Wykład 14

Obliczanie stałych równowag reakcji chemicznych w fazie gazowej z pierwszych zasad

Postęp reakcji

$\nu_A A+\nu_B B+\ldots = \nu_C C+\nu_D D+\ldots$

ν_X: współczynnik stechiometryczny przy związku X

Możemy formalnie wszystkie współczynniki stechiometryczne przenieść na jedną stronę:

$-\nu_A A-\nu_B B+\ldots+\nu_C C+\nu_D D+\ldots=0$

Współczynniki przy substratach mają znak “-” a przy produktach znak “+”. Jeżeli jakiś związek nie bierze udziału w danej reakcji przypisujemy mu współczynnik “0”.

Definiujemy postęp reakcji $\Delta\lambda$ jako ubytek liczby moli danego substratu lub przyrost liczby moli danego produktu podzielony przez współczynnik stechiometryczny.

$\Delta\lambda=-\Delta N_A/\nu_A=-\Delta N_B/\nu_B=\ldots=\Delta N_C/\nu_C=\Delta N_D/\nu_D=\ldots$

Przykład: Reakcja jodu z wodorem

$$H_2 + I_2 = 2HI$$

$$\Delta N(H_2)=\Delta N(I_2)=-\Delta\lambda$$
$$\Delta N(HI)=2\Delta\lambda$$

Warunek równowagi chemicznej

$$dF = -SdT - pdV + \sum_j \mu_j dN_j = 0$$

$$dN_j = \nu_j d\lambda, \quad dV = 0, \quad dT = 0$$

$$dF = \sum_j \mu_j dN_j = \left(\sum_j \mu_j \nu_j \right) d\lambda = 0$$

...

$$\sum_j \mu_j \nu_j = -\mu_A \nu_A - \mu_B \nu_B + \ldots + \mu_C \nu_C + \mu_D \nu_D + \ldots = 0$$

$$\mu_X = -k_B T \left(\frac{\partial \ln Q}{\partial N_X} \right)_{T,V,N_A,N_B,\ldots}$$

$$Q = \frac{q_A^{N_A}}{N_A!} \frac{q_B^{N_B}}{N_B!} \ldots \frac{q_C^{N_C}}{N_C!} \frac{q_D^{N_D}}{N_D!} \ldots$$

$$\mu_X = -k_B T \left(\frac{\partial \ln\left(N_X \ln q_X - \ln\left(N_X!\right)\right)}{\partial N_X} \right)_{T,V,N_A,N_B,\ldots} =$$

$$-k_B T \left(\ln q_X - \ln N_X\right) = -k_B T \ln \frac{q_X}{N_X}$$

$$-k_B T \nu_A \ln \frac{q_A}{N_A} - k_B T \nu_B \ln \frac{q_B}{N_B} + \ldots = -k_B T \nu_C \ln \frac{q_C}{N_C} - k_B T \nu_D \ln \frac{q_D}{N_D} + \ldots$$

$$\frac{N_C^{\nu_C} N_D^{\nu_D} \ldots}{N_A^{\nu_A} N_B^{\nu_B} \ldots} = \frac{q_c^{\nu_C} q_D^{\nu_D} \ldots}{q_A^{\nu_A} q_B^{\nu_B} \ldots}$$

$$q_X = q_X(V,T) = q_X^{'}(T)V$$

$$\frac{(N_C/V)^{\nu_C}(N_D/V)^{\nu_D}\cdots}{(N_A/V)^{\nu_A}(N_B/V)^{\nu_B}\cdots} = \frac{\rho_C^{\nu_C}\rho_D^{\nu_D}\cdots}{\rho_A^{\nu_A}\rho_B^{\nu_B}\cdots}$$

$$= \frac{(q_C/V)^{\nu_C}(q_D/V)^{\nu_D}\cdots}{(q_A/V)^{\nu_A}(q_B/V)^{\nu_B}\cdots} = K_C(T)$$

$$p_X = k_B T \rho_X$$

$$K_p = \frac{p_C^{\nu_C} p_D^{\nu_D}\cdots}{p_A^{\nu_A} p_B^{\nu_B}\cdots} = K_C(k_B T)^{\nu_C+\nu_D+\ldots-\nu_A-\nu_B-\ldots}$$

Przykład 1: asocjacja sodu w fazie gazowej

$$2Na = Na_2$$

$\Delta\varepsilon_{12}$=16000cm^{-1}=45 kcal/mol
ω_1=2 (term $^2S_{1/2}$)

$$K_p = \frac{p_{Na_2}}{p_{Na}^2} = \frac{q_{Na_2}/V}{\left(q_{Na}/V\right)^2}\left(k_B T\right)^{-1}$$

$$q_{Na} = \left(\frac{2\pi m_{Na} k_B T}{h^2}\right)^{3/2} V q_{elec} \approx 2\left(\frac{2\pi m_{Na} k_B T}{h^2}\right)^{3/2} V$$

$$q_{Na_2} = \left(\frac{2\pi m_{Na_2} k_B T}{h^2}\right)^{3/2} V \frac{8\pi^2 I k_B T}{2h^2} \frac{e^{-h\nu/2k_B T}}{\left(1-e^{-h\nu/k_B T}\right)} \omega_{1e} e^{D_e/k_B T}$$

$$= \left(\frac{2\pi m_{Na_2} k_B T}{h^2}\right)^{3/2} V \frac{T}{2\Theta_r}\left(1-e^{-\Theta_\nu/T}\right)^{-1} e^{D_0/k_B T}$$

m_{Na}=23 g/mol D_0=17.3 kcal/mol Θ_v=229 K Θ_r=0.221 K

T=1000 K

$$\frac{q_{Na}}{V}=\left(\frac{2\pi\times 0.023/6.023\times 10^{23}\,\mathrm{kg}\times 1.38\times 10^{-23}\,\mathrm{J/K}\times 1000\,\mathrm{K}}{\left(6.626\times 10^{-34}\,\mathrm{J}\times\mathrm{s}\right)^2}\right)^{3/2}\times 2=1.30989\times 10^{33}\,\mathrm{m}^{-3}$$

$$\frac{q_{Na_2}}{V}=\left(\frac{2\pi\times 0.046/6.023\times 10^{23}\,\mathrm{kg}\times 1.38\times 10^{-23}\,\mathrm{J/K}\times 1000\,\mathrm{K}}{\left(6.626\times 10^{-34}\,\mathrm{J}\times\mathrm{s}\right)^2}\right)^{3/2}\times$$

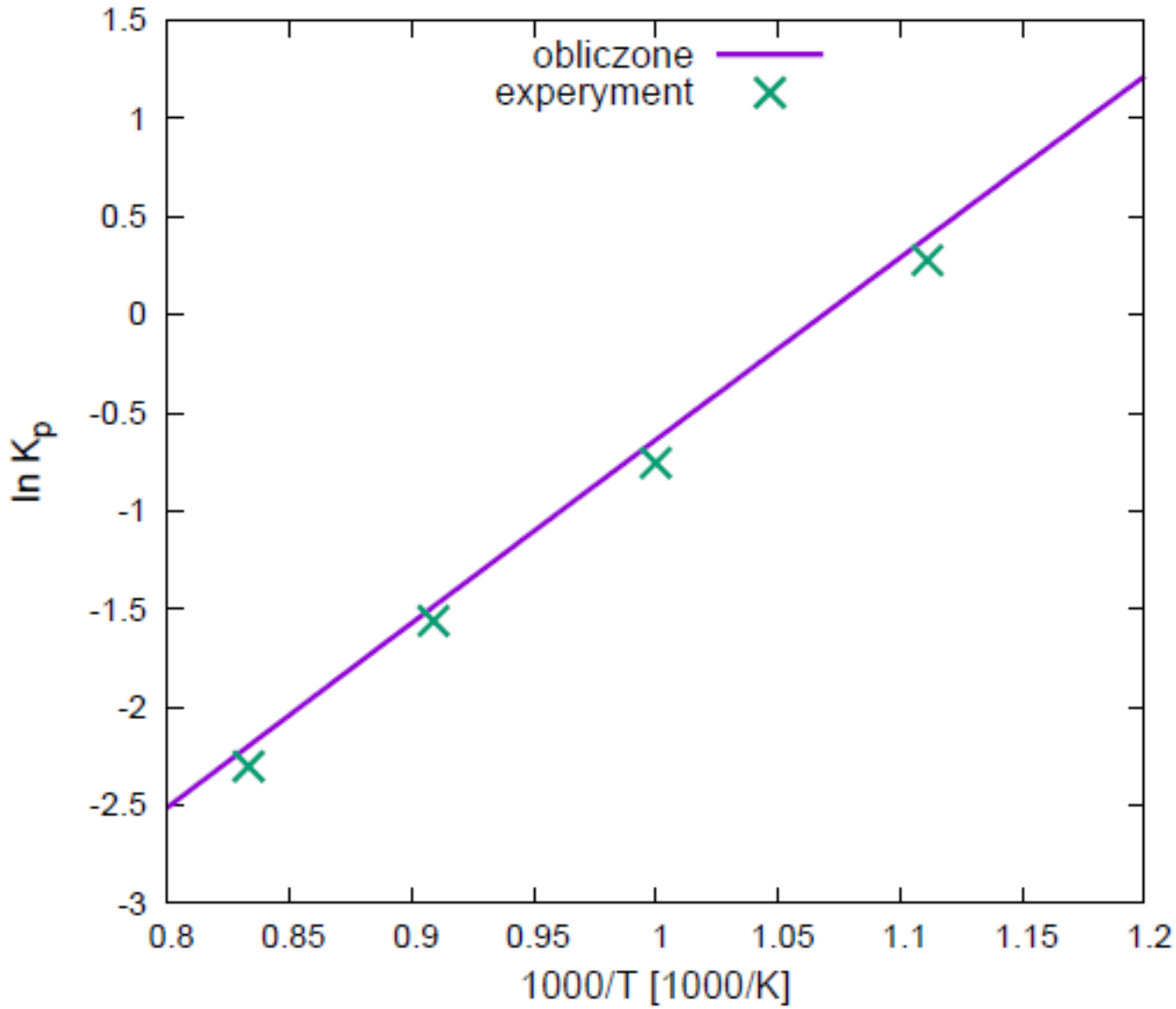
$$\frac{1000\,\mathrm{K}}{2\times 0.221\,\mathrm{K}}\left(1-e^{-229\mathrm{K}/1000\mathrm{K}}\right)^{-1}\exp\left(\frac{72383\,\mathrm{J/mol}}{8.3143\,\mathrm{J/mol}\times\mathrm{K}\times 1000\mathrm{K}}\right)=$$

$$1.85247\times 10^{33}\times 2.2624\times 10^{3}\times(1/0.204671)\times 6.038\times 10^{3}=1.2364\times 10^{41}\,\mathrm{m}^{-3}$$

$$K_p=\frac{1.2519\times 10^{41}\,\mathrm{m}^{-3}}{\left(1.3099\times 10^{33}\,\mathrm{m}^{-3}\right)^2 1.38\times 10^{-23}\,\mathrm{J/K}\times 1000\mathrm{K}}=5.221\times 10^{-6}\,\mathrm{N}^{-1}\times\mathrm{m}^2\approx 0.5\,\mathrm{atm}^{-1}$$

Porównanie obliczonych i zmierzonych wartości ciśnieniowej stałej równowagi dimeryzacji sodu w fazie gazowej (C.T. Ewing et al., *J. Chem. Phys.*, **71**, 473, 1967)

T(K)	$K_p^{obl}(atm^{-1})$	$K_p^{zm}(atm^{-1})$
900	1.44	1.32
1000	0.50	0.47
1100	0.22	0.21
1200	0.11	0.10


obliczone
experyment
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
ln K_p
0.8
0.85
0.9
0.95
1
1.05
1.1
1.15
1.2
1000/T [1000/K]

Przykład 2: Prosta reakcja wymiany izotopowej

$$H_2 + D_2 = 2HD$$

$$K(T) = K_p(T) = K_c(T) = \frac{\rho_{HD}^2}{\rho_{H_2}\rho_{D_2}} = \frac{p_{HD}^2}{p_{H_2}p_{D_2}}$$

$$= \frac{\left(\frac{2\pi m_{HD}k_BT}{h^2}\right)^3\left(\frac{T}{\Theta_{r,HD}}\right)^2\left(\frac{e^{-\Theta_{v,HD}/2T}}{1-e^{-\Theta_{v,HD}/T}}\right)^2 e^{2D_e/k_BT}}{\left(\frac{2\pi m_{H_2}k_BT}{h^2}\right)^{3/2}\left(\frac{2\pi m_{D_2}k_BT}{h^2}\right)^{3/2}\frac{T^2}{4\Theta_{r,H_2}\Theta_{r,D_2}}\left(\frac{e^{-\Theta_{v,H_2}/2T}}{1-e^{-\Theta_{v,H_2}/T}}\right)\left(\frac{e^{-\Theta_{v,D_2}/2T}}{1-e^{-\Theta_{v,D_2}/T}}\right)e^{2D_e/k_BT}}$$

$$= \frac{m_{HD}^3}{\left(m_{H_2}m_{D_2}\right)^{3/2}}\frac{4\Theta_{r,H_2}\Theta_{r,D_2}}{\Theta_{r,HD}^2}\underbrace{\frac{\left(1-e^{-\Theta_{v,H_2}/T}\right)\left(1-e^{-\Theta_{v,D_2}/T}\right)}{\left(1-e^{-\Theta_{v,HD}/T}\right)^2}}_{\text{można przyjąć za = 1 } (\Theta_v/T>>1)}\exp\left(-\frac{2\Theta_{v,HD}-\Theta_{v,D_2}-\Theta_{v,D_2}}{2T}\right)$$

$$\frac{\nu_{HD}}{\nu_{H_2}} = \left(\frac{\mu_{H_2}}{\mu_{HD}}\right)^{1/2} \quad \text{lub} \quad \frac{\Theta_{\nu,HD}}{\Theta_{\nu,H_2}} = \left(\frac{\mu_{H_2}}{\mu_{HD}}\right)^{1/2}$$

$$\frac{\nu_{D_2}}{\nu_{H_2}} = \left(\frac{\mu_{H_2}}{\mu_{D_2}}\right)^{1/2} \quad \text{lub} \quad \frac{\Theta_{\nu,D_2}}{\Theta_{\nu,H_2}} = \left(\frac{\mu_{H_2}}{\mu_{D_2}}\right)^{1/2}$$

$$\mu_{H_2} = \frac{1}{2} m_H \qquad \mu_{HD} = \frac{m_H\, 2m_H}{m_H + 2m_H} = \frac{2}{3} m_H \qquad \mu_{D_2} = \frac{(2m_H)^2}{4m_H} = m_H$$

$$\Theta_{\nu,HD} = \left(\frac{3}{4}\right)^{1/2} \Theta_{\nu,H_2} \qquad \Theta_{\nu,D_2} = \left(\frac{1}{2}\right)^{1/2} \Theta_{\nu,H_2}$$

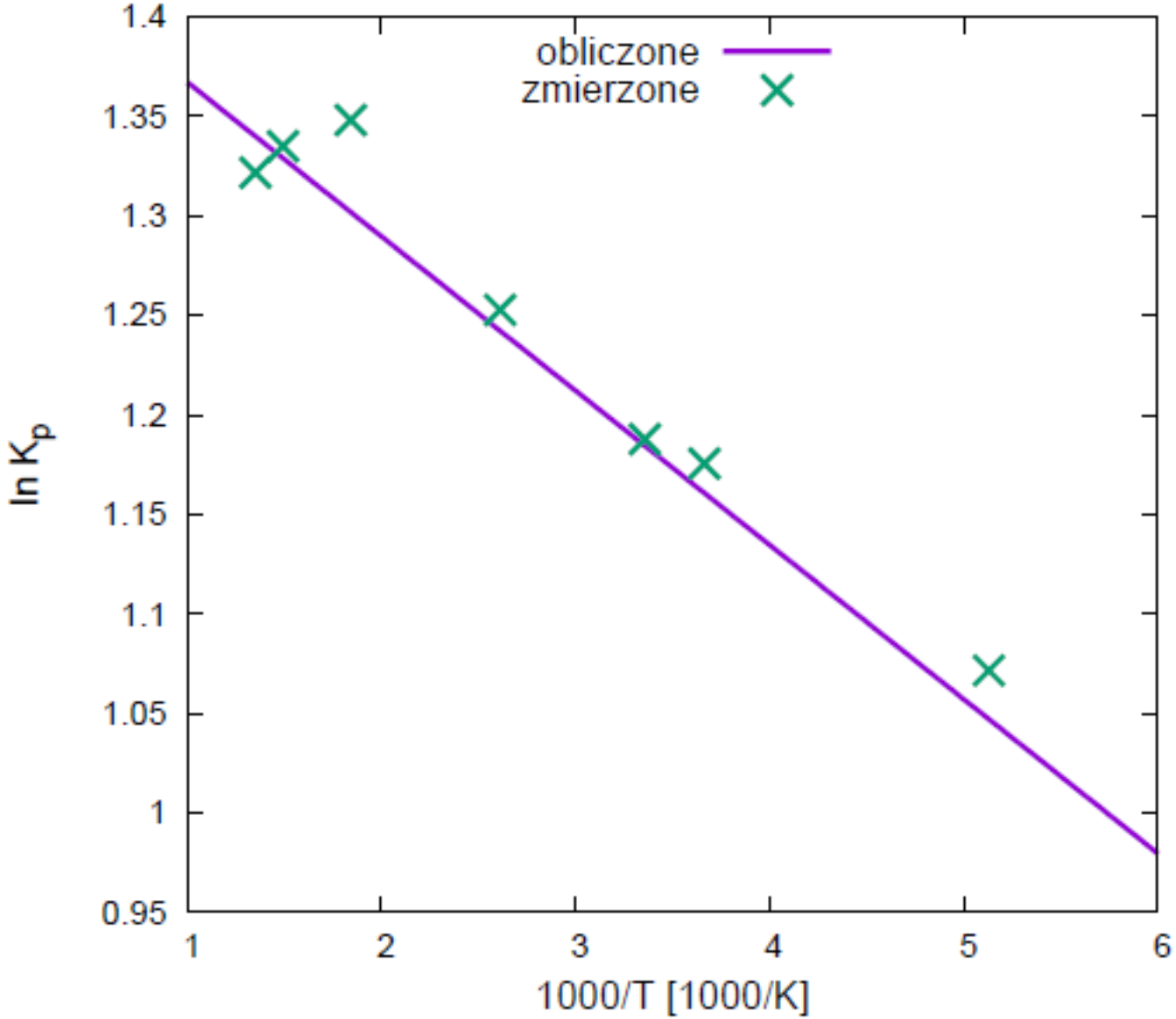
$$\frac{\Theta_{r,HD}}{\Theta_{r,H_2}} = \frac{I_{H_2}}{I_{HD}} = \frac{\mu_{H_2}}{\mu_{HD}} = \frac{3}{4} \qquad \frac{\Theta_{r,HD}}{\Theta_{r,D_2}} = \frac{I_{D_2}}{I_{HD}} = \frac{\mu_{D_2}}{\mu_{HD}} = \frac{3}{2}$$

$$K(T) = 4\left(\frac{9}{8}\right)^{3/2} \frac{8}{9} \exp\left(-\frac{\left(3^{1/2} - 1 - (1/2)^{1/2}\right)\Theta_{\nu,H_2}}{T}\right) = 4 \times 1.06 \times \exp\left(-\frac{77.7}{T}\right)$$

Porównanie obliczonych i zmierzonych wartości stałej wymiany izotopowej $H_2+D_2=2HD$ w różnych temperaturach (D. Rittenberg et al., J. Chem. Phys., 2, 362, 1934)

T(K)	K^{obl}	K^{zm}
195	2.84*	2.92
273	3.18	3.24
298	3.26	3.28
383	3.46	3.50
543	3.67	3.85
670	3.77	3.8
741	3.81	3.75

W temperaturze 185 K istotne są efekty kwantowe; po ich uwzględnieniu otrzymuje się wartość 2.87.


obliczone
zmierzone
1.4
1.35
1.3
1.25
1.2
1.15
1.1
1.05
1
0.95
ln K_p
1
2
3
4
5
6
1000/T [1000/K]

Przykład 3: bardziej skomplikowana reakcja wymiany izotopowej

$$CH_4 + DBr = CH_3D + HBr$$

$$K(T) = \frac{\rho_{CH_3D}\rho_{HBr}}{\rho_{CH_4}\rho_{DBr}} = \frac{q_{CH_3D}q_{HBr}}{q_{CH_4}q_{DBr}}$$

$$= \frac{\sigma_{CH_4}\sigma_{DBr}}{\sigma_{CH_3D}\sigma_{HBr}}\left(\frac{M_{CH_3D}M_{HBr}}{M_{CH_4}M_{DBr}}\right)^{3/2}\frac{I_{HBr}}{I_{DBr}}\frac{\left(I_{A,CH_3D}I_{B,CH_3D}I_{C,CH_3D}\right)^{\frac{1}{2}}}{\left(I_{A,CH_4}I_{B,CH_4}I_{C,CH_4}\right)^{\frac{1}{2}}}\frac{q_{vib,CH_3D}q_{vib,HBr}}{q_{vib,CH_4}q_{vib,DBr}}$$

Table 9–3. **Fundamental vibrational frequencies of CH_4, CH_3D, HBr, and DBr**

CH_4		CH_3D	
frequency	degeneracy	frequency	degeneracy
2917 cm^{-1}	1	2200 cm^{-1}	1
1534	2	2945	1
3019	3	1310	1
1306	3	1471	2
		3021	2
		1155	2

HBr		DBr	
frequency	degeneracy	frequency	degeneracy
2650 cm^{-1}	1	1880 cm^{-1}	1

Wkład oscylacyjny

$$\frac{q_{vib,CH_3D}q_{vib,HBr}}{q_{vib,CH_4}q_{vib,DBr}} \approx \exp\left[-\sum_j \frac{\Theta_{\nu,j}^{CH_3D} - \Theta_{\nu,j}^{CH_4}}{2T} - \frac{\Theta_{\nu,j}^{HBr} - \Theta_{\nu,j}^{DBr}}{2T}\right] = \exp\left(\frac{317}{T}\right)$$

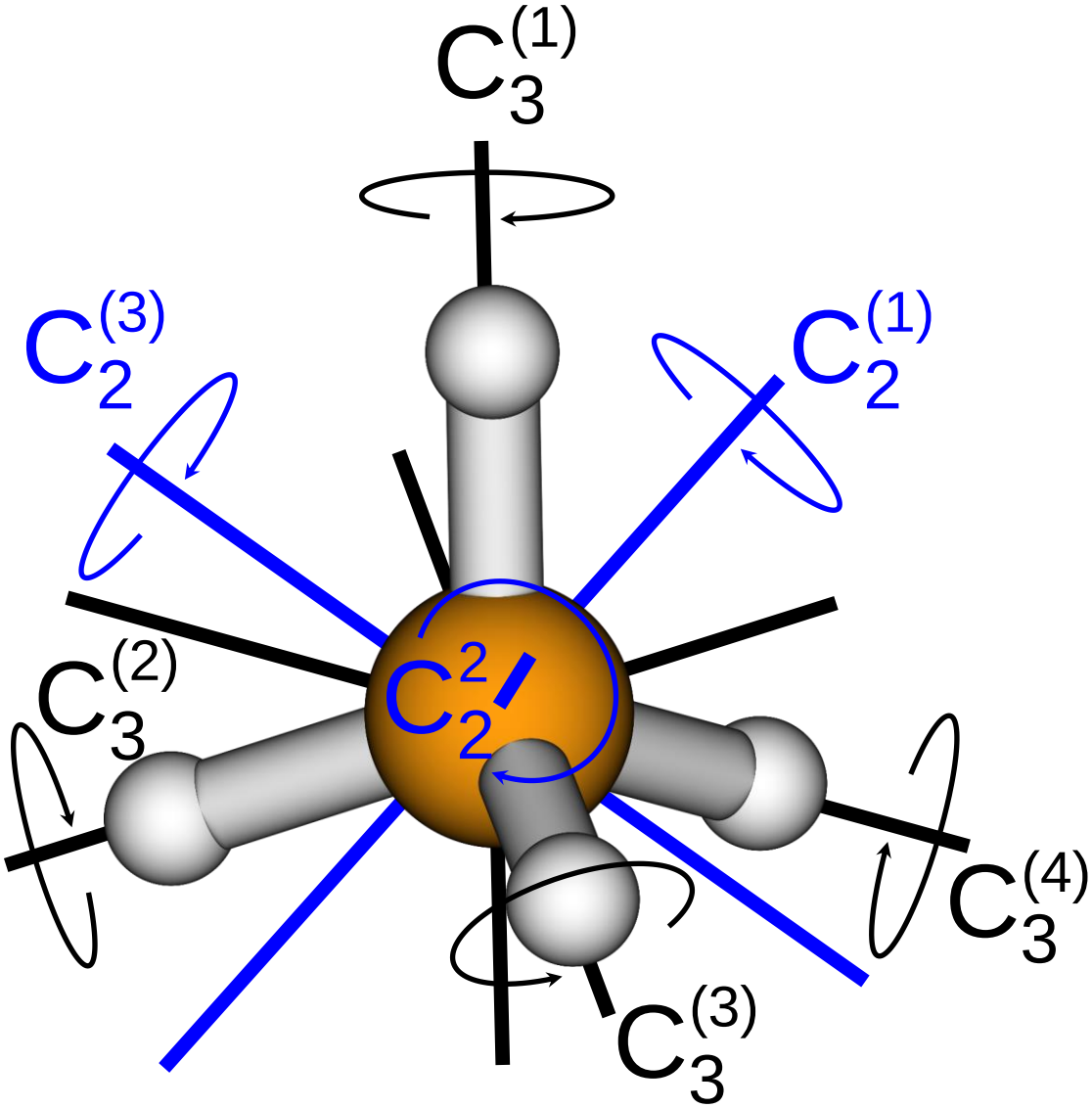
Wkład rotacyjny

$$\frac{\sigma_{CH_4}\sigma_{DBr}}{\sigma_{CH_3D}\sigma_{HBr}} \frac{I_{HBr}}{I_{DBr}} \frac{\left(I_{A,CH_3D}I_{B,CH_3D}I_{C,CH_3D}\right)^{\frac{1}{2}}}{\left(I_{A,CH_4}I_{B,CH_4}I_{C,CH_4}\right)^{\frac{1}{2}}}$$

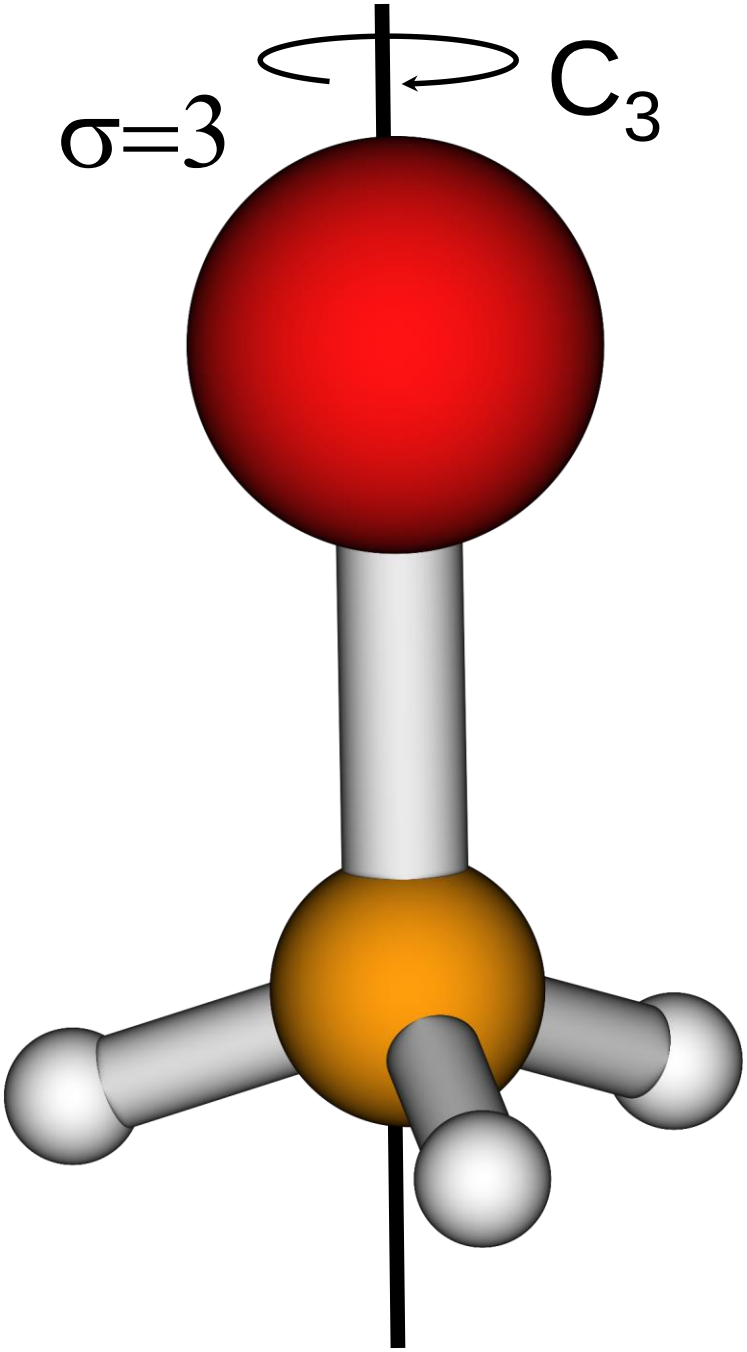
Wkład translacyjny

$$\left(\frac{M_{CH_3D}M_{HBr}}{M_{CH_4}M_{DBr}}\right)^{3/2}$$

$\sigma = 4 \times 2 + 3 + 1 = 12$



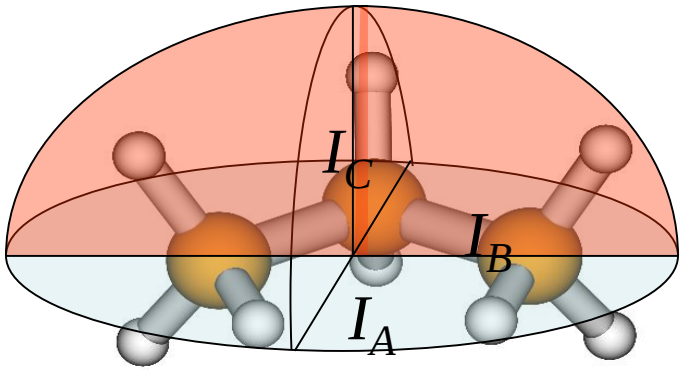
$\sigma = 3$



Wkład rotacyjny

$$\sigma_{CH_4} = 12 \qquad \sigma_{CH_3D} = 3 \qquad \sigma_{HBr} = \sigma_{DBr} = 1$$

$$\frac{\sigma_{CH_4}\sigma_{DBr}}{\sigma_{CH_3D}\sigma_{HBr}} = \frac{12\times 1}{3\times 1} = 4$$



Obliczanie momentów bezwładności

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

$$= \mathbf{U}\begin{pmatrix} I_A & & \\ & I_B & \\ & & I_C \end{pmatrix}\mathbf{U}^{\mathbf{T}}$$

Dla cząsteczek dwuatomowych mamy

$$\frac{I'}{I} = \frac{\mu'}{\mu} = \frac{M}{M'}\frac{m_1'm_2'}{m_1m_2} \qquad \frac{\nu'}{\nu} = \left(\frac{M'}{M}\frac{m_1m_2}{m_1'm_2'}\right)^{\frac{1}{2}}$$

stąd

$$\left(\frac{M'}{M}\right)^{\frac{3}{2}}\frac{I'}{I} = \left(\frac{m_1'\,m_2'}{m_1m_2}\right)^{\frac{3}{2}}\frac{\nu'}{\nu}$$

Uogólnieniem tej zależności jest reguła iloczynu Tellera-Redlicha

$$\left(\frac{M'}{M}\right)^{3/2}\frac{I'}{I} = \prod_{i=1}^{n}\left(\frac{m'_i}{m_i}\right)^{3/2}\prod_{j=1}^{3n-5}\frac{\nu'_j}{\nu_j}$$

Cząsteczki liniowe

$$\left(\frac{M'}{M}\right)^{3/2}\left(\frac{I'_A\,I'_B\,I'_C}{I_AI_BI_C}\right)^{1/2} = \prod_{i=1}^{n}\left(\frac{m'_i}{m_i}\right)^{3/2}\prod_{j=1}^{3n-6}\frac{\nu'_j}{\nu_j}$$

Cząsteczki nieliniowe

Wyrażenie na stałą równowagi przyjmuje więc następującą postać:

$$K(T) = 4\times\exp\left(\frac{317}{T}\right)\frac{\nu_{HBr}}{\nu_{DBr}}\prod_{j=1}^{9}\frac{\nu_{j,CH_{3D}}}{\nu_{j,CH_4}} = 2.99\times\exp\left(\frac{317}{T}\right)$$

Przykład 4: synteza jodowodoru w fazie gazowej

$$H_2 + I_2 = 2HI$$

$$K(T) = \frac{(q_{HI}/V)^2}{(q_{H_2}/V)(q_{I_2}/V)} = \frac{q_{HI}^{\ 2}}{q_{H_2} q_{I_2}}$$

$$= \left(\frac{m_{HI}^2}{m_{H_2} m_{I_2}}\right)^{3/2} \left(\frac{4\Theta_r^{H_2}\Theta_r^{I_2}}{\left(\Theta_r^{HI}\right)^2}\right) \frac{\left(1-e^{-\Theta_{v,H_2}/T}\right)\left(1-e^{-\Theta_{v,I_2}/T}\right)}{\left(1-e^{-\Theta_{v,HI}/T}\right)} \times \exp\left(\frac{2D_0^{HI} - D_0^{H_2} - D_0^{I_2}}{RT}\right)$$

$$d\ln K = -\frac{\Delta H}{R} d\left(\frac{1}{T}\right)$$

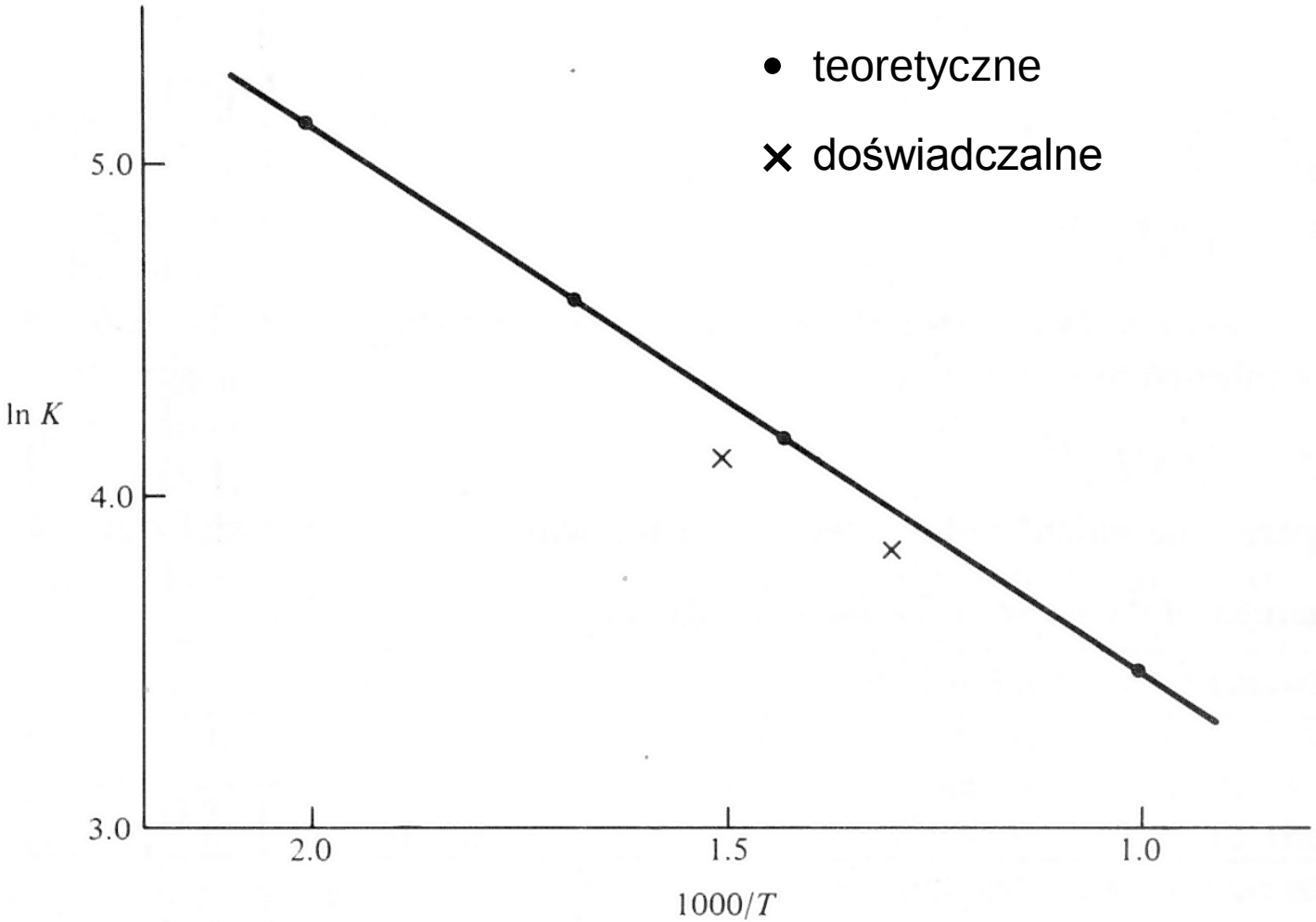


Figure 9–1. **The logarithm of the equilibrium constant versus $1/T$ for the reaction $H_2 + I_2 \rightleftharpoons 2HI$. The points are calculated from Eq. (9–32) and the crosses are the experimental values.** (From A. H. Taylor and R. H. Crist, *J. Am. Chem, Soc.*, **63**, 1377, 1941.)

Przykład 5: synteza wody w fazie gazowej

$$\mathrm{H_2} + \frac{1}{2}\mathrm{O_2} = \mathrm{H_2O}$$

$$K_p(T) = \frac{\left(\rho_{H_2O}/V\right)}{\left(k_B T\right)^{1/2}\left(\rho_{H_2}/V\right)\left(\rho_{O_2}/V\right)^{1/2}}$$

$$\frac{q_{H_2}}{V} = \left(\frac{2\pi m_{H_2} k_B T}{h^2}\right)^{3/2}\left(\frac{T}{2\Theta_r^{H_2}}\right)\left(1 - e^{-\Theta_v^{H_2}/T}\right)^{-1} e^{D_0^{H_2}/RT}$$

$$\frac{q_{O_2}}{V} = \left(\frac{2\pi m_{O_2} k_B T}{h^2}\right)^{3/2}\left(\frac{T}{2\Theta_r^{O_2}}\right)\left(1 - e^{-\Theta_v^{O_2}/T}\right)^{-1} 3e^{D_0^{O_2}/RT}$$

$$\frac{q_{H_2O}}{V} = \left(\frac{2\pi m_{H_2O} k_B T}{h^2}\right)^{3/2} \frac{\pi^{1/2}}{\sigma}\left(\frac{T}{\Theta_A^{H_2O}\Theta_B^{H_2O}\Theta_C^{H_2O}}\right)\prod_{j=1}^{3}\left(1 - e^{-\Theta_v^{H_2}/T}\right)^{-1} e^{D_0^{H_2O}/RT}$$

Porównanie obliczonych i zmierzonych wartości stałej równowagi reakcji syntezy wody w różnych temperaturach.

T(K)	$\log K^{obl}$	$\log K^{zm}$
1000	10.2	10.3
1500	5.7	5.7
2000	3.7	3.5

Korzystanie z tabel termodynamicznych w celu obliczenia stałych równowag

$$\nu_C\mu_C + \nu_D\mu_D + \ldots - \nu_A\mu_A - \nu_B\mu_B - \ldots = 0$$

$$\mu_X = -k_BT\ln\frac{q_X}{N_X} = -k_BT\ln\left[\left(\frac{q_X}{V}\right)\frac{V}{N_X}\right] = -k_BT\ln\left[\left(\frac{q_X}{V}\right)\frac{k_BT}{p_X}\right] = \mu_X^0(T) + k_BT\ln p_X$$

$$\mu_X^0 = -k_BT\ln\left[\left(\frac{q_X}{V}\right)k_BT\right]$$

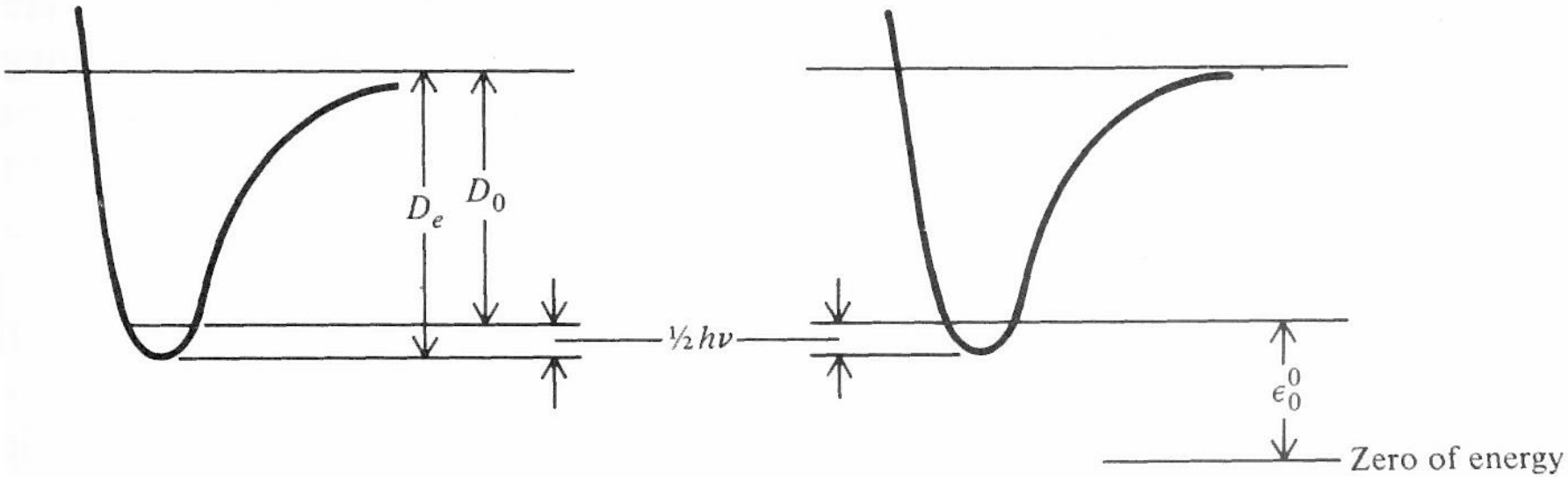
$$q(V,T) = q_{trans}(V,T)q_{rot}(V,T)q_{osc}(V,T)q_{elec}(T)$$

$$q_{elec}(T) = e^{D_e/k_BT}\left(\omega_{e1} + \omega_{e2}e^{-\Delta\varepsilon_{12}/k_BT} + \ldots\right) = e^{D_e/k_BT}q_{elec}^0(T)$$

$$q_{vib}(V,T) = \prod_j \frac{e^{-\Theta_{\nu_j}/2T}}{1-e^{-\Theta_{\nu_j}/T}}$$

$$q(V,T) = q_{trans}(V,T)q_{rot}(V,T)\left[\prod_j\left(1-e^{-\Theta_{\nu_j}/T}\right)^{-1}\right]q_{elec}^0(T)e^{\left(D_e - \sum_j \frac{1}{2}h\nu_j\right)\Big/k_BT}$$

$$= q_{trans}(V,T)q_{rot}(V,T)q_{osc}^0(V,T)q_{elec}^0(V,T)e^{D_0/k_BT}$$



$$q(V,T) = q^0(V,T)e^{-\varepsilon_0^0/k_BT}$$

$$\mu - \varepsilon_0^0 = -k_BT\ln\left[\left(\frac{q^0}{V}\right)k_BT\right] + k_BT\ln p\left(\mathrm{N/m^2}\right)$$

$$= -k_BT\ln\left[\left(\frac{q^0}{V}\right)\frac{k_BT}{1.01\times10^6}\right] + k_BT\ln p(\mathrm{atm})$$

$$G^0 - E_0^0 = -RT \ln\left[\left(\frac{q^0}{V}\right)\frac{k_B T}{1.01\times 10^6}\right]$$

$$-R\ln K_p = -N_A\left(\nu_C\mu_C^0 + \nu_D\mu_D^0 + \ldots - \nu_A\mu_A^0 - \nu_B\mu_B^0 - \ldots\right)$$

$$= \frac{\Delta E_0^0}{T} + \Delta\left(\frac{G^0 - E_0^0}{T}\right)$$

$$\Delta E_0^0 = \nu_C E_0^0 + \nu_D E_0^0 + \ldots - \nu_A E_0^0 - \nu_B E_0^0 - \ldots$$

$$\Delta\left(G^0 - E_0^0\right) = \nu_C\left(G_C^0 - E_{0,C}^0\right) + \nu_D\left(G_D^0 - E_{0,D}^0\right) + \ldots$$

$$-\nu_A\left(G_A^0 - E_{0,A}^0\right) - \nu_A\left(G_B^0 - E_{0,B}^0\right) - \ldots$$

E_0: energia pierwiastka w 0 K, odpowiadająca takiej jego formie jaką ma w warunkach standardowych (T = 298 K, p = 1 atm).

Table 9–6. **Thermodynamic functions of some selected substances**

	$-(G^0 - E_0{}^0)/T$ cal/deg-mole						
	298.15°K	500°K	1000°K	1500°K	2000°K	$H^0_{298} - E_0{}^0$	$E_0{}^0$(kcal/mole)
Ne	29.98	32.56	36.00	38.00	39.44	1.481	0
Ar	32.01	34.59	38.04	40.04	41.48	1.481	0
Kr	34.22	36.80	40.24	42.25	43.69	1.481	0
H(g)	22.42	24.99	28.44	30.45	31.88	1.481	51.62
Cl(g)	34.43	37.06	40.69	42.83	44.34	1.499	28.54
Br(g)	36.84	39.41	42.85	44.89	46.36	1.481	26.90
I(g)	38.22	40.78	44.23	46.24	47.68	1.481	25.61
O(g)	33.08	35.84	39.46	41.54	43.00	1.607	58.98
N(g)	31.65	34.22	37.66	39.67	41.10	1.481	112.54
H_2(g)	24.42	27.95	32.74	35.59	37.67	2.024	0
Cl_2(g)	45.93	49.85	55.43	58.85	61.34	2.194	0
Br_2(g)	50.85	54.99	60.80	64.31	66.83	2.325	8.37
I_2(g)	54.18	58.46	64.40	67.96	70.52	2.148	15.66
O_2(g)	42.06	45.68	50.70	53.81	56.10	2.07	0
N_2(g)	38.82	42.42	47.31	50.28	52.48	2.072	0
CO(g)	40.25	43.86	48.77	51.78	53.99	2.073	−27.202
NO(g)	42.98	46.76	51.86	54.96	57.24	2.194	21.48
HCl(g)	37.72	41.31	46.16	49.08	51.23	2.065	−22.019
HBr(g)	40.53	44.12	48.99	51.95	54.13	2.067	−8.1
HI(g)	42.40	45.99	50.90	53.90	56.11	2.069	6.7
CO_2(g)	43.56	47.67	54.11	58.48	61.85	2.238	−93.969
H_2O(g)	37.17	41.29	47.01	50.60	53.32	2.368	−57.107
NH_3(g)	37.99	42.28	48.63	53.03	56.56	2.37	−9.37
Cl_2O(g)	54.52	59.49	67.04	71.91	—	2.719	18.61
ClO_2(g)	52.79	57.48	64.65	69.33	—	2.577	25.59
N_2O(g)	44.89	49.11	55.76	60.27	—	2.291	20.31
NO_2(g)	49.19	53.60	60.23	64.58	67.88	2.465	8.68
CH_4(g)	36.46	40.75	47.65	52.84	57.1	2.397	−15.99
CH_3Cl(g)	47.45	52.06	59.78	65.54	—	2.489	−17.7
CH_2Cl_2(g)	55.08	60.36	69.58	76.17	—	2.834	−19
$CHCl_3$(g)	59.29	65.81	76.78	84.63	—	3.390	−23
CCl_4(g)	60.15	68.12	81.41	89.96	—	4.111	−25
C_2H_6(g)	45.27	50.77	61.11	69.46	—	2.856	−16.52
C_2H_4(g)	43.98	48.74	57.29	63.94	69.46	2.525	14.52
CH_2O(g)	44.25	48.54	55.11	59.81	63.58	2.393	−26.8
Na_2(g)	46.65	51.04	57.14	60.77	—	2.484	—
K_2(g)	51.06	55.57	61.76	65.47	—	2.566	—

Source: G. N. Lewis and M. Randall, *Thermodynamics*, revised by K. S. Pitzer and L. Brewer (New York: McGraw-Hill, 1961).

Przykładowo dla reakcji syntezy jodowodoru

$H_2+I_2=2HI$

$$\Delta E^o = 2E^o_{HI} - E^o_{H_2} - E^o_{I_2} = 2\times 6.7 - 0 - 15.66 = -2.26\,\text{kcal/mol}$$

$$-\Delta\left(\frac{G^o - E^o_o}{T}\right)_{|1000K} = 2\times 50.90 - 32.74 - 64.40 = 4.46\,\text{cal/mol}\times\text{K}$$

$$-R\ln K_p\left(T = 1000\,\text{K}\right) = -2.26 - 4.46 = -6.72\,\text{cal/mol}\times\text{K}$$

$$\ln K_p = \frac{6.72\,\text{cal/mol}\times\text{K}}{1.9862\,\text{cal/mol}\times\text{K}} = 3.3833$$

$$K_p = 29.47$$