

3 SLOŽKY:

(SM)

$$-\frac{1}{RT} \frac{dM_1}{dz} = x_2 \frac{v_1 - v_2}{D_{12}} + x_3 \frac{v_1 - v_3}{D_{13}}$$

$$-\frac{1}{RT} \frac{dM_2}{dz} = x_1 \frac{v_2 - v_1}{D_{12}} + x_3 \frac{v_2 - v_3}{D_{23}}$$

BINÁR. KOEF.

$$(D_{21} = D_{12})$$

(F)

$$-J_1 = c D'_{11} \frac{dx_1}{dz} + c D'_{12} \frac{dx_2}{dz}$$

$$-J_2 = c D'_{21} \frac{dx_1}{dz} + c D'_{22} \frac{dx_2}{dz}$$

KOEF. ZÁV.
NA SLOŽ.

PŘEP.

$$D'_{11} = D_{13} [x_1 D_{23} + (x_2 + x_3) D_{12}] / Z$$

$$D'_{21} = x_2 D_{13} (D_{23} - D_{12}) / Z$$

$$Z = x_1 D_{23} + x_2 D_{13} + x_3 D_{12}$$

$$D'_{12} = x_1 D_{23} (D_{13} - D_{12}) / Z$$

$$D'_{22} = D_{23} [x_2 D_{13} + (x_1 + x_3) D_{12}] / Z$$

$$[x_{cr} = 1, v_v = v_n, D_{12} = D_{21}]$$

PSEUDO BINÁR

$$J_1 = -c D_1 \frac{dx_1}{dz}$$

$$c \frac{dx_1}{dz} = \frac{x_1 j_2 - x_2 j_1}{D_{12}} + \frac{x_1 j_3 - x_3 j_1}{D_{13}}$$

$$[x_{cr} = 1]$$



$$\frac{1}{RT} \frac{dM_i}{dz} = \frac{1}{x_i} \frac{dx_i}{dz}$$

$$J_i = (v_i - v_n) c x_i$$

$$v_n = \sum x_i v_i, \sum x_i = 1$$

1. $D_{12} = D_{13} = D_{23} = D_1$

$$c D_{12} \frac{dx_1}{dz} = x_1 j_2 + x_2 j_1 - (1 - x_1) j_1 = x_1 j_2 - j_1 = -J_1$$

2. $x_1 \rightarrow 0$: bindr 1 - 2+3

BLANC

$$c \frac{dx_1}{dz} = -\left(\frac{x_2}{D_{12}} + \frac{x_3}{D_{13}}\right) j_1 = -\frac{1}{D_1} J_1 \quad (j_1 = x_1 j + J_1, x_2, x_3 = \text{const})$$

3. $x_1 \rightarrow 0, x_2 \rightarrow 0$: bindry 1-3 $D_1 = D_{13}$, 2-3 $D_2 = D_{23}$

$$c \frac{dx_1}{dz} = -\frac{x_3 j_1}{D_{13}} = -\frac{j_1}{D_{13}} = -\frac{1}{D_{13}} J_1 \quad (j_1 = J_1, x_3 = 1)$$

DIFÚZE V ROZTOCÍCH ELEKTROLYTŮ

NERNST - PLANCK

EINSTEIN

ROZP.

EL. POHYB.

$$\vec{j}_i^0 = -D_i \nabla c_i - c_i u_i \nabla \varphi$$

EL. POT.

$$u_i = \frac{z_i D_i F}{RT}$$

NA'BOJ

FARADAYOVA KONST.

$$\vec{j}_i^0 = -D_i \nabla c_i - z_i c_i D_i \frac{F}{RT} \nabla \varphi$$

FORMA STEFAN-MAXWELL

($v_0 = 0, c_0 \rightarrow c$)

$$\nabla c_i + \frac{F}{RT} z_i c_i \nabla \varphi = - \frac{\vec{j}_i}{D_{i0}} \left(- \sum_{j \neq i, 0} \frac{c_j \vec{j}_i - c_i \vec{j}_j}{c D_{ij}} \right)$$

FARADAY

$$\vec{i} = F \sum z_i \vec{j}_i^0$$

INT. EL. PROUDU

$$= -F \sum z_j D_j \nabla c_j - \underbrace{\frac{F^2}{RT} \sum z_j^2 c_j D_j}_{\kappa} \nabla \varphi$$

OHM

$$\nabla c_j = 0 \Rightarrow \vec{i} = -\kappa \nabla \varphi$$

κ

SPEC. VOD/VOST
ELEKTU

NULOVÝ PROUD

$$\frac{F}{RT} \nabla \varphi = - \frac{\sum z_j D_j \nabla c_j}{\sum z_j^2 D_j \nabla c_j} \Leftrightarrow \sum z_j \vec{j}_i^0 = 0$$

ELEKTRONEUTRALITA

$$\sum z_j c_j = 0 \Rightarrow \sum z_j \nabla c_j = 0$$

$$z_c c_c = - \sum_{j \neq c} z_j c_j, \quad z_c \nabla c_c = - \sum_{j \neq c} z_j \nabla c_j$$

a.-b



(H^+, Cl^-)

el. pot. zpomaľuje H^+
urychľuje Cl^-

$$z_a = 1, z_b = -1, c_a = c_b$$

N-P: $J_a = -D_a \nabla c_a - c_a D_a G \nabla \psi$
 $J_b = -D_b \nabla c_b + c_b D_b G \nabla \psi$

$$G = \frac{F}{RT}$$

$$\sim 40V^{-1}$$



⊕PROUD: $J_a - J_b = 0$ $(\sum z_i J_i = 0)$

ELNEUTR.: $c_a - c_b = 0$ $(\sum z_i c_i = 0)$

$$\nabla c_a - \nabla c_b = 0$$

$$0 = -(D_a - D_b) \nabla c_a - c_a (D_a + D_b) G \nabla \psi$$

$$G \nabla \psi = - \frac{D_a - D_b}{D_a + D_b} \frac{\nabla c_a}{c_a}$$

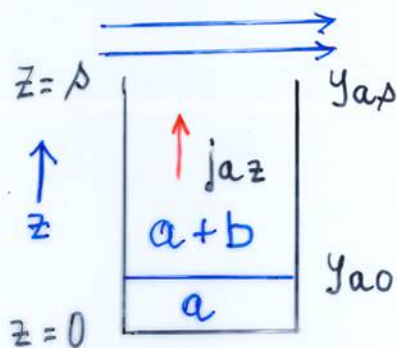
$$J_a = -D_a \left(1 - \frac{D_a - D_b}{D_a + D_b} \right) \nabla c_a = - \frac{2D_a D_b}{D_a + D_b} \nabla c_a = - \frac{2}{\frac{1}{D_a} + \frac{1}{D_b}} \nabla c_a$$

$$D = \frac{\frac{1}{|z_a|} + \frac{1}{|z_b|}}{\frac{1}{|z_a| D_a} + \frac{1}{|z_b| D_b}} = \frac{\frac{1}{|z_a|} + \frac{1}{|z_b|}}{\frac{1}{\lambda_a} + \frac{1}{\lambda_b}} \frac{RT}{F^2}$$

D

USTÁL. DIF.

(1 SMĚR, Θ CHR.)

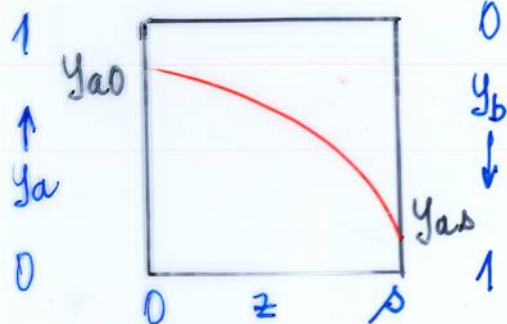


$$\frac{dj_{az}}{dz} = 0 \quad j_{az} = \text{konst.}$$

$$\left. \begin{aligned} j_{az} &= y_a j_z - c D_{ab} \frac{dy_a}{dz} \\ j_{bz} &= 0, \quad j_{az} = j_z \end{aligned} \right\} (1-y_a) j_z = -c D_{ab} \frac{dy_a}{dz}$$

$$\frac{j_z}{c D_{ab}} dz = - \frac{dy_a}{1-y_a} \Rightarrow \frac{j_z}{c D_{ab}} z = \ln(1-y_a) + B$$

$$z=0, \quad y_a = y_{a0} \Rightarrow 0 = \ln(1-y_{a0}) + B$$



$$\frac{j_z}{c D_{ab}} z = \ln \frac{1-y_a}{1-y_{a0}}$$

$$\frac{1-y_a}{1-y_{a0}} = \exp \left[\frac{j_z z}{c D_{ab}} \right]$$

$$z = \Delta, \quad y_a = y_{a\Delta}$$

$$1-y_a = y_b$$

$$\ln \frac{1-y_a}{1-y_{a0}} = \frac{z}{\Delta} \ln \frac{1-y_{a\Delta}}{1-y_{a0}}$$

$$j_{az} = j_z = \frac{c D_{ab}}{\Delta} \ln \frac{1-y_{a\Delta}}{1-y_{a0}} = \frac{c D_{ab}}{\Delta} \cdot \frac{y_{a0} - y_{a\Delta}}{(1-y_a)_{ls}}$$

$$y_{b,ls} = (1-y_a)_{ls} = \frac{(1-y_{a\Delta}) - (1-y_{a0})}{\ln \frac{1-y_{a\Delta}}{1-y_{a0}}} = \frac{y_{a0} - y_{a\Delta}}{\ln \frac{1-y_{a\Delta}}{1-y_{a0}}}$$

$$b: \quad 0 = y_b j_z - c D_{ab} \frac{dy_b}{dz}$$

STEFAN

OBEC.



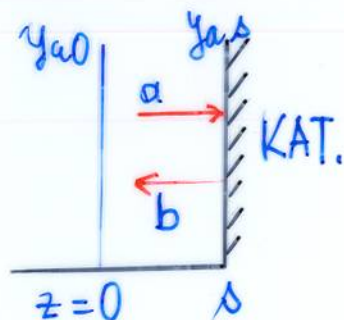
$$j_{az} = y_a j_z - c D_{ab} \frac{dy_a}{dz}$$

$$g_a \left(\frac{j_{az}}{j_z} \right) = y_a - \frac{c D_{ab}}{j_z} \frac{dy_a}{dz} \Rightarrow \frac{j_z}{c D_{ab}} dz = - \frac{dy_a}{y_a - y_a}$$

$$\ln \frac{y_a - y_{a0}}{y_a - y_{a1}} = \frac{z}{\delta} \ln \frac{y_a - y_{a0}}{y_a - y_{a1}}$$

$$j_{az} = g_a j_z = \frac{c D_{ab} g_a}{\delta} \cdot \frac{y_{a0} - y_{a1}}{(y_a - y_{a1})_{\delta}}$$

+ HET. REAKCE



(POLYM.)

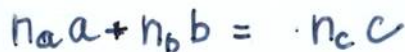
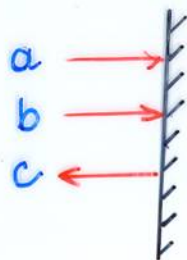
$$j_{bz} = -\frac{1}{n_a} j_{az}$$

($n_a < 0$)

$$g_a = \frac{j_{az}}{|j_{az} + j_{bz}|} = \frac{1}{1 - \frac{1}{n_a}} = \frac{n_a}{n_a - 1}$$

$$j_{a1} = k_p c^m y_{a1}^m \quad y_{a1} = \frac{1}{c} \left(\frac{j_{az}}{k_p} \right)^{\frac{1}{m}}$$

OKAMŽ. $y_{a1} = 0$



$$j_i = \frac{n_i}{n_a} j_a \Rightarrow g_i = \frac{j_i}{|j_a + j_b + j_c|} = \frac{n_i}{n_a + n_b + n_c}$$

$n_{\text{reakt.}} < 0$

$n_{\text{produkt.}} > 0$

$$j_a = k_p c^{m+n} y_{a1}^m y_{b1}^n$$

PSEUDOBIN.



OKAMŽ. $y_{a1} = 0$

ZVL. PŘ.

$$y_a j_z = 0 \quad \begin{cases} y_a \rightarrow 0 \\ j_z = 0 \end{cases} \quad \begin{aligned} (j_z = j_{az}, j_{bz} = 0) \\ (j_{az} = -j_{bz}) \end{aligned}$$

$$j_{az} = -c D_{ab} \frac{dy_a}{dz}$$

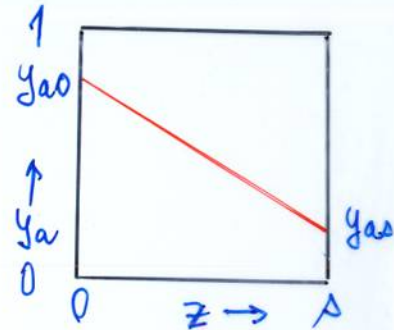
$$\left. \begin{aligned} \frac{j_{az}}{c D_{ab}} z &= -y_a + B \\ 0 &= -y_{a0} + B \end{aligned} \right\}$$

$$\frac{j_{az}}{c D_{ab}} z = y_{a0} - y_a$$

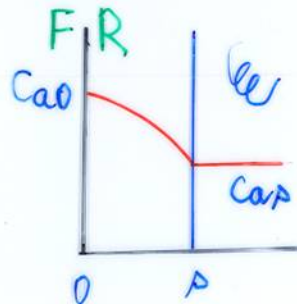
$$z = \delta, \quad y_a = y_{a\delta}$$

$$j_{az} = \frac{c D_{ab}}{\delta} (y_{a0} - y_{a\delta})$$

$$y_{a0} - y_a = \frac{z}{\delta} (y_{a0} - y_{a\delta})$$



FILM



$$j_a = k_c (C_{a0} - C_{a\delta}) = \underbrace{c k_c}_{k_g} (y_{a0} - y_{a\delta})$$

$$k_c = \frac{D_{ab}}{\delta} \frac{1}{y_{b0}}$$

$$\frac{\dot{n}_a}{V} = j_a a = k_c a (C_{a0} - C_{a\delta})$$

VIČESL.

S-M

F

$$\frac{dy_i}{d(\frac{z}{\delta})} = \sum_{k \neq i} \frac{y_i j_k - y_k j_i}{\frac{c D_{ik}}{\delta}}$$

$$j_i = \sum_{k=1}^{c-1} \frac{c D_{ik}}{\delta} (y_{i0} - y_{i\delta})$$

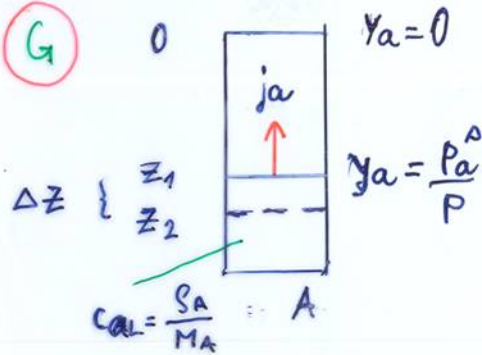
PSEUDOBIN.

$$j_i = \frac{c D_i}{\delta} (y_{i0} - y_{i\delta})$$

PSEUDOSTAC. STAY (PSS)

$\Rightarrow D_{ab}$

G

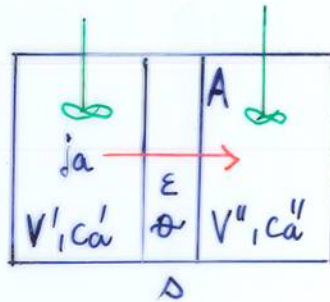


$$A j_a = c_{al} A \frac{dz}{d\tau} \quad j_a = \frac{c_{Dab}}{z} \frac{(y_a - y_{a0})}{y_{bes}}$$

$$\frac{c_{Dab}}{c_{al}} \frac{y_a - y_{a0}}{y_{bes}} \int_0^{\tau} d\tau = \int_{z_1}^{z_2} z dz$$

$$\frac{c_{Dab}}{c_{al}} \frac{y_a - y_{a0}}{y_{bes}} \tau = \frac{1}{2} (z_2^2 - z_1^2) = \frac{1}{2} (z_2 + z_1) \Delta z$$

L



$$\left. \begin{aligned} V' \frac{dc_a'}{d\tau} &= -j_a A \\ V'' \frac{dc_a''}{d\tau} &= j_a A \end{aligned} \right\} \frac{d(c_a' - c_a'')}{d\tau} = -j_a A \left(\frac{1}{V'} + \frac{1}{V''} \right)$$

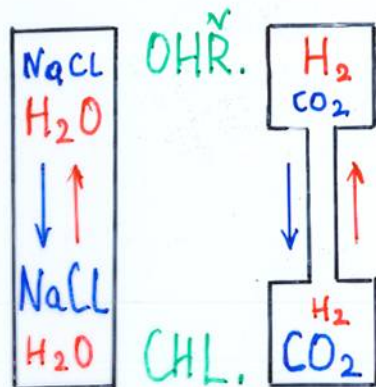
$$j_a = \frac{D_{ab} \epsilon}{\theta \rho} (c_a' - c_a'')$$

$$\frac{d(c_a' - c_a'')}{d\tau} = - D_{ab} \underbrace{\frac{A \epsilon}{\theta \rho} \left(\frac{1}{V'} + \frac{1}{V''} \right)}_B (c_a' - c_a'')$$

$$\ln \frac{c_a' - c_a''}{c_{a0}' - c_{a0}''} = - D_{ab} B \tau$$

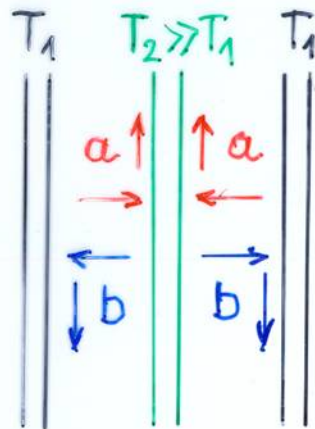
TERMODIFUZE

$$(c=2, [p], \vec{f}_i = 0)$$



SORET
(1879)

CHAPMAN
DOOTSON
(1917)



$$\alpha^T(a) < 0$$

$$\alpha^T(b) > 0$$

FOURIER DUFOR

$$-\vec{J}_e = \lambda \nabla T + c D_a^D \nabla x_a$$

$$-\vec{J}_a = \frac{D_a^T}{T} \nabla T + c D_{ab} \nabla x_a$$

SORET

FICK

$$(\vec{J}_b, \nabla x_b \text{ Lin. závis.})$$

$$-\vec{J}_a = c D_{ab} \left(\nabla x_a + \frac{D_a^T}{c D_{ab}} \frac{\nabla T}{T} \right)$$

$$k^T = \alpha^T x_a x_b = \sigma^T x_a x_b$$

T-D POMÉR, T-D FAKTOR (G), SORET (L)

$$-\vec{J}_a = c D_{ab} \left(\nabla x_a + \alpha^T x_a x_b \frac{\nabla T}{T} \right)$$

$$G, \vec{J}_a^n = 0 :$$

$$\int_{x_{a1}}^{x_{a2}} \frac{dx_a}{x_a(1-x_a)} = - \alpha^T \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\ln \frac{x_{a2}/x_{b2}}{x_{a1}/x_{b1}} = \alpha^T \ln \frac{T_1}{T_2}$$

PRO Tstř.