} m_2}} & \cdots & \frac{k_{3n,3n}}{m_{3n}} \end{pmatrix}$$

r

W

M

k_{ij}

$$\mathbf{r} = \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ \vdots \\ x_n \\ y_n \\ z_n \end{pmatrix}$$

$$\mathbf{M} = \begin{pmatrix} m_1 & 0 & 0 & \dots & 0 & 0 & 0 \\ 0 & m_1 & 0 & \dots & 0 & 0 & 0 \\ 0 & 0 & m_1 & \dots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & m_{3n} & 0 & 0 \\ 0 & 0 & 0 & \dots & 0 & m_{3n} & 0 \\ 0 & 0 & 0 & \dots & 0 & 0 & m_{3n} \end{pmatrix}$$

$$k_{ij} = \frac{\partial^2 E}{\partial r_i \partial r_j}$$

$$\mathbf{W} = \mathbf{M}^{-\frac{1}{2}} \mathbf{K} \mathbf{M}^{-\frac{1}{2}}$$

$$\mathbf{K} = \mathbf{H}$$

$$\lambda_i = \omega_i^2$$

$$3n - 6$$

$3n - 5$

16

$$18,7 \times 10^5$$

$$k = 18,7 \times 10^5 \ \frac{\mathrm{dyn}}{\mathrm{cm}} = 18,7 \times 10^5 \times \frac{10^{-5} \ \mathrm{N}}{10^{-2} \ \mathrm{m}} = 1870 \ \frac{\mathrm{N}}{\mathrm{m}}$$

$$\mu = \frac{16 \times 12}{16 + 12} = 6,8571 \ \frac{\text{g}}{\text{mol}} = \frac{6,8571 \times 10^{-3} \ \text{kg}}{6,022 \times 10^{23}} = 1,1387 \times 10^{-26} \ \text{kg}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{6,28318}\sqrt{\frac{18,7 \times 10^2}{1,1387 \times 10^{-26}}} = 6,4497 \times 10^{13}\ \mathrm{s}^{-1} = 6,4497 \times 10^{13}\ \mathrm{Hz}$$

$\overline{\nu}$

$$\overline{\nu} = \frac{\nu}{c} = \frac{6,4497 \times 10^{13}}{3 \times 10^{8}} = 2,15 \times 10^{5}\ \mathrm{m}^{-1} = 2150\ \mathrm{cm}^{-1}$$

$$\overline{\nu} = 2270\ \mathrm{cm}^{-1} = 2,27 \times 10^5\ \mathrm{m}^{-1}$$

$$\mu = \frac{1 \times 127}{1 + 127} = 0,9922\ \frac{\text{g}}{\text{mol}} = 1,6476 \times 10^{-27}\ \text{kg}$$

$$(2\pi c)^2\mu$$

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

$$k = (2\pi c\overline{\nu})^2\mu$$

μ

$$k = (6,28318 \times 3 \times 10^8 \times 2,27 \times 10^5)^2 \times 1,6476 \times 10^{-27} = 301 \ \frac{\mathrm{N}}{\mathrm{m}}$$

1

$$\frac{\overline{\nu}_{1\,HBr}}{\overline{\nu}_{2\,HBr}} = \frac{\frac{1}{2\pi c}\sqrt{\frac{k}{\mu_{1\,HBr}}}}{\frac{1}{2\pi c}\sqrt{\frac{k}{\mu_{2\,HBr}}}} = \sqrt{\frac{\mu_{2\,HBr}}{\mu_{1\,HBr}}}$$

$$\mu_{^1HBr} = \frac{1 \times 79}{1 + 79} = \frac{79}{80} = 0,9875 \ \frac{\mathrm{g}}{\mathrm{mol}}$$

$$\mu_{^2HBr} = \frac{2 \times 79}{2 + 79} = \frac{158}{81} = 1,9506\ \frac{\mathrm{g}}{\mathrm{mol}}$$

$$\frac{\overline{\nu}_{1\,HBr}}{\overline{\nu}_{2\,HBr}} = \sqrt{\frac{\mu_{2\,HBr}}{\mu_{1\,HBr}}} = \sqrt{\frac{1,9506}{0,9875}} = 1,41$$

3—

$$\overline{\nu} = 1986,5$$

$$x_1 < x_2 < x_3$$

$$E = \frac{1}{2}k[(x_2 - x_1) - d^\circ]^2 + \frac{1}{2}k[(x_3 - x_2) - d^\circ]^2$$

1

$$F_1 = -\frac{\partial E}{\partial x_1} = k[(x_2 - x_1) - d^\circ]$$

$$F_2 = -\frac{\partial E}{\partial x_2} = -k(x_2 - x_1) + k(x_3 - x_2) = k(x_1 - 2x_2 + x_3)$$

$$F_3 = -\frac{\partial E}{\partial x_3} = -k[(x_3 - x_2) - d^\circ]$$

$$m\frac{\mathrm{d}^2x_1}{\mathrm{d}t^2} = k(-x_1 + x_2 - d^\circ)$$

$$m\frac{\mathrm{d}^2x_2}{\mathrm{d}t^2} = k(x_1 - 2x_2 + x_3)$$

$$m\frac{\mathrm{d}^2x_3}{\mathrm{d}t^2} = k(x_2 - x_3 + d^\circ)$$

$$m\frac{\mathrm{d}^2(x_1 + x_2 + x_3)}{\mathrm{d}t^2} = 0$$

$$m\frac{\mathrm{d}^2(x_3 - x_1 - 2d^\circ)}{\mathrm{d}t^2} = -k(x_3 - x_1 - 2d^\circ) \;\Rightarrow\; \frac{\mathrm{d}^2(x_3 - x_1 - 2d^\circ)}{\mathrm{d}t^2} = -\frac{k}{m}(x_3 - x_1 - 2d^\circ)$$

$$\omega_s = \sqrt{\frac{k}{m}}$$

$2d^{\circ}$

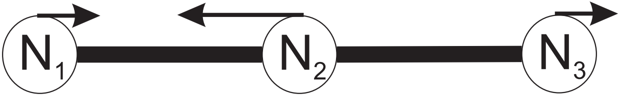
$$m\frac{\mathrm{d}^2(x_1-2x_2+x_3)}{\mathrm{d}t^2}=-3k(x_1-2x_2+x_3)\ \Rightarrow$$

$$\frac{\mathrm{d}^2(x_1 - 2x_2 + x_3)}{\mathrm{d}t^2} = -\frac{3k}{m}(x_1 - 2x_2 + x_3)$$

$$\xi = x_1 - 2x_2 + x_3$$

$$\omega_a = \sqrt{\frac{3k}{m}}$$

drganie rozciągające symetryczne



drganie rozciągające antysymetryczne

$$k = (2\pi c\overline{\nu})^2(m/3) = (6,28318 \times 3 \times 10^8 \times 1,9865 \times 10^5)^2 \frac{14 \times 10^{-3}/3}{6,022 \times 10^{23}}$$

$$= 1087 \ \frac{\text{N}}{\text{m}}$$

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 E}{\partial x_1^2} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \frac{\partial^2 E}{\partial x_1 \partial x_3} \\ \frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2^2} & \frac{\partial^2 E}{\partial x_2 \partial x_3} \\ \frac{\partial^2 E}{\partial x_3 \partial x_1} & \frac{\partial^2 E}{\partial x_3 \partial x_2} & \frac{\partial^2 E}{\partial x_3^2} \end{pmatrix} = \begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix}$$

$$\mathbf{W} = \begin{pmatrix} \frac{k}{m} & -\frac{k}{m} & 0 \\ -\frac{k}{m} & 2\frac{k}{m} & -\frac{k}{m} \\ 0 & -\frac{k}{m} & \frac{k}{m} \end{pmatrix}$$

$$\det(\mathbf{W} - \lambda\mathbf{I}) = \begin{vmatrix} \frac{k}{m} - \lambda & -\frac{k}{m} & 0 \\ -\frac{k}{m} & 2\frac{k}{m} - \lambda & -\frac{k}{m} \\ 0 & -\frac{k}{m} & \frac{k}{m} - \lambda \end{vmatrix} = \frac{k}{m} \begin{vmatrix} 1 - \lambda' & -1 & 0 \\ -1 & 2 - \lambda' & -1 \\ 0 & -1 & 1 - \lambda' \end{vmatrix} = 0$$

$$\lambda' = \frac{m}{k}\lambda$$

λ'

$$(1-\lambda')[(2-\lambda')(1-\lambda')-1]+1(-(1-\lambda'))=(1-\lambda')[(2-\lambda')(1-\lambda')-2]$$

$$= -\lambda'(\lambda' - 1)(\lambda' - 3) = 0$$

$$\lambda_1' = 0$$

$$\lambda_2' = 1$$

$$\lambda_2' = 3$$

$$\lambda_1 = \omega_1^2 = 0$$

$$\lambda_2 = \omega_2^2 = \frac{k}{m}$$

$$\lambda_3 = \omega_3^2 = \frac{3k}{m}$$

λ_i

$$\mathbf{W}\mathbf{v}_i = \lambda_i \mathbf{v}_i$$

$$k/m$$

$$\lambda_1' = 0$$

$\lambda_1', \lambda_2', \lambda_3'$

$$v_{11} - v_{21} = 0$$

$$-v_{11} + 2v_{21} - v_{31} = 0$$

$$-v_{21} + v_{31} = 0$$

$$v_{11} = v_{21}$$

$$v_{21} = v_{31}$$

$$v_{11} = v_{21} = v_{31}$$

$$\lambda_2' = 1$$

$$(1-1)v_{12} - v_{22} = 0$$

$$-v_{12} + (2-1)v_{22} - v_{32} = 0$$

$$-v_{22} + (1-1)v_{23} = 0$$

$$v_{22} = 0$$

$$v_{12} = -v_{32}$$

$$\lambda_2' = 3$$

$$(1-3)v_{13} - v_{23} = 0$$

$$-v_{13} + (2-3)v_{23} - v_{33} = 0$$

$$-v_{23} + (1-3)v_{33} = 0$$

$$v_{23} = -2v_{13}$$

$$v_{23} = -2v_{33}$$

$$v_{13} = v_{23}$$

/

$$\mathbf{v}_1' = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \quad \mathbf{v}_2' = \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \quad \mathbf{v}_3' = \begin{pmatrix} 1 \\ -2 \\ 1 \end{pmatrix}$$

$$\sqrt{1^2 + 1^2 + 1^2} = \sqrt{3}$$

$$\sqrt{1^2 + 0^2 + (-1)^2} = \sqrt{2}$$

$$\sqrt{1^2 + (-2)^2 + 1^2} = \sqrt{6}$$

$$\mathbf{v}_1$$

$$\mathbf{v}_2$$

$\mathbf{V}_3$

$$\mathbf{V} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{6}} \\ \frac{1}{\sqrt{3}} & 0 & -\frac{2}{\sqrt{6}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{6}} \end{pmatrix}$$

$$k = 3,62 \times 10^5$$

$$\overline{\nu} = 609$$

$$k = 15,7 \times 10^5$$

$$\lambda = 5297$$

$$k = 1160$$

35

$$\overline{\nu}_{1\,H^{35}Cl} = 2938$$

n

$$\overline{\nu}_{n\,H^{35}Cl} = 1743$$

$n = 3$

6×6

m_X

m_Y

$$k_{CO} = 1602$$

$$\overline{\nu} = 2300$$

$$\overline{\nu}_{sym} = \frac{1}{2\pi c}\sqrt{\frac{k}{m_X}}$$

$$\overline{\nu}_{anti} = \frac{1}{2\pi c}\sqrt{k\frac{m_Y+2m_X}{m_Y m_X}}$$

• • •

Z

E_i

$$P_i \sim \exp\left(-\frac{E_i}{k_B T}\right)$$

$$k_B = 1,3806 \times 10^{-23}$$

$$R = 8,3145$$

$$P_i \sim \exp\left(-\frac{E_i}{RT}\right)$$

$$N_A = 6,02214 \times 10^{23}$$

$$P_i = \frac{\exp\left(-\frac{E_i}{RT}\right)}{Q}$$

$$Q = \sum_{j=1}^{Z} \exp\left(-\frac{E_j}{k_B T}\right)$$

g_i

$$P_i = \frac{g_i \exp\left(-\frac{E_i}{k_B T}\right)}{Q}$$

$$Q = \sum_{j=1}^{Z} g_j \exp\left(-\frac{E_j}{k_B T}\right)$$

$$P(\mathbf{x},\mathbf{p})d^n\mathbf{x}d^n\mathbf{p} = \frac{\exp\left(-\frac{E(\mathbf{x},\mathbf{p})}{k_BT}\right)d^n\mathbf{x}d^n\mathbf{p}}{Q}$$

$$Q = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \exp\left(-\frac{E(\mathbf{x},\mathbf{p})}{k_B T}\right) d^n\mathbf{x} d^n\mathbf{p}$$

$$P(E)dE = \frac{\Omega(E)\exp\left(-\frac{E}{k_B T}\right) dE}{Q}$$

$$Q = \int_{-\infty}^{\infty} \Omega(E) \exp\left(-\frac{E}{k_B T}\right) dE$$

$$\Omega(E)$$

$$\frac{P_{II}}{P_I} = \frac{g_{II}\exp\left(-\frac{E_{II}}{k_BT}\right)}{g_I\exp\left(-\frac{E_I}{k_BT}\right)} = \frac{g_{II}}{g_I}\exp\left(-\frac{E_{II}-E_I}{k_BT}\right) = \frac{g_{II}}{g_I}\exp\left(-\frac{\Delta E}{k_BT}\right)$$

$$\Delta S = k_B \ln \frac{g_{II}}{g_I}$$

$$\Delta F = \Delta E - T\Delta S$$

$$\frac{P_{II}}{P_I} = \exp\left(-\frac{\Delta F}{k_B T}\right) = K_{I \to II}$$

R

k_B

$$T = 298$$

$$\frac{x_{enol}}{x_{keton}} = \exp\left(-\frac{E_{enol} - E_{keton}}{RT}\right) = \exp\left(-\frac{\Delta E}{RT}\right)$$

$$\Delta E$$

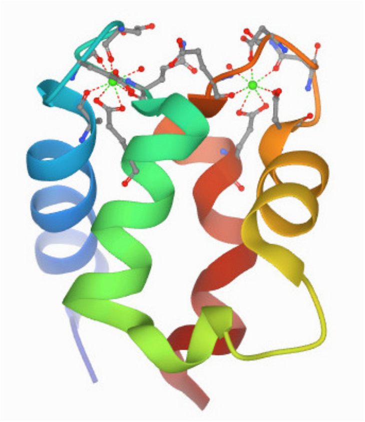
$$\Delta E = 1,2 \times 4184 = 5023,2$$

$$x_{enol}/x_{keton} = 0,1317$$

$$x_{keton} = 1 - x_{enol}$$

$$\frac{x_{enol}}{1 - x_{enol}} = 0,1317$$

$$x_{enol} = \frac{0,1317}{1 + 0,1317} = 0,1163 \approx 11,6\ \%$$



nzw

zw

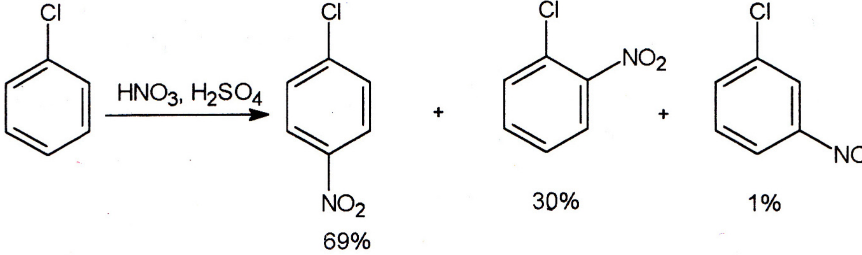
$$\Delta E = E_{zw} - E_{nzw}$$

t_{zw}

t_{nzw}

$$\frac{P_{zw}}{P_{nzw}} = \frac{t_{zw}}{t_{nzw}} = \frac{368}{632} = \exp\left(-\frac{\Delta F}{RT}\right)$$

$$\Delta F = -RT \ln\left(\frac{t_{zw}}{t_{nzw}}\right) = -8,3145 \times 298 \ln 0,5823 = 1340 \ \frac{\text{J}}{\text{mol}} = 0,32 \ \frac{\text{kcal}}{\text{mol}}$$



$$x_o$$

x_m

x_p

$$\Delta E_{o-p} = E_o - E_p$$

$$\Delta E_{m-p} = E_m - E_p$$

$$\frac{x_o}{x_p} = \frac{g_o}{g_p} \exp\left(-\frac{\Delta E_{o-p}}{RT}\right)$$

$$\Delta E_{o-p} = -RT \ln \frac{g_p x_o}{g_o x_p} = -8,3145 \times 298 \times \ln \frac{1 \times 0,3}{2 \times 0,69} = 3806 \ \frac{\mathrm{J}}{\mathrm{mol}} = 0,91 \ \frac{\mathrm{kcal}}{\mathrm{mol}}$$

$$\Delta E_{m-p} = -RT \ln \frac{g_p x_m}{g_m x_p} = -8,3145 \times 298 \times \ln \frac{1 \times 0,01}{2 \times 0,69} = 12290 \ \frac{\mathrm{J}}{\mathrm{mol}} = 2,94 \ \frac{\mathrm{kcal}}{\mathrm{mol}}$$

$$\Delta E_{m-o} = \Delta E_{m-p} - \Delta E_{o-p} = 2,94 - 0,91 = 2,01$$

v

v_x

v_y

v_z

$$E_k = \frac{1}{2} m \left(v_x^2 + v_y^2 + v_z^2 \right) = \frac{1}{2} m v^2$$

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

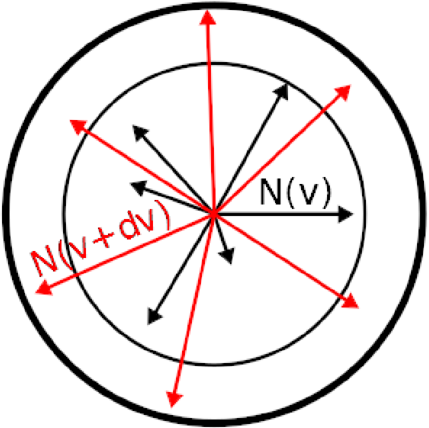
$v + dv$

$$dv$$

$$N(v)$$

$$N(v + dv)$$

$$dN = N(v + dv) - N(v)$$



N(v)
N(v + dv)

$$g(v) = 4\pi v^2 dv$$

$$P(v)dv = \frac{1}{Q} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv$$

Q

$$Q = 4\pi \int_{0}^{\infty} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv$$

$$\int_{0}^{\infty} x^2 \exp\left(-ax^2\right) dx$$

$$a = \frac{m}{2k_B T}$$

$$\frac{d}{da}\int_0^\infty \exp\left(-ax^2\right)dx = -\int_0^\infty x^2\exp\left(-ax^2\right)dx$$

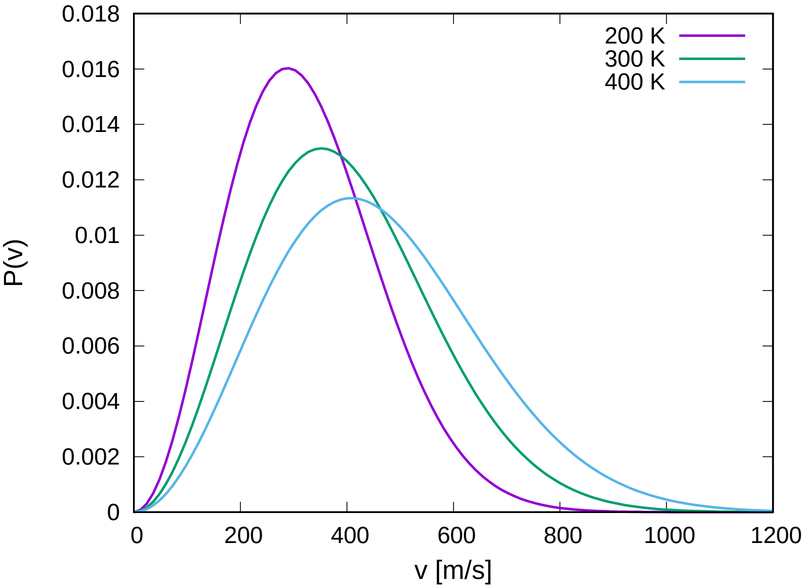
$\pm\infty$

$$\int_{0}^{\infty} x^2 \exp\left(-ax^2\right) dx = \frac{1}{2} \int_{-\infty}^{\infty} x^2 \exp\left(-ax^2\right) dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

$$-\frac{d}{da}\int_{0}^{\infty}\exp\left(-ax^2\right)dx=-\frac{d}{da}\frac{1}{2}\sqrt{\frac{\pi}{a}}=\frac{1}{4}\sqrt{\frac{\pi}{a^3}}$$

$$Q = \sqrt{\left(\frac{2\pi k_B T}{m}\right)^3}$$

$$P(v)dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 \exp\left(-\frac{mv^2}{2k_B T} \right) dv$$


0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
P(v)
0
200
400
600
800
1000
1200
v [m/s]
200 K
300 K
400 K

g_I

g_{II}

$$E_{AQ(II)}$$

$$E_{AQ(I)}$$

$$t = 20°C$$

$$x_{AQ(II)} = 0,59$$

g_I

$$t = 30^\circ$$

$$x_{AK(I)} = 0,80$$

t

g_g

g_t

$t = 25°$

x_g

x_t

E_t

E_g

$$x_t(T) = \frac{\frac{1}{2}\exp\left(-\frac{\Delta E}{RT}\right)}{1+\frac{1}{2}\exp\left(-\frac{\Delta E}{RT}\right)} = \frac{\frac{1}{2}\exp\left(-\frac{480}{T}\right)}{1+\frac{1}{2}\exp\left(-\frac{480}{T}\right)} = \frac{\exp\left(-\frac{480}{T}\right)}{2+\exp\left(-\frac{480}{T}\right)}$$

x_n

E_w

E_n

$^1\Delta_g$

$$^{3}\sum_{g}$$

$$\Delta E = 21$$

g_0

g_1

$$\mathbf{p} = m\mathbf{v}$$

$$p = m\sqrt{v_x^2 + v_y^2 + v_z^2}$$

$$E_k = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

p

$$E = E_k + E_p = \frac{p^2}{2\mu} + \frac{1}{2}kx^2$$

N

V

U

S

TS

pV

'εντροπή

$\tau\rho\acute{\epsilon}\pi\omega$

$$dS = \frac{Q_{el}^{odwr}}{T} = \frac{DQ}{T}$$

H

G

$$H = U + pV$$

$$F = U - TS$$

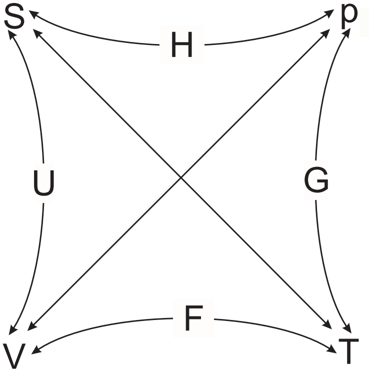
$$G = H - TS$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T; \qquad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

$$\left(\frac{\partial H}{\partial S}\right)_p = T; \qquad \left(\frac{\partial H}{\partial p}\right)_S = V$$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S; \qquad \left(\frac{\partial F}{\partial V}\right)_T = -p$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S; \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$


S
p
H
U
G
F
V
T

$$U \equiv \langle E \rangle = \frac{1}{Q} \sum_{i=1}^{Z} g_i \epsilon_i \exp\left(-\frac{\epsilon_i}{k_B T}\right)$$

$$p = \frac{1}{Q} \sum_{i=1}^{Z} -g_i \frac{\partial \epsilon_i}{\partial V} \exp\left(-\frac{\epsilon_i}{k_B T}\right)$$

ϵ_i

$$Q = Q(N, V, T) = \sum_{i=1}^{Z} g_i \exp\left(-\frac{\epsilon_i}{k_B T}\right)$$

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

$$F = -k_B T \ln Q$$

$$\mu = -\left(\frac{\partial F}{\partial N}\right)_V = -k_B T \left(\frac{\partial \ln Q}{\partial N}\right)_{V,T}$$

$$S = k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q = \frac{U}{T} + k_B \ln Q$$

$$p = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T}$$

$\ln Q$

C_V

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

$$S = \int \frac{C_V}{T} dT$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S$$

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

$$\frac{\partial^2 F}{\partial V \partial T} = -\left(\frac{\partial S}{\partial V}\right)_T$$

$$\frac{\partial^2 F}{\partial T \partial V} = -\left(\frac{\partial p}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left[\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right]_T = T\left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right]_V = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

$$\left(p + \frac{aN^2}{V^2}\right)\left(\frac{V}{N} - b\right) = k_B T$$

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_V = 0$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

$$Q = \sum_{i=1}^{3} g_i \exp\left(-\frac{\epsilon_i}{RT}\right)$$

$$= 1 \times \exp\left(-\frac{0 \times 4184}{8,3145 \times 298}\right) + 3 \times \exp\left(-\frac{1 \times 4184}{8,3145 \times 298}\right) + 5 \times \exp\left(-\frac{3 \times 4184}{8,3145 \times 298}\right)$$

$$Q = 1 + 0,5543 + 0,0315 = 1,5858$$

$$F = -RT \ln Q = -8,3145 \times 298 \times \ln 1,5858 = -1142,44 \text{ J/mol} = -0,27 \text{ kcal/mol}$$

$$E = \frac{1}{Q} \sum_{i=1}^{3} g_i \epsilon_i \exp\left(-\frac{\epsilon_i}{RT}\right) =$$

$$\frac{1}{1,5858}\left[1 \times 0 \times \exp\left(-\frac{0 \times 4184}{8,3145 \times 298}\right) + 3 \times 1 \times \exp\left(-\frac{1 \times 4184}{8,3145 \times 298}\right)\right.$$

$$+5 \times 3 \times \exp\left(-\frac{3 \times 4184}{8,3145 \times 298}\right)\Bigg] =$$

$$\frac{0 + 0,5543 + 0,0945}{1,5858} = \frac{0,6488}{1,5858} = 0,41 \text{ kcal/mol}$$

$$Q = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} V^N$$

$$N! \approx N^N e^{-N} = \left(\frac{N}{e}\right)^N$$

$$Q = \left(\frac{e}{N}\right)^N \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} V^N$$

$$\ln Q = \ln\left(\frac{e}{N}\right)^N + \ln\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} + \ln V^N =$$

$$N \ln\left(\frac{e}{N}\right) + \frac{3N}{2} \ln\left(\frac{2\pi m k_B T}{h^2}\right) + N \ln V =$$

$$N\left[\frac{3}{2}\ln\left(\frac{2\pi m k_B}{h^2}\right)+1+\ln T+\ln V-\ln N\right]$$

$$F = -k_B T \ln Q = -k_B T N \left[\frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{2\pi m k_B}{h^2} \right) + 1 + \ln V - \ln N \right]$$

$$= -Nk_BT\left[\frac{3}{2}\ln\left(\frac{2\pi m k_B}{h^2}\right) + 1 + \frac{3}{2}\ln T\right] + Nk_BT\ln\frac{N}{V}$$

$$E = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right) = k_B T^2 \left(\frac{\partial}{\partial T} \frac{3}{2} N \ln T \right) = k_B T^2 \frac{3N}{2T} = \frac{3}{2} N k_B T$$

$$p = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)$$

$$p = k_B T \left(\frac{\partial}{\partial V} N \ln V \right)$$

$$p = k_B T \frac{N}{V}$$

$$pV = Nk_BT$$

$$N = nN_A$$

$$k_B = R/N_A$$

$$pV = nRT$$

$$\mu = \frac{\partial F}{\partial N} = \frac{\partial}{\partial N}\left(-Nk_BT\left(\frac{3}{2}\ln\frac{2\pi mk_B}{h^2}\right) - \frac{3}{2}\ln T\right) + 1 + \frac{\partial}{\partial N}\left[Nk_BT\left(\ln N - \ln V\right)\right]$$

$$= -k_B T \left(\frac{3}{2} \ln \left(\frac{2\pi m k_B}{h^2} \right) + 1 + \frac{3}{2} \ln T \right) + N \left[k_B T \ln N + k_B T (\ln N + 1) \right] - k_B T \ln V$$

$$= -\frac{3}{2}k_B T \ln\left(\frac{2\pi m k_B T}{h^2}\right) + k_B T \ln \frac{N}{V}$$

$$\mu^\circ(T) = -\frac{3}{2}k_B T \ln\left(\frac{2\pi m k_B T}{h^2}\right)$$

$$C = \frac{N}{V}$$

$$\mu = \mu^{\circ}(T) + k_B T \ln C$$

V_1

$$V_2$$

$$W = \Delta F = -nRT \ln \frac{V_2}{V_1}$$

$\epsilon > 0$

$$T^* = RT/\epsilon$$

$g > 1$

3

$$g = 1$$

$$g = 5$$

$$\Delta\epsilon = \epsilon_w - \epsilon_n = 5,8$$

$t = 90^\circ$

$$E = 39,03$$

$$F = -4,86$$

$$S = 0,1209$$

$$Q = (BT)^{\frac{5N}{2}} \left(\frac{Ve}{N}\right)^{N}$$

$$U = \frac{5}{2} N k_B T$$

$$S = \frac{5}{2}Nk_B + Nk_B\left(\frac{5}{2}\ln(BT) - \ln\frac{N}{V} + 1\right)$$

$$\mu = -\frac{5}{2} k_B T \ln(BT) + k_B T \ln \frac{N}{V}$$

$$Q = \frac{1}{N!}\left[\frac{e^{-\frac{h\upsilon}{2k_BT}}}{1-e^{-\frac{h\nu}{k_BT}}}\right]^N$$

$$U = \frac{Nh\nu}{2} + \frac{Nh\nu}{e^{\frac{h\nu}{k_B T}} - 1}$$

Δ

ν

$$\Theta_{osc} = h\nu / k_B$$

$$\epsilon_n = h\nu \left(n + \frac{1}{2} \right), \quad n = 0, 1, 2, ...$$

$$Q = \frac{\exp\left(-\frac{h\nu}{2k_BT}\right)}{1-\exp\left(-\frac{h\nu}{k_BT}\right)} = \frac{\exp\left(-\frac{\Theta_v}{2T}\right)}{1-\exp\left(-\frac{\Theta_v}{T}\right)}$$

$$E = \frac{h\nu}{2} + \frac{h\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} = \frac{k_B \Theta_v}{2} + \frac{k_B \Theta_\nu}{\exp\left(\frac{\Theta_\nu}{T}\right) - 1}$$

$x_1, x_2, \ldots, x_n$

$\overline{x}$

σ_x

$$\overline{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \quad \sigma_x = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(x_i - \overline{x}\right)^2} = \sqrt{\frac{1}{n(n-1)}\left[n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2\right]}$$

$$\sigma_x^2$$

$$\sigma_{\overline{x}} = \frac{\sigma_x}{\sqrt{n}}$$

$$\sigma_E^2 = \frac{1}{Q} \sum_{i=1}^{Z} g_i (\epsilon_i - \overline{E})^2 \exp\left(-\frac{\epsilon_i}{k_B T}\right)$$

$$= \frac{1}{Q}\sum_{i=1}^{Z} g_i \epsilon_i^2 \exp\left(-\frac{\epsilon_i}{k_B T}\right) - \left[\frac{1}{Q}\sum_{i=1}^{Z} g_i \epsilon_i \exp\left(-\frac{\epsilon_i}{k_B T}\right)\right]^2 = k_B T^2 \frac{\partial \overline{E}}{\partial T} = k_B T^2 C_V$$

$$C_V = \frac{1}{k_B T^2}\sigma_E^2$$

$$\left(\frac{\sigma_N}{N}\right)^2 = \left(\frac{\sigma_p}{p}\right)^2 = \frac{k_b T \kappa}{V}$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)$$

$$= 1 \times \exp\left(-\frac{0 \times 4184}{8,3145 \times 298}\right) + 3 \times \exp\left(-\frac{1 \times 4184}{8,3145 \times 298}\right)$$

$$+5 \times \exp\left(-\frac{3 \times 4184}{8,3145 \times 298}\right) 1 + 0,5543 + 0,0315 = 1,5858$$

$$\frac{1}{1,5858}\left[1 \times 0 \times \exp\left(-\frac{0 \times 4184}{8,3145 \times 298}\right) + 3 \times 1 \times \exp\left(-\frac{1 \times 4184}{8,3145 \times 298}\right)\right.$$

$$\frac{0 + 0,5543 + 0,0946}{1,5858} = \frac{0,6488}{1,5858} = 0,4092 \text{ kcal/mol}$$

$$\overline{E^2} = \frac{1}{Q} \sum_{i=1}^{3} g_i \epsilon_i^2 \exp\left(-\frac{\epsilon_i}{RT}\right) =$$

$$\frac{0 + 0,5543 + 0,2835}{1,5858} = 0,5283 \text{ (kcal/mol)}^2$$

$$\sigma_E^2 = \overline{E^2} - \overline{E}^2 = 0,5283 - 0,4092^2 = 0,3609 \text{ (kcal/mol)}^2$$

$$C_V = \frac{\sigma_E^2}{RT^2} = \frac{0,3609}{1,9872 \times 10^{-3} \times 298^2} = 2,05 \times 10^{-3} \ \text{kcal/(mol} \times \text{K)}$$

$$R = 1,9872 \times 10^{-3}$$

$$E = \frac{3}{2} N k_B T$$

$$C_V = \frac{\partial E}{\partial T} = \frac{3}{2} N k_B$$

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial p} = \frac{N k_B T}{V p^2} = \frac{1}{p}$$

$$g = 10$$

$$C_V = \frac{g\epsilon^2 \exp\left(-\frac{\epsilon}{RT}\right)}{RT^2 \left[1 + g\exp\left(-\frac{\epsilon}{RT}\right)\right]^2}$$

C_V

$$C_V^* = \frac{g \exp\left(-\frac{1}{T^*}\right)}{T^{*2}\left[1 + g \exp\left(-\frac{1}{T^*}\right)\right]^2}$$

$$C_V = \frac{5}{2} N k_B$$

$$C_V = \frac{N(h\nu)^2}{k_B T^2 \left(e^{\frac{h\nu}{k_B T}} - 1\right)^2}$$

$$Q = \frac{1}{N!} q^N$$

q

$$1/N!$$

$$\epsilon_{ijk} = \epsilon_{ti} + \epsilon_{ej} + \epsilon_{nk}$$

$$q = q_t q_e q_n$$

$$\epsilon_{ti}$$

ϵ_{ej}

ϵ_{nk}

$$q_n = \omega_{n\circ}.$$

ω_{e0}

$\omega_{e1}, \ldots$

$\Delta\epsilon_1$

$\Delta\epsilon_2 \ldots$

$$q_e = \omega_\circ + \omega_1 \exp\left(-\beta\Delta\epsilon_1\right) + \omega_2 \exp\left(-\beta\Delta\epsilon_2\right) \ldots$$

$$\beta = 1/k_B T$$

$$\beta = 1/RT$$

$$P_{ei} = \frac{\omega_{ei} \exp\left(-\frac{\Delta\epsilon_{ei}}{k_B T}\right)}{q_e}$$

$$q_t = \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} V$$

$N!$

$$Q = Q(N, V, T) = \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} \left(\frac{Ve}{N} \right)^N \times$$

$$\times \left[\omega_{e\circ} + \omega_{e1} \exp\left(-\frac{\Delta\epsilon_{e1}}{k_B T}\right) + \omega_{e2} \exp\left(-\frac{\Delta\epsilon_{e2}}{k_B T}\right) + \ldots\right]^N \times \omega_{n\circ}^N$$

$$q_n = 1$$

$$U = \frac{3}{2}Nk_BT + N\frac{\Delta\epsilon_1\omega_{e1}\exp\left(-\frac{\Delta\epsilon_{e1}}{k_BT}\right) + \Delta\epsilon_2\omega_{e2}\exp\left(-\frac{\Delta\epsilon_{e2}}{k_BT}\right) + \dots}{\omega_{e\circ} + \omega_{e1}\exp\left(-\frac{\Delta\epsilon_{e1}}{k_BT}\right) + \omega_{e2}\exp\left(-\frac{\Delta\epsilon_{e2}}{k_BT}\right) + \dots}$$

$$C_V = \frac{3}{2}Nk_B + N\frac{\Delta\epsilon_1^2\omega_{e1}\exp\left(-\frac{\Delta\epsilon_{e1}}{k_BT}\right) + \Delta\epsilon_2^2\omega_{e2}\exp\left(-\frac{\Delta\epsilon_{e2}}{k_BT}\right) + \ldots}{k_BT^2\left[\omega_{e\circ} + \omega_{e1}\exp\left(-\frac{\Delta\epsilon_{e1}}{k_BT}\right) + \omega_{e2}\exp\left(-\frac{\Delta\epsilon_{e2}}{k_BT}\right) + \ldots\right]}$$

$$-N\frac{\left[\Delta\epsilon_1\omega_{e1}\exp\left(-\frac{\Delta\epsilon_{e1}}{k_BT}\right)+\Delta\epsilon_2\omega_{e2}\exp\left(-\frac{\Delta\epsilon_{e2}}{k_BT}\right)+\ldots\right]^2}{k_BT^2\left[\omega_{e\circ}+\omega_{e1}\exp\left(-\frac{\Delta\epsilon_{e1}}{k_BT}\right)+\omega_{e2}\exp\left(-\frac{\Delta\epsilon_{e2}}{k_BT}\right)+\ldots\right]^2}$$

$$C_V = \frac{3}{2}Nk_B + N\frac{\Delta\epsilon_1^2\omega_{e\circ}\omega_{e1}\exp\left(-\frac{\Delta\epsilon_{e1}}{k_BT}\right)}{k_BT^2\left[\omega_{e\circ} + \omega_{e1}\exp\left(-\frac{\Delta\epsilon_{e1}}{k_BT}\right)\right]^2}$$

$$\epsilon_{ijklm} = \epsilon_{ti} + \epsilon_{rj} + \epsilon_{\nu k} + \epsilon_{el} + \epsilon_{nm}$$

$$q = q_t q_r q_\nu q_e q_n$$

ϵ_{rj}

$\epsilon_{\nu k}$

ϵ_{el}

ϵ_{nm}

$$m_1 + m_2$$

$$q_t = \left[\frac{2\pi(m_1 + m_2)k_B T}{h^2}\right]^{\frac{3}{2}} V$$

$$\epsilon_e = \epsilon_{e\circ} = -D_e$$

$$q_e = \omega_{e\circ} \exp\left(\frac{D_e}{k_B T}\right)$$

$$\epsilon_n = h\nu\left(n + \frac{1}{2}\right),\ n = 0, 1, 2, \ldots$$

$$q_\nu = \sum_{n=0}^{\infty} a_\circ r^n$$

$$a_\circ = \exp\left(-\frac{h\nu}{2k_B T}\right)$$

$$r = \exp\left(-\frac{h\nu}{k_B T}\right)$$

$$q_\nu = \frac{\exp\left(-\frac{h\nu}{2k_B T}\right)}{1 - \exp\left(-\frac{h\nu}{k_B T}\right)}$$

$$\Theta_\nu = \frac{h\nu}{k_B}$$

q_{ν}

$$q_\nu = \frac{\exp\left(-\frac{\Theta_\nu}{2T}\right)}{1 - \exp\left(-\frac{\Theta_\nu}{T}\right)}$$

$$P_n = \frac{\exp\left[-\frac{\Theta_\nu\left(n+\frac{1}{2}\right)}{T}\right]}{q_\nu} = \left[1 - \exp\left(-\frac{\Theta_\nu}{T}\right)\right] \exp\left(-\frac{n\Theta_\nu}{T}\right)$$

J

$$\epsilon_J = \frac{h^2}{8\pi^2 I} J(J+1) = \overline{B} J(J+1), \;\; J = 0, 1, 2 \ldots$$

$$\overline{B} = \frac{h^2}{8\pi^2 I}$$

$$I = \mu d^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

I

$$\overline{B}$$

$$2J + 1$$

$$q_r = \sum_{J=0}^{\infty} (2J+1) \exp\left[-\frac{\overline{B}J(J+1)}{k_B T}\right]$$

$$q_r = \frac{T}{\Theta_r}$$

$$\Theta_r = \frac{h^2}{8\pi^2 I k_B}$$

Θ_r

$$P_J = \frac{(2J+1)\exp\left[-\frac{\Theta_r}{T}J(J+1)\right]}{q_r}$$

$$Q = \left[\frac{2\pi(m_1+m_2)k_BT}{h^2}\right]^{\frac{3N}{2}} \left(\frac{Ve}{N}\right)^N \times \left(\frac{T}{\Theta_r}\right)^N \times$$

$$\times \frac{\exp\left(-\frac{N\Theta_\nu}{2T}\right)}{\left[1-\exp\left(-\frac{\Theta_\nu}{T}\right)\right]^N} \times \omega_{e\circ} \exp\left(\frac{ND_e}{k_B T}\right) \times \left[(2S_1+1)(2S_2+1)\right]^N$$

S_1

S_2

$$D_{\circ} = D_e - \frac{1}{2}h\nu$$

$$Q = \left[\frac{2\pi(m_1+m_2)k_B T}{h^2}\right]^{\frac{3N}{2}} \left(\frac{Ve}{N}\right)^N \times \left(\frac{T}{\Theta_r}\right)^N \times \left[1-\exp\left(-\frac{\Theta_\nu}{T}\right)\right]^{-N} \times$$

$$\omega_{e\circ} \exp\left(\frac{ND_\circ}{k_B T}\right) \times \left[(2S_1+1)(2S_2+1)\right]^N$$

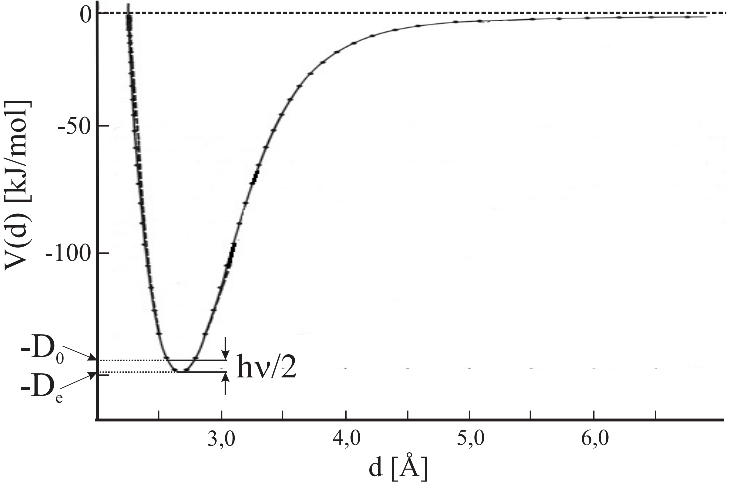
$-D_\circ$

$$\frac{1}{2}h\nu$$

D_e

$D_{\circ}$

$$D_e - D_\circ = 1,3$$



0
-50
-100
-D0
-De
hν/2
V(d) [kJ/mol]
3,0
4,0
5,0
6,0
d [Å]

$$U = \frac{5}{2} N k_B T + \frac{N h \nu}{2} + \frac{N h \nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} - N D_e$$

$$= \frac{5}{2} N k_B T + \frac{N h \nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} - N D_\circ = \frac{5}{2} N k_B T + \frac{N k_B \Theta_\nu}{\exp\left(\frac{\Theta_\nu}{T}\right) - 1} - N D_\circ$$

$$C_V = \frac{5}{2} N k_B + N k_B \left(\frac{h\nu}{k_B T} \right)^2 \frac{\exp\left(\frac{h\nu}{k_B T}\right)}{\left[\exp\left(\frac{h\nu}{k_B T}\right) - 1\right]^2} =$$

$$\frac{5}{2}Nk_B + Nk_B\left(\frac{\Theta_\nu}{T}\right)^2 \frac{\exp\left(\frac{\Theta_\nu}{T}\right)}{\left[\exp\left(\frac{\Theta_\nu}{T}\right) - 1\right]^2}$$

$$\frac{5}{2}k_BT$$

$\frac{5}{2} k_B$

$$\frac{3}{2}k_BT$$

$$\frac{2}{2}k_B T$$

$$\frac{3}{2}k_B$$

$$\frac{2}{2}k_B$$

$$\frac{1}{2}k_B T$$

$\frac{1}{2}k_B$

$$\Delta\epsilon = 0,05$$

$^3P_{3/2}$

$$^2P_{1/2}$$

$$\omega_\circ = 4$$

$$\omega_1 = 2$$

$$T = 400$$

$$0,05 \times 96590,5 = 4830$$

q_{el}

$$q_{el} = 4 + 2\exp\left(-\frac{4830}{8,3145 \times 298}\right) = 4 + 2 \times 0,14235 = 4,2847$$

$$P_1 = \frac{0,2847}{4,2847} = 0,066 = 6,6\ \%$$

$$q_{el} = 4 + 2\exp\left(-\frac{4830}{8,3145 \times 400}\right) = 4 + 2 \times 0,2340 = 4,4680$$

$$P_1 = \frac{0,4680}{4,4680} = 0,105 = 10,5\ \%$$

$$U_t = \frac{3}{2}nRT = \frac{3}{2} \times 1 \times 8,3145 \times 400 = 4989 \text{ J}$$

$$C_{Vt} = \frac{3}{2}nR = \frac{3}{2} \times 1 \times 8,3145 = 12,47 \text{ J/K}$$

$$U_e = n\frac{\Delta\epsilon_1 \omega_1 \exp\left(-\frac{\Delta\epsilon_1}{RT}\right)}{q_e} = 1 \times \frac{4830 \times 2 \times 0,2340}{4,4680} = 506 \text{ J}$$

$$C_{Ve} = n\frac{\Delta\epsilon_1^2\omega_\circ\omega_1 \exp\left(-\frac{\Delta\epsilon_1}{RT}\right)}{RT^2 q_e^2} = 1 \times \frac{4830^2 \times 4 \times 2 \times 0,2340}{8,3145 \times 400^2 \times 4,4680^2} = 1,64 \text{ J/K}$$

$$U = U_t + U_e = 4989 + 506 = 5495 \text{ J} = 1,31 \text{ kcal}$$

$$C_V = C_{Vt} + C_{Ve} = 12,47 + 1,64 = 14,11 \text{ J/K} = 3,37 \text{ cal/K}$$

1

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2} = \frac{1 \times 35}{1 + 35} = \frac{35}{36} = 0,9722 \text{ g/mol} = 1,6145 \times 10^{-27} \text{ kg}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2 \times 3,14159}\sqrt{\frac{490}{1,6145 \times 10^{-27}}} = 8,7680 \times 10^{13} \ \ 1/\mathrm{s}$$

$$I = \mu d^2 = 1,6145 \times 10^{-27} \times \left(1,29 \times 10^{-10}\right)^2 = 2,6867 \times 10^{-47}\ \mathrm{kg} \times \mathrm{m}^2$$

$$\Theta_\nu = \frac{h\nu}{k_B} = \frac{6,63 \times 10^{-34} \times 8,7680 \times 10^{13}}{1,38 \times 10^{-23}} = 4212,4 \text{ K}$$

$$\Theta_r = \frac{h^2}{8\pi^2 I k_B} = \frac{\left(6,63 \times 10^{-34}\right)^2}{8 \times 3,14159^2 \times 2,6867 \times 10^{-47} \times 1,38 \times 10^{-23}} = 15\ \mathrm{K}$$

$n > 0$

$$J = 1$$

$J > 0$

$$\Theta_\nu$$

$$\Theta_{rot}$$

$$P_n = \frac{\exp\left[\left(-\frac{\Theta_\nu}{T}\right)\left(n + \frac{1}{2}\right)\right]}{q_\nu}$$

$$q_\nu = \frac{\exp\left(-\frac{\Theta_\nu}{2T}\right)}{1 - \exp\left(-\frac{\Theta_\nu}{T}\right)}$$

$$P_n = \frac{\exp\left[\left(-\frac{\Theta_\nu}{T}\right)\left(n+\frac{1}{2}\right)\right]}{\frac{\exp\left(-\frac{\Theta_\nu}{2T}\right)}{1-\exp\left(-\frac{\Theta_\nu}{T}\right)}} = \exp\left(-\frac{n\Theta_\nu}{T}\right)\left[1-\exp\left(-\frac{\Theta_\nu}{T}\right)\right]$$

$$P_1 = \exp\left(-\frac{1 \times 4212,4}{298}\right)\left[1 - \exp\left(-\frac{4212,4}{298}\right)\right] = 7 \times 10^{-7}$$

$$n = 0$$

$$P_{n>0} = 1 - P_0 = 1 - \exp\left(-\frac{0 \times \Theta_\nu}{T}\right)\left[1 - \exp\left(-\frac{\Theta_\nu}{T}\right)\right] = \exp\left(-\frac{\Theta_\nu}{T}\right)$$

$$= \exp\left(-\frac{4212,4}{298}\right) = 7 \times 10^{-7}$$

$$P_J = \frac{\exp\left[\left(-\frac{\Theta_{rot}}{T}\right)(J+1)\,J\right](2J+1)}{q_{rot}}$$

$$q_{rot} \approx \frac{T}{\Theta_{rot}} = \frac{298}{15} = 19,8667$$

$$P_1 = \frac{\exp\left[\left(-\frac{15}{298}\right)(1+1)\,1\right](2\times 1+1)}{19,8667} = \frac{2,7127}{19,8667} = 0,14$$

$$P_{J>0} = 1 - P_0 = 1 - (2 \times 0 + 1)\frac{\exp\left[-\frac{\Theta_r}{T}0(0+1)\right]}{q_r} \approx 1 - \frac{\Theta_r}{T} = \frac{T - \Theta_r}{T}$$

$$P_{J>0} = \frac{298 - 15}{298} = 0,95$$

$$T >> \Theta_r$$

$$t = 1330^\circ$$

$$\omega_\circ = 2$$

$^2S_{1/2}$

$$\omega_1 = 2$$

$$\Delta\epsilon_1 = 1,85$$

$$^2P_{1/2}$$

$$\omega_2 = 4$$

$$\Delta\epsilon_2 = 1,85$$

$^2P_{3/2}$

$$x_1 = P_1 = 1,5 \times 10^{-6}$$

$$x_2 = P_2 = 3,0 \times 10^{-6}$$

$$T = 2000$$

$$\omega_0 = 1$$

$^3P_0$

$$\omega_1 = 3$$

$$\Delta\epsilon_1 = 20,2$$

$^3D_1$

$$U = 26,488$$

$$U_e = 1,544$$

$$C_V = 16,32$$

$$C_{Ve} = 3,85$$

d_{HH}

$$k = 550$$

d_{NO}

$k = 1570$

37

d_{ClCl}

$$k = 320$$

$$\nu_{^1\mathrm{H}^2\mathrm{H}} = 1,1218 \times 10^{14}$$

$$I_{^1\mathrm{H}^2\mathrm{H}} = 6,0624 \times 10^{-48}\mathrm{kg} \times \mathrm{m}^2$$

$$\Theta_{\nu}^{^1\mathrm{H}^2\mathrm{H}} = 5386,4$$

$$\Theta_r^{^1\mathrm{H}^2\mathrm{H}} = 66,5$$

$$\nu_{\mathrm{NO}} = 5,6634 \times 10^{13}$$

$$I_{\mathrm{NO}} = 1,6398 \times 10^{-46}$$

$$\Theta_{\nu}^{\mathrm{NO}} = 2719,3$$

$$\Theta_r^{\mathrm{NO}} = 2,45$$

$$\nu_{^{35}\mathrm{Cl}^{37}\mathrm{Cl}} = 1,6474 \times 10^{13}$$

$$I_{^{35}\mathrm{Cl}^{37}\mathrm{Cl}} = 1,1828 \times 10^{-45} \mathrm{kg} \times \mathrm{m}^2$$

$$\Theta_{\nu}^{^{35}\mathrm{Cl}^{37}\mathrm{Cl}} = 791,0$$

$$\Theta_r^{^{35}\mathrm{Cl}^{37}\mathrm{Cl}} = 0,34$$

$$\Theta_{\nu}^{H_2}$$

$$\Theta_r^{\mathrm{H}_2}$$

$\Theta_{\nu}^{Cl_2}$

$$\Theta_r^{\mathrm{Cl}_2}$$

$\Theta_{\nu}^{\mathrm{HCl}}$

$$\Theta_r^{\mathrm{HCl}}$$

$$\Theta_r^{\mathrm{Cl2}} < \Theta_r^{\mathrm{HCl}} < \Theta_r^{\mathrm{H_2}} < \Theta_\nu^{\mathrm{Cl_2}} < \Theta_\nu^{\mathrm{HCl}} < \Theta_\nu^{\mathrm{H_2}}$$

$$T = 404$$

$$P(n = 1) = 0,12$$

$$P(n > 0) = 0,14$$

$$P(J=1)=0,0025$$

$$P(J > 0) = 0,9992$$

$$T = \Theta_r$$

$$T = 2\Theta_r$$

$$T = 10\Theta_r$$

$$q = T/\Theta_r$$

$$T = \Theta_r$$

$$q_r = 1,42$$

$$q_r \approx 1$$

$$T = 2\Theta_r$$

$$q_r = 2,37$$

$$q_r \approx 2$$

$$T = 10\Theta_r$$

$$q_r = 10,34$$

$$q_r \approx 10$$

$$q = \sum_{ijklm} \exp\left(-\frac{\epsilon_{ijklm}}{k_B T}\right)$$

$$q = q_t q_r q_\nu q_e q_n$$

$$q = q_t q_{rn} q_\nu q_e$$

q_{rn}

$$(S+1)(2S+1)$$

$$S(2S+1)$$

$$q_{rn} = \begin{cases} S(2S+1) \sum\limits_{\substack{J \\ parzyste}} (2J+1) \exp\left[-\frac{J(J+1)\Theta_r}{T}\right] + \\ (S+1)(2S+1) \sum\limits_{\substack{J \\ nieparzyste}} (2J+1) \exp\left[-\frac{J(J+1)\Theta_r}{T}\right] \quad S \text{ niecalkowita} \\ \\ (S+1)(2S+1) \sum\limits_{\substack{J \\ parzyste}} (2J+1) \exp\left[-\frac{J(J+1)\Theta_r}{T}\right] + \\ S(2S+1) \sum\limits_{\substack{J \\ nieparzyste}} (2J+1) \exp\left[-\frac{J(J+1)\Theta_r}{T}\right] \quad S \text{ calkowita} \end{cases}$$

$$\sum_{\substack{J \\ parzyste}} (2J+1)\exp\left[-\frac{J(J+1)\Theta_r}{T}\right] \approx \sum_{\substack{J \\ nieparzyste}} (2J+1)\exp\left[-\frac{J(J+1)\Theta_r}{T}\right]$$

$$\approx \frac{1}{2} \sum_{wszystkie\ J} (2J+1) \exp\left[-\frac{J(J+1)\Theta_r}{T}\right]$$

$$q_{rn} \approx [S(2S+1)+(S+1)(2S+1)]\frac{1}{2}\sum_J (2J+1)\exp\left[-\frac{J(J+1)\Theta_r}{T}\right] =$$

$$(2S+1)^2 \frac{T}{2\Theta_r} = q_n \frac{T}{\sigma\Theta_r} = q_n q_r$$

$$q_n = (2S+1)^2$$

$$\sigma = 2$$

$$q_r = \frac{T}{\sigma \Theta_r}$$

$$Q = \left[\frac{2\pi(m_1 + m_2)k_B T}{h^2}\right]^{\frac{3N}{2}} \left(\frac{Ve}{N}\right)^N \times \left(\frac{T}{\sigma\Theta_r}\right)^N \times$$

$$\frac{\exp\left(-\frac{N\Theta_\nu}{2T}\right)}{\left[1-\exp\left(-\frac{\Theta_\nu}{T}\right)\right]^N} \times \omega_{e\circ}^N \exp\left(\frac{ND_e}{k_B T}\right) =$$

$$\left[\frac{2\pi(m_1+m_2)k_BT}{h^2}\right]^{\frac{3N}{2}} \left(\frac{Ve}{N}\right)^N \times \left(\frac{T}{\sigma\Theta_r}\right)^N \times \left[1-\exp\left(-\frac{\Theta_\nu}{T}\right)\right]^{-N} \times$$

$$\omega_{e\circ}^{N} \exp\left(\frac{N D_\circ}{k_B T}\right)$$

Θ_{ν}

$$D_\circ = D_e - \frac{1}{2}h\nu$$

$$= \frac{5}{2} N k_B T + \frac{N h\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} - N D_\circ = \frac{5}{2} N k_B T + \frac{N k_B \Theta_\nu}{\exp\left(\frac{\Theta_\nu}{T}\right) - 1} - N D_\circ$$

$$C_V = \frac{5}{2} N k_B + \frac{N (h\nu)^2 \exp\left(\frac{h\nu}{k_B T}\right)}{k_B T^2 \left[\exp\left(\frac{h\nu}{k_B T}\right) - 1\right]^2} = \frac{5}{2} N k_B + N k_B \left(\frac{\Theta_\nu}{T}\right)^2 \frac{\exp\left(\frac{\Theta_\nu}{T}\right)}{\left[\exp\left(\frac{\Theta_\nu}{T}\right) - 1\right]^2}$$

$$q_\nu = \prod_{i=1}^{\alpha} \frac{\exp\left(-\frac{h\nu_i}{2k_BT}\right)}{1 - \exp\left(-\frac{h\nu_i}{k_BT}\right)}$$

$$\alpha = 3n - 5$$

$$\alpha = 3n - 6$$

$$I = \sum_{i=1}^{n} m_i \left(x_i - x_{CM}\right)^2$$

$$x_{CM} = \frac{\sum_{i=1}^{n} m_i x_i}{\sum_{i=1}^{n} m_i}$$

m_i

$$\mathbf{I} = \begin{pmatrix} \sum_{i=1}^{n} r_i^2 - \left(x_i - x_{CM}\right)^2 & \sum_{i=1}^{n} \left(x_i - x_{CM}\right)\left(y_i - y_{CM}\right) & \sum_{i=1}^{n} \left(x_i - x_{CM}\right)\left(z_i - z_{CM}\right) \\ \sum_{i=1}^{n} \left(y_i - y_{CM}\right)\left(x_i - x_{CM}\right) & \sum_{i=1}^{n} r_i^2 - \left(y_i - y_{CM}\right)^2 & \sum_{i=1}^{n} \left(y_i - y_{CM}\right)\left(z_i - z_{CM}\right) \\ \sum_{i=1}^{n} \left(z_i - z_{CM}\right)\left(x_i - x_{CM}\right) & \sum_{i=1}^{n} \left(z_i - z_{CM}\right)\left(y_i - y_{CM}\right) & \sum_{i=1}^{n} r_i^2 - \left(z_i - z_{CM}\right)^2 \end{pmatrix} =$$

$$\begin{pmatrix} \mathbf{V}_A & \mathbf{V}_B & \mathbf{V}_C \end{pmatrix} \begin{pmatrix} I_A & & \\ & I_B & \\ & & I_C \end{pmatrix} \begin{pmatrix} \mathbf{V}_A & \mathbf{V}_B & \mathbf{V}_C \end{pmatrix}^T$$

x_{CM}

y_{CM}

z_{CM}

r_i

$$I_A$$

$$I_B$$

I_C

$\mathbf{V}_A$

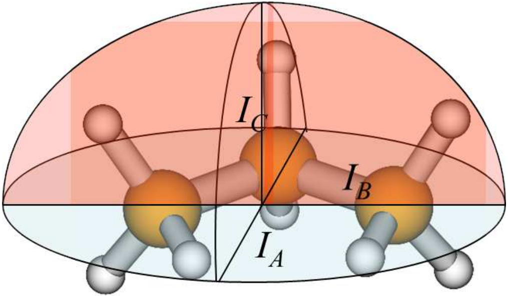
$$\mathbf{V}_B$$

$$\mathbf{V}_C$$

$$x_{CM} = \frac{\sum_{i=1}^{n} m_i x_i}{m}, \quad y_{CM} = \frac{\sum_{i=1}^{n} m_i y_i}{m}, \quad z_{CM} = \frac{\sum_{i=1}^{n} m_i z_i}{m}$$

$$r_i = \sqrt{(x_i - x_{CM})^2 + (y_i - y_{CM})^2 + (z_i - z_{CM})^2}$$

$$m = \sum_{i=1}^{n} m_i$$



I_C
I_B
I_A

$$q_r = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{8\pi^2 I_A k_B T}{h^2}}\sqrt{\frac{8\pi^2 I_B k_B T}{h^2}}\sqrt{\frac{8\pi^2 I_C k_B T}{h^2}} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_A \Theta_B \Theta_C}}$$

Θ_A

Θ_B

Θ_C

$$\Theta_X = \frac{8\pi^2 I_X k_B}{h^2}$$

X

$$Q = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} \left(\frac{Ve}{N}\right)^N \times \left(\frac{T}{\sigma\Theta_r}\right)^N \times$$

$$\left[\prod_{i=1}^{3n-5} \frac{\exp\left(-\frac{\Theta_{\nu i}}{2T}\right)}{1-\exp\left(-\frac{\Theta_{\nu i}}{T}\right)}\right]^N \times \omega_{e\circ}^N \exp\left(\frac{ND_e}{k_B T}\right) =$$

$$\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} \left(\frac{Ve}{N}\right)^N \times \left(\frac{T}{\sigma\Theta_r}\right)^N \times \left\{\prod_{i=1}^{3n-5}\left[1-\exp\left(-\frac{\Theta_{\nu i}}{T}\right)\right]\right\}^{-N} \times$$

$$Q = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} \left(\frac{Ve}{N}\right)^N \times \left(\frac{\sqrt{\pi}}{\sigma}\right)^N \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C}\right)^{\frac{N}{2}} \times$$

$$\left[\prod_{i=1}^{3n-6} \frac{\exp\left(-\frac{\Theta_{\nu i}}{2T}\right)}{1-\exp\left(-\frac{\Theta_{\nu i}}{T}\right)}\right]^N \times \omega_{e\circ}^N \exp\left(\frac{ND_e}{k_B T}\right) =$$

$$\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} \left(\frac{Ve}{N}\right)^N \times \left(\frac{\sqrt{\pi}}{\sigma}\right)^N \left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{\frac{N}{2}} \times$$

$$\left\{\prod_{i=1}^{3n-6}\left[1-\exp\left(-\frac{\Theta_{\nu i}}{T}\right)\right]\right\}^{-N} \times \omega_{e\circ}^{N}\exp\left(\frac{ND_{\circ}}{k_B T}\right)$$

$$f = 5$$

$$f = 6$$

$$\alpha = 3n - f$$

f

$k = 5$

$$k = 6$$

$$U = \frac{f}{2} N k_B T + \frac{N h \nu}{2} + N \sum_{i=1}^{\alpha} \frac{h \nu_i}{\exp\left(\frac{h \nu_i}{k_B T}\right) - 1} - N D_e$$

$$= \frac{f}{2} N k_B T + N \sum_{i=1}^{\alpha} \frac{h\nu_i}{\exp\left(\frac{h\nu_i}{k_B T}\right) - 1} - N D_\circ$$

$$= \frac{f}{2} N k_B T + \sum_{i=1}^{\alpha} \frac{\Theta_{\nu i}}{\exp\left(\frac{\Theta_{\nu i}}{T}\right) - 1} - N D_\circ$$

$$C_V = \frac{f}{2}Nk_B + N\sum_{i=1}^{\alpha}\frac{(h\nu_i)^2\exp\left(\frac{h\nu_i}{k_BT}\right)}{k_BT^2\left[\exp\left(\frac{h\nu_i}{k_BT}\right)-1\right]^2}$$

$$= \frac{f}{2} N k_B + N k_B \sum_{i=1}^{\alpha} \left(\frac{\Theta_{\nu i}}{T} \right)^2 \frac{\exp\left(\frac{\Theta_{\nu i}}{T}\right)}{\left[\exp\left(\frac{\Theta_{\nu i}}{T}\right) - 1\right]^2}$$

$$\overline{\nu} = 214$$

$$D_{\circ} = 35,6$$

$$R = N_A k_B$$

$$E = \overbrace{\frac{3n}{2}RT}^{translacyjny} + \overbrace{nRT}^{rotacyjny} + \overbrace{\frac{1}{2}nR\Theta_\nu + \frac{nR\Theta_\nu}{\exp\frac{\Theta_\nu}{T} - 1}}^{oscylacyjny} + \overbrace{-nD_e}^{elektronowy}$$

$$\Theta_\nu = \frac{h\nu}{k_B} = \frac{hc\overline{\nu}}{k_B} = \frac{6,626 \times 10^{-34} \times 3 \times 10^8 \times 2,14 \times 10^4}{1,381 \times 10^{-23}} = 308,0 \text{ K}$$

$$D_e = D_\circ + \frac{1}{2} R\Theta_\nu = 35,6 \times 4184 + \frac{1}{2} \times 8,3145 \times 308,0 = 150231 \text{ J/mol}$$

$$E_t = 1 \times 1,5 \times 8,3145 \times 400 = 4989 \text{ J} = 5,0 \text{ kJ}$$

$$E_r = 1 \times 8,3145 \times 400 = 3326 \text{ J} = 3,3 \text{ kJ}$$

$$E_\nu = 1 \times 0,5 \times 8,3145 \times 308,0 + \frac{8,3145 \times 308,0}{\exp\left(\frac{308,0}{400}\right) - 1} = 3489 \text{ J} = 3,5 \text{ kJ}$$

$$E_e = -1 \times 150231 = -150231 \text{ J} = -150,1 \text{ kJ}$$

$$E = E_t + E_r + E_\nu + E_e = 4989 + 3326 + 3489 - 150231 =$$

$$-138427 \text{ J} = -138,4 \text{ kJ} = -33,1 \text{ kcal}$$

$$C_V = \overbrace{\frac{3n}{2}R}^{translacyjny} + \overbrace{nR}^{rotacyjny} + \overbrace{nR\left(\frac{\Theta_\nu}{T}\right)^2 \frac{\exp\left(\frac{\Theta_\nu}{T}\right)}{\left(\exp\left(\frac{\Theta_\nu}{T}\right)-1\right)^2}}^{oscylacyjny}$$

$$C_{Vt} = 1 \times 1,5 \times 8,3145 = 12,47 \text{ J/K}$$

$$C_{Vr} = 1 \times 8,3145 = 8,31 \text{ J/K}$$

$$C_{V\nu} = 1 \times 8,3145 \left(\frac{308,0}{400} \right)^2 \frac{\exp\left(\frac{308,0}{400}\right)}{\left[\exp\left(\frac{308,0}{400}\right) - 1\right]^2} = 7,92 \text{ J/K}$$

$$C_V = C_{Vt} + C_{Vr} + C_{V\nu} = 12,47 + 8,31 + 7,92 = 28,70 \text{ J/K}$$

$$\Theta_{\nu 1} = \Theta_{\nu 2} = 310$$

$$\Theta_{\nu 3} = \Theta_{\nu 4} = \Theta_{\nu 5} = 450$$

$$\Theta_{\nu 6} = 660$$

$$\Theta_{\nu 7} = \Theta_{\nu 8} = \Theta_{\nu 9} = 1120$$

$$D_{\circ} = 308,8$$

$$E_t = E_r = \frac{3}{2}RT = 1,5 \times 8,3145 \times 500 = 6236 \text{ J} = 6,2 \text{ kJ}$$

$$E_\nu = \frac{R}{2}\sum_{i=1}^{9}\Theta_{\nu i} + R\sum_{i=1}^{9}\frac{\Theta_{\nu i}}{\exp\left(\frac{\Theta_{\nu i}}{T}\right)-1} =$$

$$\frac{8,3145}{2}\left(2\times 310+3\times 450+660+3\times 1120\right)+$$

$$R \times \left(2 \times \frac{310}{\exp\left(\frac{310}{500}\right) - 1} + 3 \times \frac{450}{\exp\left(\frac{450}{500}\right) - 1} + \right.$$

$$\frac{660}{\exp\left(\frac{660}{500}\right)-1}+3\times\frac{1120}{\exp\left(\frac{1120}{500}\right)-1}\Bigg)=24902+19021=43923\ \mathrm{J}=4,4\ \mathrm{kJ}$$

$$E_e = -D_\circ - \frac{R}{2}\sum_{i=1}^{9}\Theta_{\nu i} = -308,8 \times 4184 - 24902 = -1316921 \text{ J} = -1316,9 \text{ kJ} =$$

$$-314,8 \text{ kcal}$$

$$E = E_t + E_r + E_\nu + E_e = 6236 + 6236 + 43923 - 1316921 =$$

$$-1260526 \text{ J} = -1260,5 \text{ kJ} = -301,3 \text{ kcal}$$

$$C_{Vt} = C_{Vr} = \frac{3}{2}R = 1,5 \times 8,3145 = 12,47 \text{ J/K}$$

$$C_{V\nu} = R \sum_{i=1}^{9} \left(\frac{\Theta_{\nu i}}{T} \right)^2 \frac{\exp\left(\frac{\Theta_{\nu i}}{T}\right)}{\left[\exp\left(\frac{\Theta_{\nu i}}{T}\right) - 1\right]^2} =$$

$$8,3145\left\{2 \times \left(\frac{310}{500}\right)^2 \frac{\exp\left(\frac{310}{500}\right)}{\left[\exp\left(\frac{310}{500}\right)-1\right]^2} + 3 \times \left(\frac{450}{500}\right)^2 \frac{\exp\left(\frac{450}{500}\right)}{\left[\exp\left(\frac{400}{500}\right)-1\right]^2} + \right.$$

$$\left(\frac{660}{500}\right)^2 \frac{\exp\left(\frac{660}{500}\right)}{\left[\exp\left(\frac{660}{500}\right)-1\right]^2} + 3 \times \left(\frac{1120}{500}\right)^2 \frac{\exp\left(\frac{1120}{500}\right)}{\left[\exp\left(\frac{1120}{500}\right)-1\right]^2} \Bigg\} = 63,33 \ \mathrm{J/K}$$

$$C_V = C_{Vt} + C_{Vr} + C_{V\nu} = 12,47 + 12,47 + 63,33 = 88,27 \text{ J/K}$$

200°

$$\Delta E = E_p - E_s = 2E_I - E_{I_2}$$

E_{I2}

E_I

e

$$2 \times \frac{3}{2}RT$$

$$\frac{3}{2}RT$$

RT

$$\frac{R\Theta_{\nu}}{2} + \frac{R\Theta_{\nu}}{\exp\left(\frac{\Theta_{\nu}}{T}\right) - 1}$$

$$-RT$$

$$-\frac{R\Theta_\nu}{2} - \frac{R\Theta_\nu}{\exp\left(\frac{\Theta_\nu}{T}\right)-1}$$

$$\Delta E = \frac{1}{2}RT - \frac{R\Theta_\nu}{2} - \frac{R\Theta_\nu}{\exp\left(\frac{\Theta_\nu}{T}\right) - 1} + D_e = \frac{1}{2}RT - \frac{R\Theta_\nu}{\exp\left(\frac{\Theta_\nu}{T}\right) - 1} + D_\circ$$

$$T = 200 + 273 = 473$$

$$\Delta E = 0,5 \times 8,3145 \times 473 - \frac{8,3145 \times 308}{\exp\left(\frac{308}{473}\right) - 1} + 35,6 \times 4184 =$$

$$1,97 - 2,79 + 148,95 = 148,1 \text{ kJ} = 35,4 \text{ kcal}$$

$$\Delta E_t = 1,5 \times 8,3145 \times 473 = 5,9 \text{ kJ}$$

$$\Delta E_r = -8,3145 \times 473 = -3,9 \text{ kJ}$$

$$\Delta E_{\nu} = -\frac{8,3145 \times 308}{2} - \frac{8,3145 \times 308}{\exp\left(\frac{308}{473}\right) - 1} = -4,1 \text{ kJ}$$

$$\Delta E_e = 35,6 \times 4184 + \frac{8,3145 \times 308}{2} = 150,2 \text{ kJ} = 35,6 \text{ kcal}$$

$$D_{\circ} = 82,4$$

$$E_t = 3,7$$

$$E_r = 2,5$$

$$E_\nu = 13,6$$

$$E_e = -358,3$$

$$E = -338.6$$

$$C_{Vt} = 12,47$$

$$C_{Vr} = 8,31$$

$$C_{V\nu} = 0,02$$

$$D_{\circ}^{H_2O} = 219,3$$

$$\Theta_{\nu 1}^{H_2O}$$

$$\Theta_{\nu 2}^{H_2O}$$

$$\Theta_{\nu 3}^{H_2O}$$

$$E_t = E_r = 5,0$$

$$E_\nu = 53,3$$

$$E_e = -970,8$$

$$E = -907,5$$

$$C_{Vt} = C_{Vr} = 12,47$$

$$C_{Ve} = 0$$

$$C_{V\nu} = 0,90$$

$$C_V = 25,84$$

$$D_\circ = 17,3$$

$$\Delta E = -\frac{1}{2}RT + \frac{R\Theta_\nu}{2} + \frac{R\Theta_\nu}{\exp\left(\frac{\Theta_\nu}{T}\right)-1} - D_\circ$$

$$\Delta E(1157\ \mathrm{K}) = -68,5$$

$$t = 1000^\circ$$

$$D_{\circ}^{H_2} = 103,2$$

$\Theta_{\nu}^{H_2}$

$$D_{\circ}^{O_2} = 118$$

$\Theta_{\nu}^{O_2}$

$$\Delta E = -\frac{3}{2}RT + 2R\left[\frac{\Theta_{\nu 1}^{H_2O}}{\exp\left(\frac{\Theta_{\nu 1}^{H_2O}}{T}\right)-1} + \frac{\Theta_{\nu 2}^{H_2O}}{\exp\left(\frac{\Theta_{\nu 2}^{H_2O}}{T}\right)-1} + \frac{\Theta_{\nu 3}^{H_2O}}{\exp\left(\frac{\Theta_{\nu 3}^{H_2O}}{T}\right)-1}\right] -$$

$$-R\left[\frac{2\Theta_{\nu}^{H_2}}{\exp\left(\frac{\Theta_{\nu}^{H_2}}{T}\right)-1}-\frac{\Theta_{\nu}^{O_2}}{\exp\left(\frac{\Theta_{\nu}^{O_2}}{T}\right)-1}\right]-$$

$$\left(2D_{\circ}^{H_2O} - 2D_{\circ}^{H_2} - D_{\circ}^{O_2}\right)$$

$$\Delta E(1273 \text{ K}) = -116,6$$

$$k = 5,5 \times 10^5$$

$$\Delta E \approx \left(\sqrt{3} - 1 - 1/\sqrt{2}\right) R\Theta_{\nu}^{H_2}/2 = 644,5$$

ν_A

ν_B

ν_C

ν_D

$$\lambda = -\frac{\Delta N_A}{\nu_A} = -\frac{\Delta N_B}{\nu_B} = \dots \frac{\Delta N_C}{\nu_C} = \frac{\Delta N_D}{\nu_D} = \dots$$

$$\Delta N_A = -\lambda \nu_A$$

$$\Delta N_B = -\lambda \nu_B$$

•
•
•

$$\Delta N_C = \lambda \nu_C$$

$$\Delta N_D = \lambda \nu_D$$

$$\nu_{H_2} = 1$$

$$\nu_{I_2} = 1$$

$$\nu_{HI} = 2$$

$$\Delta n_{H_2} = -\lambda$$

$$\Delta n_{I_2} = -\lambda$$

$$\Delta n_{HI} = 2\lambda$$

$$dF = \left(\frac{\partial F}{\partial T}\right) dT + \left(\frac{\partial F}{\partial V}\right) dV +$$

$$\left(\frac{\partial F}{\partial N_A}\right) dN_A + \left(\frac{\partial F}{\partial N_B}\right) dN_B + \ldots + \left(\frac{\partial F}{\partial N_C}\right) dN_C + \left(\frac{\partial F}{\partial N_D}\right) dN_D + \ldots =$$

$$-SdT + pdV + \mu_A dN_A + \mu_B dN_B + \ldots + \mu_C dN_C + \mu_D dN_D + \ldots = 0$$

μ_X

$$dT = 0$$

$$dV = 0$$

$$\mu_A dN_A + \mu_B dN_B + \ldots + \mu_C dN_C + \mu_D dN_D + \ldots = 0$$

$d\lambda$

$$(-\nu_A\mu_A - \nu_B\mu_B - \ldots + \nu_C\mu_C + \nu_D\mu_D + \ldots)d\lambda = 0$$

$$\nu_A \mu_A + \nu_B \mu_B + \ldots = \nu_C \mu_C + \nu_D \mu_D + \ldots$$

$$\mu_X = -k_B T \left(\frac{\partial \ln Q_X}{\partial N_X} \right)$$

$$Q_X(N_X, V, T) = \frac{q^N}{N!} = [q'(T)]^N \frac{V^N}{N!} \approx [q'(T)]^N \frac{V^N e^N}{N^N}$$

$$\mu_X = -k_B T \frac{\partial}{\partial N}\left(N \ln q' + N \ln V + N - N \ln N\right) = -k_B T \ln q' + k_B T \ln \frac{N}{V}$$

$$q'$$

N/V

$$k_B T \left(\nu_C \ln q'_C + \nu_D \ln q'_D + \ldots - \nu_A \ln q'_A - \nu_B \ln q'_B - \ldots \right) =$$

$$k_B T \left(\nu_C \ln \frac{N_C}{V} + \nu_C \ln \frac{N_D}{V} + \ldots - \nu_A \ln \frac{N_A}{V} - \nu_B \ln \frac{N_B}{V} - \ldots \right)$$

$k_B T$

$$\rho_X = \frac{N_X}{V}$$

ρ_X

$$K(T) = \frac{[q'_C]^{\nu_C}\,[q'_D]^{\nu_D}\,\ldots}{[q'_A]^{\nu_A}\,[{}'_B]^{\nu_B}\,\ldots} = \frac{\rho_C^{\nu_C}\,\rho_D^{\nu_D}\,\ldots}{\rho_A^{\nu_A}\,\rho_B^{\nu_B}\,\ldots}$$

$$K(T)$$

$$K_C$$

K_p

$$K_C = \frac{[q'_C]^{\nu_C}[q'_D]^{\nu_D}\cdots}{[q'_A]^{\nu_A}[q'_B]^{\nu_B}\cdots} N_A^{\nu_A+\nu_B+\ldots-\nu_C-\nu_D-\ldots} = \frac{C_C^{\nu_C} C_D^{\nu_D}\cdots}{C_A^{\nu_A} C_B^{\nu_B}\cdots}$$

$$K_p = \frac{[q'_C]^{\nu_C}[q'_D]^{\nu_D}\cdots}{[q'_A]^{\nu_A}[{}'_B]^{\nu_B}\cdots} k_B T^{\nu_C+\nu_D+\ldots-\nu_A-\nu_B-\ldots} = \frac{p_C^{\nu_C} p_D^{\nu_D}\cdots}{p_A^{\nu_A} p_B^{\nu_B}\cdots}$$

$$C_X = \rho_X / N_A$$

$$p_X = k_B T \rho_X$$

$$T = 900, 1000, 1100$$

1200

$$K_p(900 \text{ K}) = 1,32 \text{ atm}^{-1}$$

$$K_p(1000\ \mathrm{K}) = 0,47\ \mathrm{atm}^{-1}$$

$$K_p(1100 \text{ K}) = 0,21 \text{ atm}^{-1}$$

$$K_p(1200\ \mathrm{K}) = 0,10\ \mathrm{atm}^{-1}$$

$$\Theta_\nu = 229$$

$$\Theta_r = 0,221$$

$\rightleftharpoons$

$$K_p = \frac{p_{Na_2}}{p_{Na}^2} = \frac{q_{Na_2}/V}{(q_{Na}/V)^2}(k_BT)^{1-2} = \frac{q_{Na_2}/V}{(q_{Na}/V)^2}(k_BT)^{-1}$$

q_{Na_2}/V

$$q_{Na}/V$$

$$q_{Na_2}/V = \left(\frac{2\pi m_{Na_2} k_B T}{h^2}\right)^{\frac{3}{2}} \frac{T}{2\Theta_r^{Na_2}} \left[\exp\left(\frac{\Theta_\nu^{Na_2}}{T}\right) - 1\right]^{-1} \exp\left(\frac{D_\circ^{Na_2}}{k_B T}\right)$$

$$q_{Na}/V = \left(\frac{2\pi m_{Na} k_B T}{h^2}\right)^{\frac{3}{2}} \omega_{\circ}^{Na} = 2\left(\frac{2\pi m_{Na} k_B T}{h^2}\right)^{\frac{3}{2}}$$

$$\omega_{\circ}^{Na}$$

$$K_p = \frac{\left(\frac{2\pi m_{Na_2} k_B T}{h^2}\right)^{\frac{3}{2}} \frac{T}{2\Theta_r^{Na_2}} \left[\exp\left(\frac{\Theta_\nu^{Na_2}}{T}\right) - 1\right]^{-1} \exp\left(\frac{D_\circ^{Na_2}}{k_B T}\right)}{\left[2\left(\frac{2\pi m_{Na} k_B T}{h^2}\right)^{\frac{3}{2}}\right]^2} (k_B T)^{-1} =$$

$$\frac{1}{8}\frac{h^3}{k_B{}^{\frac{5}{2}}\,\Theta_r^{Na_2}}\frac{m_{Na_2}^{\frac{3}{2}}}{m_{Na}^3}T^{-\frac{3}{2}}\left[\exp\left(\frac{\Theta_\nu^{Na_2}}{T}\right)-1\right]^{-1}\exp\left(\frac{D_\circ^{Na_2}}{k_BT}\right)$$

m_{Na}

m_{Na2}

$D_{\circ}^{Na_2}/k_B$

$$m_{Na} = \frac{23}{1000 \times 6,022 \times 10^{23}} = 3,8193 \times 10^{-26} \text{ kg}$$

$$m_{Na_2} = 2m_{Na} = 7,6387 \times 10^{-26} \text{ kg}$$

$$\frac{D_\circ^{Na_2}}{k_B} = \frac{17,3 \times 4184}{8,3145} = 8706 \text{ K}$$

$$K_p = \frac{1}{8} \times \frac{\left(6,626 \times 10^{-34}\right)^3}{\left(2 \times 3,14159\right)^{\frac{3}{2}} \times \left(1,381 \times 10^{-23}\right)^{\frac{5}{2}} 0,221} \times$$

$$\frac{(7,6387 \times 10^{-26})^{\frac{3}{2}}}{(3,8193 \times 10^{-26})^3} T^{-\frac{3}{2}} \left[1 - \exp\left(-\frac{229}{T}\right)\right]^{-1} \exp\left(\frac{8706}{T}\right) =$$

$$\frac{5,586 \times 10^{-6} \exp\left(\frac{8706}{T}\right)}{T^{\frac{3}{2}} \left[1 - \exp\left(-\frac{229}{T}\right)\right]}$$

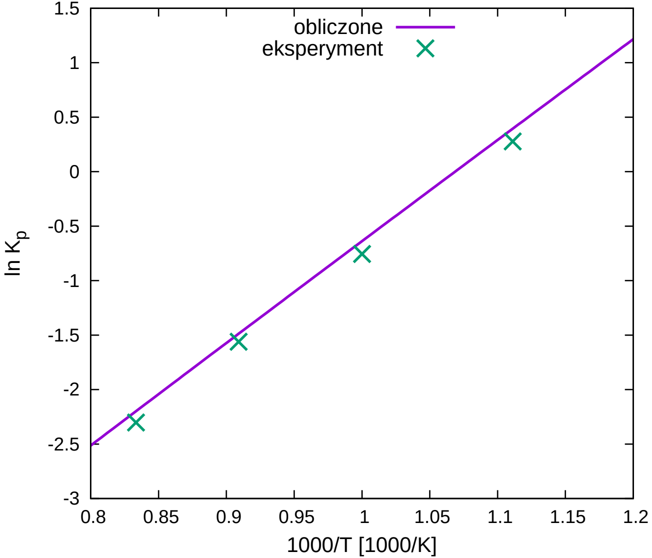
$$K_p = \frac{0,5660 \exp\left(\frac{8706}{T}\right)}{T^{\frac{3}{2}} \left[1 - \exp\left(-\frac{229}{T}\right)\right]}$$

$$K_p(900\ \mathrm{K}) = 1,48\ \mathrm{atm}^{-1}$$

$$K_p(1000\ \mathrm{K}) = 0,53\ \mathrm{atm}^{-1}$$

$$K_p(1100\ \mathrm{K}) = 0,23\ \mathrm{atm}^{-1}$$

$$K_p(1100 \text{ K}) = 0,11 \text{ atm}^{-1}$$



obliczone
eksperyment
ln K_p
1000/T [1000/K]
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
0.8
0.85
0.9
0.95
1
1.05
1.1
1.15
1.2

$$T = 195$$

$$K(195\ \mathrm{K}) = 2,92$$

$$K(273\ \mathrm{K}) = 3,24$$

$$K(298\ \mathrm{K}) = 3,28$$

$$K(383\ \mathrm{K}) = 3{,}50$$

$$K(670\ \mathrm{K}) = 3,8$$

$$\Theta_{\nu}^{^1H_2} = 6215$$

$$K = \frac{\left(q_{HD}/V\right)^2}{\left(q_{H_2}/V\right)\left(q_{D_2}/V\right)} =$$

$$\frac{\left(\frac{2\pi m_{HD} k_B T}{h^2}\right)^3 \left(\frac{\Theta_r^{HD}}{T}\right)^2 \frac{\exp\left(-\frac{\Theta_\nu^{HD}}{T}\right)}{\left[1-\exp\left(-\frac{\Theta_\nu^{HD}}{T}\right)\right]^2} \exp\left(\frac{2D_e}{k_B T}\right)}{\left(\frac{2\pi m_{H_2} k_B T}{h^2}\right)^{\frac{3}{2}} \frac{\Theta_r^{H_2}}{2T} \frac{\exp\left(-\frac{\Theta_\nu^{H_2}}{2T}\right)}{1-\exp\left(-\frac{\Theta_\nu^{H_2}}{T}\right)} \exp\left(\frac{D_e}{k_B T}\right) \left(\frac{2\pi m_{D_2} k_B T}{h^2}\right)^{\frac{3}{2}} \frac{\Theta_r^{D_2}}{2T} \frac{\exp\left(-\frac{\Theta_\nu^{D_2}}{2T}\right)}{1-\exp\left(-\frac{\Theta_\nu^{D_2}}{T}\right)} \exp\left(\frac{D_e}{k_B T}\right)} =$$

$$\frac{m_{HD}^3}{\left(m_{H_2} m_{D_2}\right)^{\frac{3}{2}}} \frac{4\Theta_r^{H_2}\Theta_r^{D_2}}{\left(\Theta_r^{HD}\right)^2} \frac{\left[1-\exp\left(-\frac{\Theta_\nu^{HD}}{T}\right)\right]^2}{\left[1-\exp\left(-\frac{\Theta_\nu^{H_2}}{T}\right)\right]\times\left[1-\exp\left(-\frac{\Theta_\nu^{D_2}}{T}\right)\right]} \exp\left(\frac{2\Theta_\nu^{HD}-\Theta_\nu^{H_2}-\Theta_\nu^{D_2}}{2T}\right)$$

$$m_{H2} = 2 \text{ g/mol}, \ m_{D2} = 4 \text{ g/mol}, \ m_{HD} = 3 \text{ g/mol}$$

$$\mu_{H_2} = \frac{1 \times 1}{1+1} = \frac{1}{2}\ \text{g/mol},\ \ \mu_{D_2} = \frac{2 \times 2}{2+2} = 1\ \text{g/mol},\ \ \mu_{HD} = \frac{1 \times 2}{1+2} = \frac{2}{3}\ \text{g/mol}$$

$$\frac{m_{HD}^3}{\left(m_{H_2} m_{D_2}\right)^{\frac{3}{2}}} = \frac{3^3}{2^{\frac{3}{2}} 4^{\frac{3}{2}}} = \frac{27}{16\sqrt{2}} \approx 1,1932$$

$$\frac{\Theta_r^{H_2}\Theta_r^{D_2}}{\left(\Theta_r^{HD}\right)^2} = \frac{I_{HD}^2}{I_{H_2}I_{D_2}} = \frac{\mu_{HD}^2}{\mu_{H_2}\mu_{D_2}} = \frac{\left(\frac{2}{3}\right)^2}{\frac{1}{2}\times 1} = \frac{8}{9} \approx 0,8889$$

$$\Theta_r = \frac{h^2}{8\pi^2 I k_B}$$

$$I = \mu d^2$$

$$\Theta_\nu^{D_2} = \sqrt{\frac{\mu_{H_2}}{\mu_{D_2}}}\Theta_\nu^{H_2} = \frac{1}{\sqrt{2}}\Theta_\nu^{H_2} = 4395\ \mathrm{K}$$

$$\Theta_\nu^{HD} = \sqrt{\frac{\mu_{H_2}}{\mu_{HD}}}\Theta_\nu^{H_2} = \frac{3}{\sqrt{2 \times 2}}\Theta_\nu^{H_2} = 5382 \text{ K}$$

$$K = 4,24 \times \frac{\left[1 - \exp\left(-\frac{6215}{T}\right)\right]\left[1 - \exp\left(-\frac{4395}{T}\right)\right]}{\left[1 - \exp\left(-\frac{5382}{T}\right)\right]^2} \exp\left(\frac{-77,5}{T}\right) \approx$$

$$4,24 \times \exp\left(\frac{-77,5}{T}\right)$$

$$K(195\ \text{K}) = 2,85$$

$$K(273\ \mathrm{K}) = 3,19$$

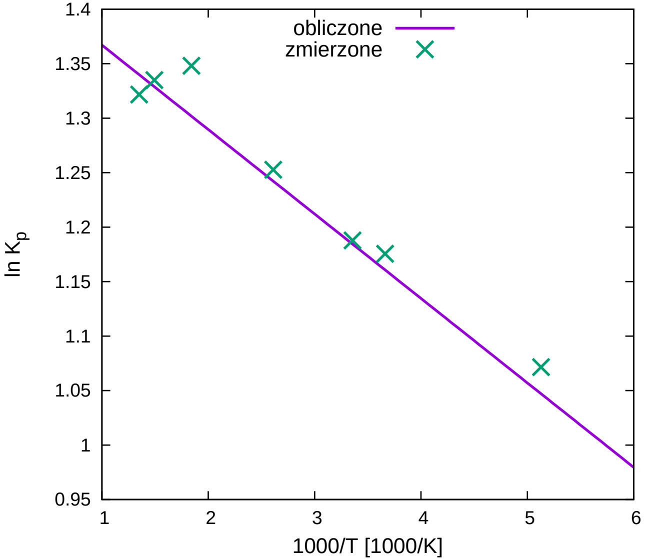
$$K(298\ \mathrm{K}) = 3,27$$

$$K(383\ \mathrm{K}) = 3,46$$

$$K(670\ \mathrm{K}) = 3,78$$

H_2

$$\ln(K) = f(1000/T)$$



obliczone
zmierzone
ln K$_p$
1000/T [1000/K]
1.4
1.35
1.3
1.25
1.2
1.15
1.1
1.05
1
0.95
1
2
3
4
5
6

$$\Theta_{\nu} = 133$$

$$\Theta_r = 0,081$$

$$D_{\circ} = 15,8$$

$$T = 872$$

$$\Theta_\nu = 308$$

$$\Theta_r = 0,0537$$

$$1,81 \times 10^{-4}$$

$$1,801 \times 10^{-3}$$

σ_K

$$0,19 \times 10^{-4}$$

$$0,060 \times 10^{-3}$$

$$\Theta_{\nu}^{HCl} = 4227$$

$$\Theta_{\nu}^{HBr} = 3787$$

$$\Theta_{\nu}^{\ 14}{}^{N_2} = 3374$$

$$T = 465^\circ$$

$$T = 500^\circ$$

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