10. PŘEHLED KINETICKÝCH ROVNIC PRO JEDNODUCHÉ HOMOGENNÍ REAKCE VE VSÁDKOVÝCH REAKTORECH

10.1 JEDNOSMĚRNÉ REAKCE NULTÉHO ŘÁDU $\nu_A\,A \rightarrow$ PRODUKTY

Bilance: $c_A = c_{A0} - |\nu_A|\,x = c_{A0} - c_{A0}\cdot\alpha_A$

Diferenciální rovnice:

$$-\frac{dc_A}{d\tau} = |\nu_A|\cdot k_c$$

$$\frac{dx}{d\tau} = |\nu_A|\cdot k_c$$

$$\frac{d\alpha_A}{d\tau} = \frac{|\nu_A|}{c_{A0}}\cdot k_c$$

Integrální rovnice:

$$c_A = c_{A0} - |\nu_A|\cdot k_c\cdot\tau$$

$$x = -|\nu_A|\cdot k_c\cdot\tau$$

$$\alpha_A = -\frac{|\nu_A|}{c_{A0}}\cdot k_c\cdot\tau$$

Poločas

$$\tau_{1/2} = \frac{c_{A0}}{2|\nu_A|\cdot k_c}$$

10.2 JEDNOSMĚRNÉ REAKCE PRVÉHO ŘÁDU $\nu_A\,A \rightarrow$ PRODUKTY

Bilance: $c_A = c_{A0} - |\nu_A|\,x = c_{A0} - c_{A0}\cdot\alpha_A$

Diferenciální rovnice:

$$-\frac{dc_A}{d\tau} = |\nu_A|\cdot k_c\cdot c_A$$

$$\frac{dx}{d\tau} = |\nu_A|\cdot k_c\cdot(c_{A0} - x)$$

$$\frac{d\alpha_A}{d\tau} = |\nu_A|\cdot k_c\cdot(1-\alpha_A)$$

Integrální rovnice:

$$\ln\frac{c_{A0}}{c_A} = |\nu_A|\cdot k_c\cdot\tau$$

$$\ln\frac{c_{A0}}{c_{A0}-x} = |\nu_A|\cdot k_c\cdot\tau$$

$$\ln\frac{1}{1-\alpha_A} = |\nu_A|\cdot k_c\cdot\tau$$

Poločas

$$\tau_{1/2} = \frac{\ln 2}{|\nu_A|\cdot k_c}$$

10.3 JEDNOSMĚRNÉ REAKCE DRUHÉHO ŘÁDU

10.3.1 $\nu_A\,A \rightarrow$ PRODUKTY

$\nu_A\,A + \nu_A\,B \rightarrow$ **PRODUKTY,** $\alpha = \beta = 1$, *stejné počáteční koncentrace* $c_{A0} = c_{B0}$

Bilance:

$$c_A = c_{A0} - |\nu_A|\,x = c_{A0} - c_{A0}\cdot\alpha_A$$

$$c_B = c_{A0} - |\nu_A|\,x = c_{A,0} - c_{A0}\cdot\alpha_A = c_A$$

Diferenciální rovnice:

$$-\frac{dc_A}{d\tau} = |\nu_A|\cdot k_c\cdot c_A^2$$

$$\frac{dx}{d\tau} = |\nu_A|\cdot k_c\cdot(c_{A0} - x)^2$$

$$\frac{d\alpha_A}{d\tau} = |\nu_A|\cdot k_c\cdot c_{A0}\cdot(1-\alpha_A)^2$$

Integrální rovnice:

$$\frac{1}{c_A} - \frac{1}{c_{A0}} = |\nu_A|\cdot k_c\cdot\tau$$

$$\frac{1}{c_{A0}-x} - \frac{1}{c_{A0}} = |\nu_A|\cdot k_c\cdot\tau$$

$$\frac{1}{1-\alpha_A} - 1 = |\nu_A|\cdot k_c\cdot c_{A0}\cdot\tau$$

Poločas

$$\tau_{1/2} = \frac{1}{c_{A0}\cdot|\nu_A|\cdot k_c}$$

10.3.2 $\nu_A A + \nu_B B \rightarrow$ PRODUKTY, $\alpha = \beta = 1$, $c_{A0}/|\nu_A| = c_{B0}/|\nu_B|$

počáteční koncentrace ve *stechiometrickém poměru* $\dfrac{c_{A0}}{|\nu_A|} = \dfrac{c_{B0}}{|\nu_B|}$

Bilance:

$$c_A = c_{A0} - |\nu_A|\,x = c_{A0} - c_{A0}\cdot\alpha_A$$

$$c_B = c_{B0} - |\nu_B|\,x = |\nu_B|\left(\frac{c_{A,0}}{|\nu_A|} - x\right) = \frac{|\nu_B|}{|\nu_A|}\left(c_{A,0} - |\nu_A|\cdot x\right) = \frac{|\nu_B|}{|\nu_A|}\cdot c_A$$

$$= c_{B0} - c_{A0}\cdot\alpha_A = \frac{|\nu_B|}{|\nu_A|}\cdot c_{A0}(1-\alpha_A)$$

Diferenciální rovnice:

$$-\frac{dc_A}{|\nu_A|\cdot d\tau} = -\frac{dc_B}{|\nu_B|\cdot d\tau} = k_c\cdot c_A\cdot c_B =$$

$$= k_c\cdot\left(\frac{|\nu_B|}{|\nu_A|}\right)\cdot c_A^2 = k_c\cdot\left(\frac{|\nu_A|}{|\nu_B|}\right)\cdot c_B^2$$

$$\frac{dx}{d\tau} = |\nu_B|\,k_c\cdot(c_{A0} - |\nu_A|\,x)^2$$

$$= |\nu_A|\,k_c\cdot(c_{B0} - |\nu_B|\,x)^2$$

$$\frac{d\alpha_A}{d\tau} = |\nu_B|\,k_c\cdot c_{A0}\cdot(1-\alpha_A)^2 =$$

$$= |\nu_A|\,k_c\cdot c_{B0}\cdot(1-\alpha_A)^2$$

Integrální rovnice:

$$\frac{1}{c_A} - \frac{1}{c_{A0}} = |\nu_B|\cdot k_c\cdot\tau$$

$$\frac{1}{c_B} - \frac{1}{c_{B0}} = |\nu_A|\cdot k_c\cdot\tau$$

$$\frac{1}{c_{A0} - |\nu_A|\cdot x} - \frac{1}{c_{A0}} = |\nu_B|\cdot k_c\cdot\tau$$

$$\frac{1}{c_{B0} - |\nu_B|\cdot x} - \frac{1}{c_{B0}} = |\nu_A|\cdot k_c\cdot\tau$$

$$\frac{1}{1-\alpha_A} - 1 = |\nu_B|\cdot k_c\cdot c_{A0}\cdot\tau =$$

$$= |\nu_A|\cdot k_c\cdot c_{B0}\cdot\tau$$

Poločas:

$$\tau_{1/2} = \frac{1}{|\nu_B|\cdot k_c\cdot c_{A0}} = \frac{1}{|\nu_A|\cdot k_c\cdot c_{B0}}$$

10.3.3 $\nu_A A + \nu_B B \rightarrow$ PRODUKTY, $\alpha = \beta = 1$, $c_{A0}/|\nu_A| \neq c_{B0}/|\nu_B|$

počáteční koncentrace v *nestechiometrickém poměru* $\dfrac{c_{A0}}{|\nu_A|} \neq \dfrac{c_{B0}}{|\nu_B|}$

bilance:
(klíčová složka A)

$$c_A = c_{A0} - |\nu_A|\,x = c_{A0} - c_{A0}\cdot\alpha_A$$

$$c_B = c_{B0} - |\nu_B|\,x = c_{B0} - c_{A0}\cdot\alpha_A = c_{B0} - \frac{|\nu_B|}{|\nu_A|}\cdot c_{A0}\cdot\alpha_A$$

Diferenciální rovnice:

$$-\frac{dc_A}{d\tau} = |\nu_A|\,k_c\cdot c_A\cdot c_B$$

$$-\frac{dc_B}{d\tau} = |\nu_B|\,k_c\cdot c_A\cdot c_B$$

$$\frac{dx}{d\tau} = k_c\cdot(c_{A0} - |\nu_A|\cdot x)\cdot(c_{B0} - |\nu_B|\cdot x)$$

$$\frac{d\alpha_A}{d\tau} = |\nu_A|\cdot k_c\cdot(1-\alpha_A)\cdot\left(c_{B0} - c_{A0}\cdot\frac{|\nu_B|}{|\nu_A|}\cdot\alpha_A\right)$$

Integrální rovnice:

$$\ln\frac{c_{A0}\cdot c_B}{c_{B0}\cdot c_A} = \left(|\nu_A|\cdot c_{B0} - |\nu_B|\cdot c_{A0}\right)\cdot k_c\cdot\tau$$

$$\ln\frac{c_{A0}\cdot(c_{B0} - |\nu_B|\cdot x)}{c_{B0}\cdot(c_{A0} - |\nu_A|\cdot x)} = \left(|\nu_A|\cdot c_{B0} - |\nu_B|\cdot c_{A0}\right)\cdot k_c\cdot\tau$$

$$\ln\frac{1-\alpha_A\cdot\dfrac{c_{A0}\cdot|\nu_B|}{c_{B0}\cdot|\nu_A|}}{1-\alpha_A} = \left(|\nu_A|\cdot c_{B0} - |\nu_B|\cdot c_{A0}\right)\cdot k_c\cdot\tau$$

Poločas:
(vzhledem k A)

$$\tau_{1/2} = \frac{1}{k_c\cdot\left(|\nu_A|\cdot c_{B0} - |\nu_B|\cdot c_{A0}\right)}\cdot\ln\left(2 - \frac{c_{A0}\cdot|\nu_B|}{c_{B0}\cdot|\nu_A|}\right)$$

10.4 JEDNOSMĚRNÉ REAKCE *n*-TÉHO ŘÁDU

10.4.1 ν_A A → PRODUKTY

Bilance: $c_A = c_{A0} - |\nu_A|\, x = c_{A0} - c_{A0}\cdot\alpha_A$

Diferenciální rovnice:

$$-\frac{dc_A}{d\tau} = |\nu_A|\cdot k_c\cdot c_A^n$$

$$\frac{dx}{d\tau} = |\nu_A|\cdot k_c\cdot (c_{A0}-x)^n$$

$$\frac{d\alpha_A}{d\tau} = |\nu_A|\cdot k_c\cdot c_{A0}^{n-1}\cdot(1-\alpha_A)^n$$

Integrální rovnice:

$$c_A^{1-n} - c_{A0}^{1-n} = |\nu_A|\cdot k_c\cdot(n-1)\cdot\tau$$

$$(c_{A0}-x)^{1-n} - c_{A0}^{1-n} = |\nu_A|\cdot k_c\cdot(n-1)\cdot\tau$$

$$(1-\alpha_A)^{1-n} - 1 = |\nu_A|\cdot k_c\cdot c_{A0}^{n-1}\cdot(n-1)\cdot\tau$$

Poločas

$$\tau_{1/2} = \left[\frac{2^{n-1}-1}{|\nu_A|(n-1)\cdot k_c}\right]\cdot c_{A0}^{1-n}$$

10.4.2 ν_A A + ν_B B → PRODUKTY, $n = \alpha + \beta,\ \alpha \neq \beta$

počáteční koncentrace ve *stechiometrickém poměru* $\dfrac{c_{A0}}{|\nu_A|} = \dfrac{c_{B0}}{|\nu_B|}$

Bilance:

$$c_A = c_{A0} - |\nu_A|\, x = c_{A0} - c_{A0}\cdot\alpha_A$$

$$c_B = c_{B0} - |\nu_B|\, x = |\nu_B|\left(\frac{c_{A0}}{|\nu_A|} - x\right) = \frac{|\nu_B|}{|\nu_A|}\left(c_{A0} - |\nu_A|\cdot x\right) = \frac{|\nu_B|}{|\nu_A|}\cdot c_A$$

$$= c_{B0} - c_{A0}\cdot\alpha_A = \frac{|\nu_B|}{|\nu_A|}\cdot c_{A0}(1-\alpha_A)$$

Diferenciální rovnice:

$$-\frac{dc_A}{|\nu_A|\cdot d\tau} = -\frac{dc_B}{|\nu_B|\cdot d\tau} = k_c\cdot c_A^{\alpha}\cdot c_B^{\beta} =$$

$$= k_c\cdot\left(\frac{|\nu_B|}{|\nu_A|}\right)^{\alpha}\cdot c_A^n = k_c\cdot\left(\frac{|\nu_A|}{|\nu_B|}\right)^{\beta}\cdot c_B^n$$

$$\frac{dx}{d\tau} = k_c\cdot\left(\frac{|\nu_B|}{|\nu_A|}\right)^{\beta}\cdot\left(c_{A0} - |\nu_A|\, x\right)^n$$

$$= k_c\cdot\left(\frac{|\nu_A|}{|\nu_B|}\right)^{\alpha}\cdot\left(c_{B0} - |\nu_B|\, x\right)^n$$

$$\frac{d\alpha_A}{d\tau} = k_c\cdot\left(\frac{|\nu_B|^{\beta}}{|\nu_A|^{\beta-1}}\right)\cdot c_{A0}^{n-1}\cdot(1-\alpha_A)^n$$

$$= k_c\cdot\left(\frac{|\nu_A|^{\alpha}}{|\nu_B|^{\alpha-1}}\right)\cdot c_{B0}^{n-1}\cdot(1-\alpha_A)^n$$

Integrální rovnice:

$$c_A^{1-n} - c_{A0}^{1-n} = k_c\left(\frac{|\nu_B|}{|\nu_A|}\right)^{\beta}\cdot(n-1)\cdot\tau$$

$$c_B^{1-n} - c_{B0}^{1-n} = k_c\left(\frac{|\nu_A|}{|\nu_B|}\right)^{\alpha}\cdot(n-1)\cdot\tau$$

$$\left(c_{A0} - |\nu_A|\cdot x\right)^{1-n} - c_{A0}^{1-n} = k_c\left(\frac{|\nu_B|}{|\nu_A|}\right)^{\beta}\cdot(n-1)\cdot\tau$$

$$\left(c_{B0} - |\nu_B|\cdot x\right)^{1-n} - c_{B0}^{1-n} = k_c\left(\frac{|\nu_A|}{|\nu_B|}\right)^{\alpha}\cdot(n-1)\cdot\tau$$

$$(1-\alpha_A)^{1-n} - 1 = k_c\cdot\left(\frac{|\nu_B|^{\beta}}{|\nu_A|^{\beta-1}}\right)\cdot(n-1)\cdot c_{A0}^{n-1}\cdot\tau$$

$$= k_c\cdot\left(\frac{|\nu_A|^{\alpha}}{|\nu_B|^{\alpha-1}}\right)\cdot(n-1)\cdot c_{B0}^{n-1}\cdot\tau$$

Poločas:

$$\tau_{1/2} = \frac{|\nu_A|^{\beta-1}\cdot\left(2^{n-1}-1\right)}{|\nu_B|^{\beta}\cdot k_c\cdot(n-1)}\cdot c_{A0}^{1-n} = \frac{|\nu_B|^{\alpha-1}\cdot\left(2^{n-1}-1\right)}{|\nu_A|^{\alpha}\cdot k_c\cdot(n-1)}\cdot c_{B0}^{1-n}$$

10.5 Protisměrné reakce

10.5.1 Reakce oboustranně prvého řádu $\mathbf{A} \underset{k_{c-}}{\overset{k_{c+}}{\rightleftarrows}} \mathbf{D}$

Bilance:
$$c_\mathrm{A} = c_\mathrm{A0} - x = c_\mathrm{A0} - c_\mathrm{A0} \cdot \alpha_\mathrm{A}$$
$$c_\mathrm{D} = c_\mathrm{D0} + x = c_\mathrm{D0} + c_\mathrm{A0} \cdot \alpha_\mathrm{A}$$

Diferenciální rovnice:

$$-\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}\tau} = +\frac{\mathrm{d}c_\mathrm{D}}{\mathrm{d}\tau} = k_{c+} \cdot c_\mathrm{A} - k_{c-} \cdot c_\mathrm{D}$$

$$\frac{\mathrm{d}x}{\mathrm{d}\tau} = k_{c+} \cdot (c_\mathrm{A0} - x) - k_{c-} \cdot (c_\mathrm{D0} + x)$$

$$\frac{\mathrm{d}\alpha_\mathrm{A}}{\mathrm{d}\tau} = k_{c+} \cdot (1 - \alpha_\mathrm{A}) - k_{c-} \cdot \left(\frac{c_\mathrm{D0}}{c_\mathrm{A0}} + \alpha_\mathrm{A} \right)$$

Integrální rovnice:

$$\ln \frac{c_\mathrm{A0} \cdot K_c - c_\mathrm{D0}}{c_\mathrm{A0} \cdot K_c - c_\mathrm{D0} - x \cdot (K_c + 1)} = k_{c+} \cdot \frac{K_c + 1}{K_c} \cdot \tau$$

$$\ln \frac{c_\mathrm{A0} \cdot K_c - c_\mathrm{D0}}{c_\mathrm{A0} \cdot K_c - c_\mathrm{D0} - \alpha \cdot c_\mathrm{A0} \cdot (K_c + 1)} = k_{c+} \cdot \frac{K_c + 1}{K_c} \cdot \tau$$

Rovnováha:

$$K_c = \frac{c_\mathrm{Drov}}{c_\mathrm{Arov}} = \frac{c_\mathrm{D0} + x_\mathrm{rov}}{c_\mathrm{A0} - x_\mathrm{rov}} = \frac{c_\mathrm{D0} + c_\mathrm{A0} \cdot \alpha_\mathrm{Arov}}{c_\mathrm{A0}(1 - \alpha_\mathrm{Arov})}$$

10.5.2 Přímá reakce prvého řádu, zpětná druhého řádu $\mathbf{A} \underset{k_{c-}}{\overset{k_{c+}}{\rightleftarrows}} \mathbf{D + E}$

Bilance:
$$c_\mathrm{A} = c_\mathrm{A0} - x = c_\mathrm{A0} - c_\mathrm{A0} \cdot \alpha_\mathrm{A} \quad , \quad c_\mathrm{D} = c_\mathrm{D0} + x = c_\mathrm{D0} + c_\mathrm{A0} \cdot \alpha_\mathrm{A}$$
$$c_\mathrm{E} = c_\mathrm{E0} + x = c_\mathrm{E0} + c_\mathrm{A0} \cdot \alpha_\mathrm{A}$$

Diferenciální rovnice:

$$-\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}\tau} = +\frac{\mathrm{d}c_\mathrm{D}}{\mathrm{d}\tau} = +\frac{\mathrm{d}c_\mathrm{E}}{\mathrm{d}\tau} = k_{c+} \cdot c_\mathrm{A} - k_{c-} \cdot c_\mathrm{D} \cdot c_\mathrm{E}$$

$$\frac{\mathrm{d}x}{\mathrm{d}\tau} = k_{c+} \cdot (c_\mathrm{A0} - x) - k_{c-} \cdot (c_\mathrm{D0} + x) \cdot (c_\mathrm{E0} + x)$$

$$\frac{\mathrm{d}\alpha_\mathrm{A}}{\mathrm{d}\tau} = k_{c+} \cdot (1 - \alpha_\mathrm{A}) + $$
$$- k_{c-} \cdot c_\mathrm{A0} \cdot \left(\frac{c_\mathrm{D0}}{c_\mathrm{A0}} + \alpha_\mathrm{A} \right) \cdot \left(\frac{c_\mathrm{E0}}{c_\mathrm{A0}} + \alpha_\mathrm{A} \right)$$

Integrální rovnice:

$$\ln \frac{(1 - \mathrm{M}) \cdot [\mathrm{N} \cdot (1 + \mathrm{M}) + x]}{(1 + \mathrm{M}) \cdot [\mathrm{N} \cdot (1 - \mathrm{M}) + x]} = k_{c+} \cdot \frac{2 \cdot \mathrm{M} \cdot \mathrm{N}}{K_c} \cdot \tau$$

$$\ln \frac{(1 - \mathrm{M}) \cdot [\mathrm{N} \cdot (1 + \mathrm{M}) + c_\mathrm{A0} \cdot \alpha_\mathrm{A}]}{(1 + \mathrm{M}) \cdot [\mathrm{N} \cdot (1 - \mathrm{M}) + c_\mathrm{A0} \cdot \alpha_\mathrm{A}]} = k_{c+} \cdot \frac{2 \cdot \mathrm{M} \cdot \mathrm{N}}{K_c} \cdot \tau$$

kde $\mathrm{M} = \left[1 + \dfrac{c_\mathrm{A0} \cdot K_c - c_\mathrm{D0} \cdot c_\mathrm{E0}}{\mathrm{N}^2} \right]^{1/2}$

$\mathrm{N} = \frac{1}{2}(K_c + c_\mathrm{D0} + c_\mathrm{E0})$

Rovnováha:

$$K_c = \frac{c_\mathrm{Drov} \cdot c_\mathrm{Erov}}{c_\mathrm{Arov}} = \frac{(c_\mathrm{D0} + x_\mathrm{Arov}) \cdot (c_\mathrm{E0} + x_\mathrm{Arov})}{c_\mathrm{A0} - x_\mathrm{Arov}} = \frac{(c_\mathrm{D0} + c_\mathrm{A0} \cdot \alpha_\mathrm{Arov}) \cdot (c_\mathrm{E,0} + c_\mathrm{A0} \cdot \alpha_\mathrm{Arov})}{c_\mathrm{A0}(1 - \alpha_\mathrm{Arov})}$$

10.5.3 PŘÍMÁ REAKCE DRUHÉHO ŘÁDU, ZPĚTNÁ PRVÉHO ŘÁDU $\mathbf{A+B \underset{k_{c-}}{\overset{k_{c+}}{\rightleftarrows}} D}$

Bilance:

$$c_A = c_{A0} - x = c_{A0} - c_{A0}\cdot\alpha_A \quad , \quad c_D = c_{D0} + x = c_{D0} + c_{A0}\cdot\alpha_A$$
$$c_B = c_{B0} - x = c_{B0} - c_{A0}\cdot\alpha_A$$

Diferenciální rovnice:

$$-\frac{dc_A}{d\tau} = -\frac{dc_B}{d\tau} = +\frac{dc_D}{d\tau} = k_{c+}\cdot c_A\cdot c_B - k_{c-}\cdot c_D$$

$$\frac{dx}{d\tau} = k_{c+}\cdot(c_{A0}-x)\cdot(c_{B0}-x) - k_{c-}\cdot(c_{D0}+x)$$

$$\frac{d\alpha_A}{d\tau} = k_{c+}\cdot c_{A0}\cdot(1-\alpha_A)\cdot\left(\frac{c_{B0}}{c_{A0}}+\alpha_A\right) + \\ - k_{c-}\cdot\left(\frac{c_{D0}}{c_{A0}}+\alpha_A\right)$$

Integrální rovnice:

$$\ln\frac{(1-M)\cdot[N\cdot(1+M)-x]}{(1+M)\cdot[N\cdot(1-M)-x]} = k_{c+}\cdot 2\cdot M\cdot N\cdot\tau$$

$$\ln\frac{(1-M)\cdot[N\cdot(1+M)-c_{A0}\cdot\alpha_A]}{(1+M)\cdot[N\cdot(1-M)-c_{A0}\cdot\alpha_A]} = k_{c+}\cdot 2\cdot M\cdot N\cdot\tau$$

kde $$M = \left[1+\frac{c_{D0}-K_c\cdot c_{A0}\cdot c_{B0}}{K_c\cdot N^2}\right]^{1/2}$$

$$N = \frac{1+K_c\cdot(c_{A0}+c_{B0})}{2\,K_c}$$

Rovnováha:

$$K_c = \frac{c_{Drov}}{c_{Arov}\cdot c_{Brov}} = \frac{(c_{D0}+x_{Arov})}{(c_{A0}-x_{Arov})\cdot(c_{B0}-x_{Arov})} = \frac{(c_{D0}+c_{A0}\cdot\alpha_{Arov})}{c_{A0}(1-\alpha_{Arov})\cdot(c_{B0}+c_{A0}\cdot\alpha_{Arov})}$$

10.5.4 PŘÍMÁ I ZPĚTNÁ REAKCE DRUHÉHO ŘÁDU $\mathbf{A+B \underset{k_{c-}}{\overset{k_{c+}}{\rightleftarrows}} D+E}$

Bilance:

$$c_A = c_{A0} - x = c_{A0} - c_{A0}\cdot\alpha_A \quad , \quad c_D = c_{D0} + x = c_{D0} + c_{A0}\cdot\alpha_A$$
$$c_B = c_{B0} - x = c_{B0} - c_{A0}\cdot\alpha_A \quad , \quad c_D = c_{E0} + x = c_{E0} + c_{A0}\cdot\alpha_A$$

Diferenciální rovnice:

$$-\frac{dc_A}{d\tau} = -\frac{dc_B}{d\tau} = +\frac{dc_D}{d\tau} = +\frac{dc_E}{d\tau} = \\ = k_{c+}\cdot c_A\cdot c_B - k_{c-}\cdot c_D\cdot c_E$$

$$\frac{dx}{d\tau} = k_{c+}(c_{A0}-x)(c_{B0}-x) - k_{c-}(c_{D0}+x)(c_{E0}+x)$$

$$\frac{d\alpha_A}{d\tau} = k_{c+}\cdot c_{A0}\cdot(1-\alpha_A)\cdot\left(\frac{c_{B0}}{c_{A0}}-\alpha_A\right) + \\ - k_{c-}\cdot c_{A0}\cdot\left(\frac{c_{D0}}{c_{A0}}+\alpha_A\right)\cdot\left(\frac{c_{E0}}{c_{A0}}+\alpha_A\right)$$

Integrální rovnice:

$$\ln\frac{(1-M)\cdot[N\cdot(1+M)-x]}{(1+M)\cdot[N\cdot(1-M)-x]} = k_{c+}\cdot 2\cdot M\cdot N\cdot\frac{K_c-1}{K_c}\cdot\tau$$

$$\ln\frac{(1-M)[N(1+M)-c_{A0}\cdot\alpha_A]}{(1+M)[N(1-M)-c_{A0}\cdot\alpha_A]} = k_{c+}\cdot 2M\cdot N\frac{K_c-1}{K_c}\cdot\tau$$

kde $$M = \left[1+\frac{c_{D0}\cdot c_{E0}-K_c\cdot c_{A0}\cdot c_{B0}}{(K_c-1)\cdot N^2}\right]^{1/2}$$

$$N = \frac{K_c\cdot(c_{A0}+c_{B0})+c_{D0}+c_{E0}}{2\,(K_c-1)}$$

Rovnováha:

$$K_c = \frac{c_{Drov}\cdot c_{Erov}}{c_{Arov}\cdot c_{Brov}} = \frac{(c_{D0}+x_{rov})\cdot(c_{E0}-x_{rov})}{(c_{A0}-x_{rov})\cdot(c_{B0}-x_{rov})} = \frac{(c_{D0}+c_{A0}\cdot\alpha_{Arov})\cdot(c_{E0}+c_{A0}\cdot\alpha_{Arov})}{c_{A0}(1-\alpha_{Arov})\cdot(c_{B0}-c_{A0}\cdot\alpha_{Arov})}$$

10.6 BOČNÉ REAKCE

10.6.1 ROZVĚTVENÉ REAKCE PRVÉHO ŘÁDU $\quad \mathbf{A} \begin{array}{l} \xrightarrow{k_1} \nu_R\,\mathbf{R} \\ \xrightarrow[k_2]{} \nu_S\,\mathbf{S} \end{array}$

Bilance: $\quad c_A = c_{A0} - x_1 - x_2 \quad , \quad c_R = c_{R0} + \nu_R\, x_1 \quad \mathrm{d}\, c_R = \nu_R \cdot \mathrm{d}\, x_1$

$c_S = c_{S0} + \nu_S\, x_2 \quad \mathrm{d}\, c_S = \nu_S \cdot \mathrm{d}\, x_2$

Diferenciální rovnice:

$$-\frac{\mathrm{d}c_A}{\mathrm{d}\tau} = (k_1 + k_2) \cdot c_A$$

$$\frac{\mathrm{d}c_R}{\nu_R \cdot \mathrm{d}\tau} = k_1 \cdot c_A$$

$$\frac{\mathrm{d}c_S}{\nu_S \cdot \mathrm{d}\tau} = k_2 \cdot c_A$$

Integrální rovnice:

$$c_A = c_{A0} \cdot \mathrm{e}^{-(k_1+k_2)\cdot\tau}$$

$$c_R = c_{R0} + \frac{\nu_R \cdot k_1 \cdot c_{A0}}{k_1 + k_2} \cdot \left(1 - \mathrm{e}^{-(k_1+k_2)\cdot\tau}\right)$$

$$c_S = c_{S0} + \frac{\nu_S \cdot k_2 \cdot c_{A0}}{k_1 + k_2} \cdot \left(1 - \mathrm{e}^{-(k_1+k_2)\cdot\tau}\right)$$

10.6.2 ROZVĚTVENÉ REAKCE DRUHÉHO ŘÁDU $\quad \mathbf{2\,A} \begin{array}{l} \xrightarrow{k_1} \nu_R\,\mathbf{R} \\ \xrightarrow[k_2]{} \nu_S\,\mathbf{S} \end{array}$

Bilance: $\quad c_A = c_{A0} - 2\,x_1 - 2\,x_2 \quad , \quad c_R = c_{R0} + \nu_R\, x_1 \quad \mathrm{d}\, c_R = \nu_R \cdot \mathrm{d}\, x_1$

$c_S = c_{S0} + \nu_S\, x_2 \quad \mathrm{d}\, c_S = \nu_S \cdot \mathrm{d}\, x_2$

Diferenciální rovnice:

$$-\frac{\mathrm{d}c_A}{2\,\mathrm{d}\tau} = (k_1 + k_2) \cdot c_A^2$$

$$+\frac{\mathrm{d}c_R}{\nu_R \cdot \mathrm{d}\tau} = k_1 \cdot c_A^2$$

$$+\frac{\mathrm{d}c_S}{\nu_S \cdot \mathrm{d}\tau} = k_2 \cdot c_A^2$$

Integrální rovnice:

$$\frac{1}{c_A} - \frac{1}{c_{A0}} = 2\,(k_1 + k_2) \cdot \tau \quad , \quad c_A = \frac{c_{A0}}{1 + 2\,c_{A0} \cdot (k_1 + k_2) \cdot \tau}$$

$$c_R = c_{R0} + \frac{\nu_R \cdot k_1 \cdot c_{A0}^2 \cdot \tau}{1 + 2 \cdot c_{A0} \cdot (k_1 + k_2) \cdot \tau}$$

$$c_S = c_{S0} + \frac{\nu_S \cdot k_2 \cdot c_{A0}^2 \cdot \tau}{1 + 2 \cdot c_{A0} \cdot (k_1 + k_2) \cdot \tau}$$

10.6.3 ROZVĚTVENÉ REAKCE DRUHÉHO ŘÁDU $\quad \mathbf{A + B} \begin{array}{l} \xrightarrow{k_1} \nu_R\,\mathbf{R} \\ \xrightarrow[k_2]{} \nu_S\,\mathbf{S} \end{array}$

Bilance: $\quad c_A = c_{A0} - x_1 - x_2 \quad , \quad c_R = c_{R0} + \nu_R\, x_1 \quad \mathrm{d}\, c_R = \nu_R \cdot \mathrm{d}\, x_1$

$c_B = c_{B0} - x_1 - x_2 \quad , \quad c_S = c_{S0} + \nu_S\, x_2 \quad \mathrm{d}\, c_S = \nu_S \cdot \mathrm{d}\, x_2$

Diferenciální rovnice:

$$-\frac{\mathrm{d}c_A}{\mathrm{d}\tau} = -\frac{\mathrm{d}c_B}{\mathrm{d}\tau} = (k_1 + k_2) \cdot c_A \cdot c_B$$

$$\frac{\mathrm{d}c_R}{\nu_R \cdot \mathrm{d}\tau} = k_1 \cdot c_A \cdot c_B$$

$$\frac{\mathrm{d}c_S}{\nu_S \cdot \mathrm{d}\tau} = k_2 \cdot c_A \cdot c_B$$

Integrální rovnice:

$$\ln \frac{c_{A0} \cdot c_B}{c_{B0} \cdot c_A} = (k_1 + k_2) \cdot (c_{B0} - c_{A0}) \cdot \tau$$

$$c_R = c_{R0} + \frac{\nu_R \cdot k_1 \cdot c_{A0}}{(k_1 + k_2)} \cdot \frac{(1 - \mathrm{e}^{(k_1+k_2)\cdot(c_{B0}-c_{A0})\cdot\tau})}{(c_{A0} - c_{B0} \cdot \mathrm{e}^{(k_1+k_2)\cdot(c_{B0}-c_{A0})\cdot\tau})}$$

$$c_S = c_{S0} + \frac{\nu_S \cdot k_2 \cdot c_{A0}}{(k_1 + k_2)} \cdot \frac{(1 - \mathrm{e}^{(k_1+k_2)\cdot(c_{B0}-c_{A0})\cdot\tau})}{(c_{A0} - c_{B0} \cdot \mathrm{e}^{(k_1+k_2)\cdot(c_{B0}-c_{A0})\cdot\tau})}$$

10.6.4 KONKURENČNÍ BOČNÉ REAKCE

$$\nu_{A1}\,\mathbf{A(g)} + \nu_B\,\mathbf{B(g)} \xrightarrow{k_1} \nu_R\,\mathbf{R(g)}$$

α_1- řád vzhledem k A, β - vzhledem k B

$$\nu_{A2}\,\mathbf{A(g)} + \nu_C\,\mathbf{C(g)} \xrightarrow{k_2} \nu_S\,\mathbf{S(g)}$$

α_2 -řád vzhledem k A, γ - vzhledem k C

Bilance:

$$c_A = c_{A0} + \nu_{A1}\,x_1 + \nu_{A2}\,x_2$$
$$c_B = c_{B0} + \nu_B\,x_1$$
$$c_C = c_{C0} + \nu_C\,x_2$$
$$c_R = c_{R0} + \nu_R\,x_1$$
$$c_S = c_{S0} + \nu_S\,x_2$$

Diferenciální rovnice:

$$\frac{dc_A}{\nu_A\,d\tau} = k_1 \cdot c_A^{\alpha_1} \cdot c_B^{\beta} + k_2 \cdot c_A^{\alpha_2} \cdot c_C^{\gamma}$$

$$\frac{dc_R}{\nu_R\,d\tau} = \frac{dc_B}{\nu_B\,d\tau} = k_1 \cdot c_A^{\alpha_1} \cdot c_B^{\beta}$$

$$\frac{dc_S}{\nu_S\,d\tau} = \frac{dc_C}{\nu_C\,d\tau} = k_2 \cdot c_A^{\alpha_2} \cdot c_C^{\gamma}$$

$$\frac{d\,c_R}{d\,c_S} = \frac{k_1}{k_2} \cdot \frac{\nu_R}{\nu_S} c_A^{(\alpha_1-\alpha_2)} \cdot \frac{c_B^{\beta}}{c_C^{\gamma}}$$

$$\frac{d\,x_1}{d\,x_2} = \frac{k_1}{k_2} \cdot (c_{A0} + \nu_{A_1} \cdot x_1 + \nu_{A_1} \cdot x_2)^{(\alpha_1-\alpha_2)} \cdot \frac{(c_{B0} + \nu_B \cdot x_1)^{\beta}}{(c_{C0} + \nu_C \cdot x_2)^{\gamma}}$$

Integrální rovnice:
(pro speciální případy)

$\alpha_1 = \alpha_2$ a $\beta = \gamma = 1$

$$\ln\frac{c_B - \nu_B \cdot x_1}{c_{B0}} = \frac{k_1}{k_2} \cdot \frac{\nu_B}{\nu_C} \cdot \ln\frac{c_{C0} - \cdot x_2}{c_{C0}}$$

$\alpha_1 = \alpha_2$ a $\beta = 1$, $\gamma = 2$

$$\ln\frac{c_{B0} + \nu_B \cdot x_1}{c_{B0}} = \frac{k_1}{k_2} \cdot \frac{\nu_B \cdot \nu_C \cdot x_2}{c_{C0} \cdot (c_{C0} + \nu_C \cdot x_2)}$$

10.7 Následné reakce $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

10.7.1 Reakce prvého řádu, $k_1 \neq k_2$

Diferenciální rovnice:

$$-\frac{dc_A}{d\tau} = k_1 \cdot c_A$$

$$\frac{dc_B}{d\tau} = k_1 \cdot c_A - k_2 \cdot c_B$$

$$\frac{dc_C}{d\tau} = k_2 \cdot c_B \quad c_C = c_{A0} + c_{B0} + c_{C0} - c_A - c_B$$

Integrální rovnice:

$$c_A = c_{A0} \cdot e^{-k_1 \cdot \tau}$$

$$c_B = c_{B0} \cdot e^{-k_2 \cdot \tau} + \frac{c_{A0} \cdot k_1}{k_2 - k_1} \cdot \left(e^{-k_1 \cdot \tau} - e^{-k_2 \cdot \tau} \right)$$

$$\tau_{max} = \frac{1}{k_2 - k_1} \cdot \ln \frac{k_1 \cdot k_2 \cdot (c_{A0} + c_{B0}) - k_2^2 \cdot c_{B0}}{k_1^2 \cdot c_{A0}}$$

$$c_{B0} = 0: \quad \tau_{max} = \frac{\ln (k_2 / k_1)}{k_2 - k_1}, \quad c_{Bmax} = c_{A0} \left(\frac{k_1}{k_2} \right)^{\frac{k_1}{k_2 - k_1}}$$

$$c_C = c_{C0} + c_{B0} \left(1 - e^{-k_2 \cdot \tau} \right) + c_{A0} \left(1 + \frac{e^{-k_1 \cdot \tau} - e^{-k_2 \cdot \tau}}{k_2 - k_1} \right)$$

10.7.2 Reakce prvého řádu, $k_1 >> k_2$,

Řídící děj $B \rightarrow C$

$$c_A \rightarrow 0$$

$$c_B = (c_{A0} + c_{B0}) \; e^{-k_2 \cdot \tau}$$

$$c_C = c_{C0} + (c_{A0} + c_{B0}) \cdot (1 - e^{-k_2 \cdot \tau})$$

10.7.3 Reakce prvého řádu, $k_1 << k_2$

Řídící děj $A \rightarrow B$

$$c_A = c_{A0} \cdot e^{-k_1 \cdot \tau}$$

$$c_B = c_{A0} \cdot \frac{k_1}{k_2} \cdot e^{-k_1 \cdot \tau}$$

$$c_C = c_{C0} + c_{B0} + c_{A0} \cdot (1 - e^{-k_1 \cdot \tau})$$

10.7.4 Reakce prvého řádu, $k_1 = k_2$

Diferenciální rovnice:

$$-\frac{dc_A}{d\tau} = k \cdot c_A$$

$$\frac{dc_B}{d\tau} = k \cdot (c_A - c_B)$$

$$\frac{dc_C}{d\tau} = k \cdot c_B$$

Integrální rovnice:

$$c_A = c_{A0} \cdot e^{-k \cdot \tau}$$

$$c_B = e^{-k \cdot \tau} \cdot (c_{B0} + k \cdot c_{A0} \cdot \tau)$$

$$\tau_{max} = \frac{c_{A0} - c_{B0}}{k \cdot c_{A0}} \; ; \quad c_{B\,max} = c_{A0} \cdot \exp \left(\frac{c_{B0} - c_{A0}}{c_{A0}} \right)$$

$$c_{B0} = 0: \quad \tau_{max} = \frac{1}{k} \quad , \; c_{Bmax} = c_{A0} \cdot \exp(-1)$$

$$c_C = c_{A0} + c_{B0} + c_{C0} - c_A - c_B$$

$$c_C = c_{C0} + c_{A0} \left(1 - (1 + k \cdot \tau) \cdot e^{-k \cdot \tau} \right) + c_{B0} \left(1 - e^{-k \cdot \tau} \right)$$