

## Rozwiązania zadań – kolokwium 1 (z 21.04.2017)

### Zad. 1

$$v = kC_A C_B$$

$$k = 1 \cdot 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

$$C_{0A} = 5 \text{ mol/dm}^3$$

$$C_{0B} = 2 \text{ mol/dm}^3$$

$$t_{max} - ?$$

Bilans stężenia:

Reagenty	t=0	t ∈ (0, ∞)
A	$C_{0A}$	$C_{0A} - x$
B	$C_{0B}$	$C_{0B} + x$
C	0	x

$$v = kC_A C_B = \frac{dx}{dt} \Rightarrow \frac{dx}{dt} = k(C_{0A} - x)(C_{0B} + x)$$

$$\int_0^x \frac{dx}{(C_{0A} - x)(C_{0B} + x)} = \int_0^t k dt$$

$$\frac{1}{C_{0A} + C_{0B}} \ln \frac{C_{0A}(C_{0B} + x)}{C_{0B}(C_{0A} - x)} = kt$$

Po jakim czasie uzyskamy  $v_{max}$  - ?

Osiągnięcie maksymalnej szybkości związane jest ze spełnieniem zależności:  $\frac{dv}{dt} = 0 = \frac{dx}{dt}$

$$(C_{0B} + x) \left[ \frac{d}{dt}(kC_{0A}) + \frac{d}{dt}(-kx) \right] + (C_{0A} - x) \left[ \frac{d}{dt}(kC_{0B}) + \frac{d}{dt}(kx) \right] = 0$$

$$-(C_{0B} + x) \frac{dx}{dt} + (C_{0A} - x) \frac{dx}{dt} = 0$$

$$C_{0B} + x = C_{0A} - x \Rightarrow 2x = C_{0A} - C_{0B} \Rightarrow x = \frac{C_{0A} - C_{0B}}{2} = \frac{3}{2} \text{ mol/dm}^3$$

$$t_{max} = \frac{1}{k} \frac{1}{C_{0A} + C_{0B}} \ln \frac{C_{0A}(C_{0B} + x)}{C_{0B}(C_{0A} - x)} = 1308,9 \text{ s} = 21,82 \text{ min}$$

### Zad. 2

a)

Bilans

Reagenty	t=0	t ∈ (0, ∞)	t <sup>∞</sup>
A	$p_{0A}$	$p_{0A} - x$	0
B	0	x	$p_{0A}$
C	0	x	$p_{0A}$
Σ	$p_{0A}$	$p_{0A} + x$	$2p_{0A}$

$$p = p_{0A} + x \Rightarrow x = p - p_{0A}$$

$$p_A = p_{0A} - x = p_{0A} - p + p_{0A} = 2p_{0A} - p = 220 - p$$

$$p^\infty = 2p_{0A} = 220 \text{ Tr} \Rightarrow p_{0A} = 110 \text{ Tr}$$

t/min	5	7	9	12
t/s	300	420	540	720
p/Tr	123	126	129	133
p <sub>A</sub> /Tr	97	94	91	87
ln p <sub>A</sub>	4,575	4,543	4,511	4,466
1/p <sub>A</sub> · 10 <sup>2</sup>	1,03	1,06	1,10	1,05

Zał.: r=0

$$\begin{aligned}
 -\frac{dp_A}{dt} &= k \\
 p_A - p_{0A} &= -kt \\
 p_A &= -kt + p_{0A} \\
 y &= -2,28 \cdot 10^{-2}x + 1,04 \cdot 10^2 \\
 R^2 &= 9,989 \cdot 10^{-1}
 \end{aligned}$$

Zał.: r=1

$$\begin{aligned}
 -\frac{dp_A}{dt} &= kp_A \\
 \ln \frac{p_{0A}}{p_A} &= kt \\
 \ln p_A &= -kt + \ln p_{0A} \\
 y &= -2,596 \cdot 10^{-4}x + 4,65 \\
 R^2 &= 9,997 \cdot 10^{-1}
 \end{aligned}$$

Zał.: r=2

$$\begin{aligned}
 -\frac{dp_A}{dt} &= kp_A^2 \\
 \frac{1}{p_A} - \frac{1}{p_{0A}} &= kt \\
 \frac{1}{p_A} &= kt + \frac{1}{p_{0A}} \\
 y &= 2,83 \cdot 10^{-6}x + 9,457 \cdot 10^{-3} \\
 R^2 &= 9,9999 \cdot 10^{-1}
 \end{aligned}$$

Odp. r=2; k=2,83 · 10<sup>-6</sup> Tr<sup>-1</sup>s<sup>-1</sup>

$$v = \frac{1}{4} v_0 \Rightarrow kp_A^2 = \frac{1}{4} p_{0A}^2 \Rightarrow p_A = \frac{1}{2} p_{0A}$$

$$\text{Dla } r=2 \Rightarrow t = \frac{1}{k} \left( \frac{1}{p_A} - \frac{1}{p_{0A}} \right) = \frac{1}{k} \left( \frac{2}{p_{0A}} - \frac{1}{p_{0A}} \right) = 3212,34 \text{ s} = 53,54 \text{ min}$$

b)

$$\Delta H_{430}^\ddagger = ?; \Delta S_{430}^\ddagger = ?; \Delta G_{430}^\ddagger = ?$$

$$T_1 = 430^\circ\text{C} = 703,15 \text{ K}; \quad k_1 = 12k_2$$

$$T_2 = 400^\circ\text{C} = 673,15 \text{ K}; \quad k_2$$

$$\begin{cases} k_1 = Ae^{-E_a/RT_1} \\ k_2 = Ae^{-E_a/RT_2} \end{cases} \Rightarrow \begin{cases} \ln k_1 = \ln A - \frac{E_a}{RT_1} \\ \ln k_2 = \ln A - \frac{E_a}{RT_2} \end{cases}$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \Rightarrow \ln \frac{12k_2}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$E_a = \frac{R \cdot \ln 12}{\frac{1}{T_2} - \frac{1}{T_1}} = 325955,8 \text{ J/mol} = 325,96 \text{ kJ/mol}$$

$$\Delta H_{430(703)}^\ddagger = E_a - fRT = 314263 \text{ J/mol} = 314,26 \text{ kJ/mol}$$

$$k_1 = \frac{k_B T_1}{h} e^{\frac{\Delta S_1^\ddagger}{R}} e^{-\frac{\Delta H_1^\ddagger}{RT_1}} \Rightarrow \ln k_1 = \ln \frac{k_B T_1}{h} + \frac{\Delta S_1^\ddagger}{R} - \frac{\Delta H_1^\ddagger}{RT_1}$$

$$\frac{\Delta S_1^\ddagger}{R} = \ln k_1 - \ln \frac{k_B T_1}{h} + \frac{\Delta H_1^\ddagger}{RT_1} = 23,44 \Rightarrow \Delta S_{430(703)}^\ddagger = 194,90 \text{ J/mol K}$$

$$\Delta G_{430(703)}^\ddagger = \Delta H_{430(703)}^\ddagger - T \cdot \Delta S_{430(703)}^\ddagger = 177217,95 \text{ J/mol} = 177,22 \text{ kJ/mol}$$

**Zad. 3**

$$K_c = 2,5; \quad k_1 = 2,7 \cdot 10^{-3} \text{ s}^{-1}; \quad y = 30 \text{ min} = 1800 \text{ s}$$

$$\frac{x}{x_r} = ? \%$$

Reakcja odwracalna pierwszego rzędu.

Reagenty	t=0	t ∈ (0, ∞)	t <sup>∞</sup>
A	C <sub>0A</sub>	C <sub>0A</sub> - x	C <sub>0A</sub> - x <sub>r</sub>
B	0	x	x <sub>r</sub>

W stanie równowagi:  $v = v_1 - v_{-1} = k_1(C_{0A} - x_r) - k_{-1}x_r = 0$

$$k_1 C_{0A} - k_1 x_r - k_{-1} x_r = 0 \Rightarrow k_1 C_{0A} - x_r(k_1 + k_{-1}) = 0 \Rightarrow k_1 + k_{-1} = \frac{k_1 C_{0A}}{x_r}$$

$$\frac{k_1}{k_{-1}} = \frac{x_r}{C_{0A} - x_r} = K_c = 2,5 \Rightarrow C_{0A} K_c - x_r K_c = x_r \Rightarrow C_{0A} K_c = x_r(1 + K_c) \Rightarrow \frac{C_{0A}}{x_r} = \frac{1 + K_c}{K_c}$$

$$v = v_1 - v_{-1} = k_1(C_{0A} - x) - k_{-1}x = \frac{dx}{dt}$$

$$\frac{dx}{dt} = k_1 C_{0A} - k_1 x - k_{-1} x = k_1 C_{0A} - x(k_1 + k_{-1}) = k_1 C_{0A} - x \frac{k_1 C_{0A}}{x_r} = k_1 C_{0A} \left(1 - \frac{x}{x_r}\right)$$

$$\frac{x_r}{x_r - x} dx = k_1 C_{0A} dt$$

$$(x_r - x) dx = \frac{k_1 C_{0A}}{x_r} dt \Rightarrow \ln \frac{x_r}{x_r - x} = \frac{C_{0A}}{x_r} k_1 t$$

$$\ln \frac{x_r}{x_r - x} = \frac{1 + K_c}{K_c} k_1 t = 6,804$$

$$\frac{x_r}{x_r - x} = 901,4 \Rightarrow \frac{x_r - x}{x_r} = \frac{1}{901,4} \Rightarrow 1 - \frac{x}{x_r} = 0,0011$$

$$\frac{x}{x_r} = 0,9989 = 99,89\%$$

**Zad. 4**

Zależność Bronsteda-Bjerruma wiąże stałą szybkości  $k$  reakcji jonowej z siłą jonową  $I$  roztworu:

$$\log k = \log k_0 + 2A z_1 z_2 \sqrt{I}$$

$k_0$  - stała szybkości dla zerowej siły jonowej – stała szybkości reakcji, gdy współ. aktywności = 1;

$A$  – współczynnik D-H =  $0,509 \text{ dm}^{3/2} \text{ mol}^{-1/2}$ ;

$z_1, z_2$  - ładunki jonów reagujących;  $z_1 z_2 = 2$ ;

$I$  - siła jonowa;

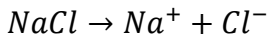
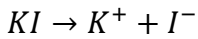
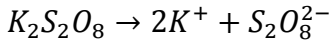
$$\log k = \log k_0 + 2 \cdot 0,509 \cdot 2 \cdot \sqrt{I} \Rightarrow \log k = \log k_0 + 2,036 \sqrt{I}$$

Całkowita siła jonowa zmienia się w skutek dodania NaCl.

$$I = \frac{1}{2} \sum C_i z_i^2 = \frac{1}{2} (2(+1)^2 C_{ON} + 1(-2)^2 C_{ON} + 1(+1)^2 C_{OI} + 1(-1)^2 C_{OI} + 1(+1)^2 C_{NaCl} + 1(-1)^2 C_{NaCl})$$

$$= \frac{1}{2} (6C_{ON} + 2C_{OI} + 2C_{NaCl}) = 9,5 \cdot 10^{-4} + C_{NaCl}$$

W roztworze mamy:



$I \cdot 10^3 / \frac{mol}{dm^3}$	2,75	4,55	6,95	9,95	19,95	15,35
$x = \sqrt{I} \cdot 10^2$	5,24	6,75	8,34	9,97	11,38	12,39
$y = \ln k$	-4,761	-4,730	-4,699	-4,668	-4,638	-4,617

$$y = 2,0037x - 4,8661$$

z zależność Bronsteda-Bjerruma  $2,036 \cong 2,0037$

$$\log k_0 = -4,8661 \Rightarrow k_0 = 1,36 \cdot 10^{-5} dm^3 mol^{-1} s^{-1}$$

### Zad. 5

Zal. etapem limitującym jest nieodwracalna reakcja powierzchniowa

$$v = k\theta_A\theta_B$$

$$\theta_A = b_A p_A (1 - \theta_A - \theta_B - \theta_C - \theta_W) = b_A p_A S$$

$$\theta_B = b_B p_B S$$

$$\theta_C = b_C p_C S$$

$$\theta_W = b_W p_W S$$

$$\theta_A = \frac{b_A p_A}{1 + b_A p_A + b_B p_B + b_C p_C + b_W p_W}$$

$$\theta_B = \frac{b_B p_B}{1 + b_A p_A + b_B p_B + b_C p_C + b_W p_W}$$

$$v = \frac{k_{exp} p_A p_B}{(1 + b_A p_A + b_B p_B + b_C p_C + b_W p_W)^2}$$