RYCHLOST SLOŽKY

$$\boxed{\vec{v}_i^{\,r} = \vec{v}_i - \vec{v}_r}$$

DIFÚZNÍ (VŮČI POHYB. SOUŘ.) | VŮČI NEHYB. S. | REF. (KONVEKČNÍ)

REF. R.	$\vec{v}_r = \sum b_i \vec{v}_i \quad (\sum b_i = 1)$	
OBJ. STŘ.	$\vec{v}_v = \sum c_i \bar{v}_{Ni} \vec{v}_i = \sum \underline{c}_i \bar{v}_{Mi} \vec{v}_i$	TEKUTINY
MOL. STŘ.	$\vec{v}_n = \sum x_i \vec{v}_i$	PLYNY
HMOT. STŘ.	$\vec{v}_m = \sum \underline{x}_i \vec{v}_i$	KAP.
REF. SL.	$\vec{v}_j = \sum \delta_{ij} \vec{v}_j$ $\delta_{ij} = \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases}$	PEVNÉ L. ELLYTY MEMBR.

$$\bar{v}_{Ni} = \left(\frac{\partial V}{\partial n_i}\right)_{n_{j \neq i}}, \quad \bar{v}_{Mi} = \left(\frac{\partial V}{\partial m_i}\right)_{m_{j \neq i}}$$

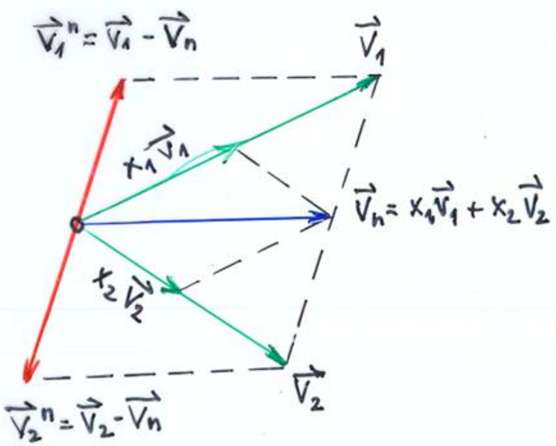
INTENZITA TOKU SLOŽKY

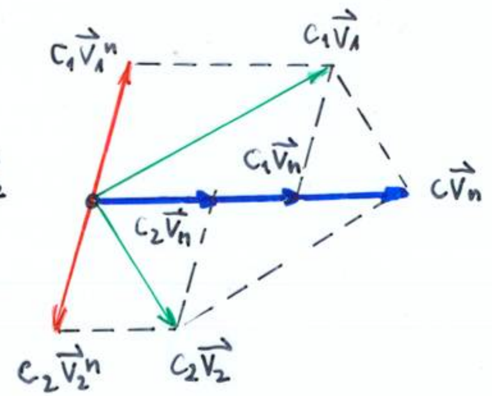
	mol.	hmot.
CELK.	$\vec{j}_i = c_i \vec{v}_i = c x_i \vec{v}_i$	$\underline{\vec{j}_i} = \underline{c_i} \vec{v}_i$ $(\underline{\vec{j}_i} = M_i \vec{j}_i)$
DIF.	$\vec{J}_i^n = c_i \vec{v}_i^n$	
KONV.	$\vec{j}_i^n = c_i \vec{v}_n = x_i \vec{j}^n$	atd.

SLOŽKY $\quad \vec{j}_i = \vec{J}_i^n + \vec{j}_i^n$

SMĚSI (Σ_i) $\quad \vec{j} = \vec{J}^n + \vec{j}^n$

$c\vec{v}_n$





VAZNÉ PODM.

$$\sum \frac{b_i}{x_i}\vec{J}_i^r = \sum \frac{b_i}{x_i} c_i \vec{V}_i^r = c \sum b_i (\vec{V}_i - \vec{V}_r) =$$

$$= c \left[\underbrace{\sum b_i \vec{V}_i}_{\vec{V}_r} - \vec{V}_r \underbrace{\sum b_i}_{1} \right] = 0$$

$\sum \frac{b_i}{x_i}\vec{J}_i^r = 0$	$\sum \frac{\underline{b_i}}{\underline{x_i}}\underline{\vec{J}}_i^r = 0$	r
$\sum \bar{v}_{Mi}\vec{J}_i^v = 0$	$\sum \bar{v}_{Mi}\underline{\vec{J}}_i^v = 0$	v
$\sum \vec{J}_i^n = 0$		n
	$\sum \underline{\vec{J}}_i^m = 0$	m
$\vec{J}_j^j = 0$	$\underline{\vec{J}}_j^j = 0$	j

$\vec{j} = \vec{j}^n = c\vec{V}_n$

$\underline{\vec{j}} = \underline{\vec{j}}^m = \rho\vec{V}_m$

1. FICK

[T, p, a-b]

TEK. $\vec{J}_a^v = -D_{ab}\nabla c_a$ $\qquad \vec{\underline{J}}_a^v = -D_{ab}\nabla \underline{c}_a$ $\qquad (\vec{\underline{J}}_a^v = M_a \vec{J}_a^v)$

SMĚR z: $J_{az}^v = -D_{ab}\dfrac{dc_a}{dz}$

*g: $\vec{J}_a^v = \vec{J}_a^n$ $\qquad$ g: $\vec{J}_a^n = -c\,D_{ab}\nabla x_a$

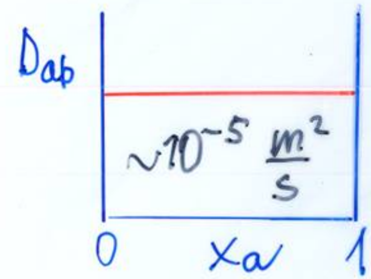
NESTL. l.: $\vec{\underline{J}}_a^v = \underline{J}_a^m$ $\qquad$ l: $\vec{\underline{J}}_a^m = -\rho\, D_{ab}\nabla \underline{x}_a$

g: $\bar{v}_{Na} = \bar{v}_{Nb}$: $\vec{J}_a^v + \vec{J}_b^v = 0$

$c_a + c_b = c$, $\nabla c_a + \nabla c_b = 0$

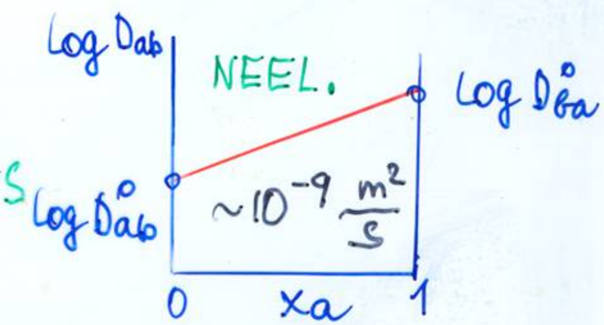
$D_{ab}\nabla c_a + D_{ba}\nabla c_b = 0$

$\Rightarrow \quad D_{ab} = D_{ba}$



l: $D_{ab} = \alpha_{CT}\, Ð_{ab}$, $\alpha_{CT} = 1 + \dfrac{\partial \ln \gamma_a}{\partial \ln x_a}$

$Ð_{ab} = (D^0_{ab})^{x_b}\,(D^0_{ba})^{x_a}$ $\qquad$ VIGNES

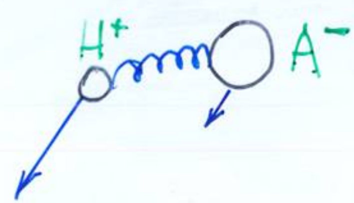


⊙POLYM (NEHYDRAT.)

$D_a \sim M^{-1/3}$

EL.LYTY: IONTY "SVÁZÁNY"

PODM. EL. NEUTR.



STEFAN MAXWELL

$$\frac{d\mu_a}{dz} = -f_{ab}\, c_b \,(v_a - v_b)$$

1. FICK

$$\frac{1}{RT}\frac{d\mu_a}{dz} = -\frac{c_b (v_a - v_b)}{c\, \mathcal{D}_{ab}}$$

$$J_a^v = -D_{ab}\frac{dc_a}{dz}$$

V HYBNÉ SÍLE ← NEIDEALITA → V KOEFICIENTU

$$\alpha_{cT}\frac{dc_a}{dz} = -\frac{c_b j_a - c_a j_b}{c\, \mathcal{D}_{ab}}$$

$$\frac{1}{RT}\frac{d\mu_a}{dz} = -\frac{x_b (v_a - v_b)}{\mathcal{D}_{ab}}$$

$$\alpha_T\frac{dx_a}{dz} = -\frac{x_b j_a - x_a j_b}{c\, \mathcal{D}_{ab}}$$

NEZÁV. VAZ. PODM.

$$\sum b_i v_i = 0$$

$$D_{ab} = \mathcal{D}_{ab}\,\alpha_{cT}$$

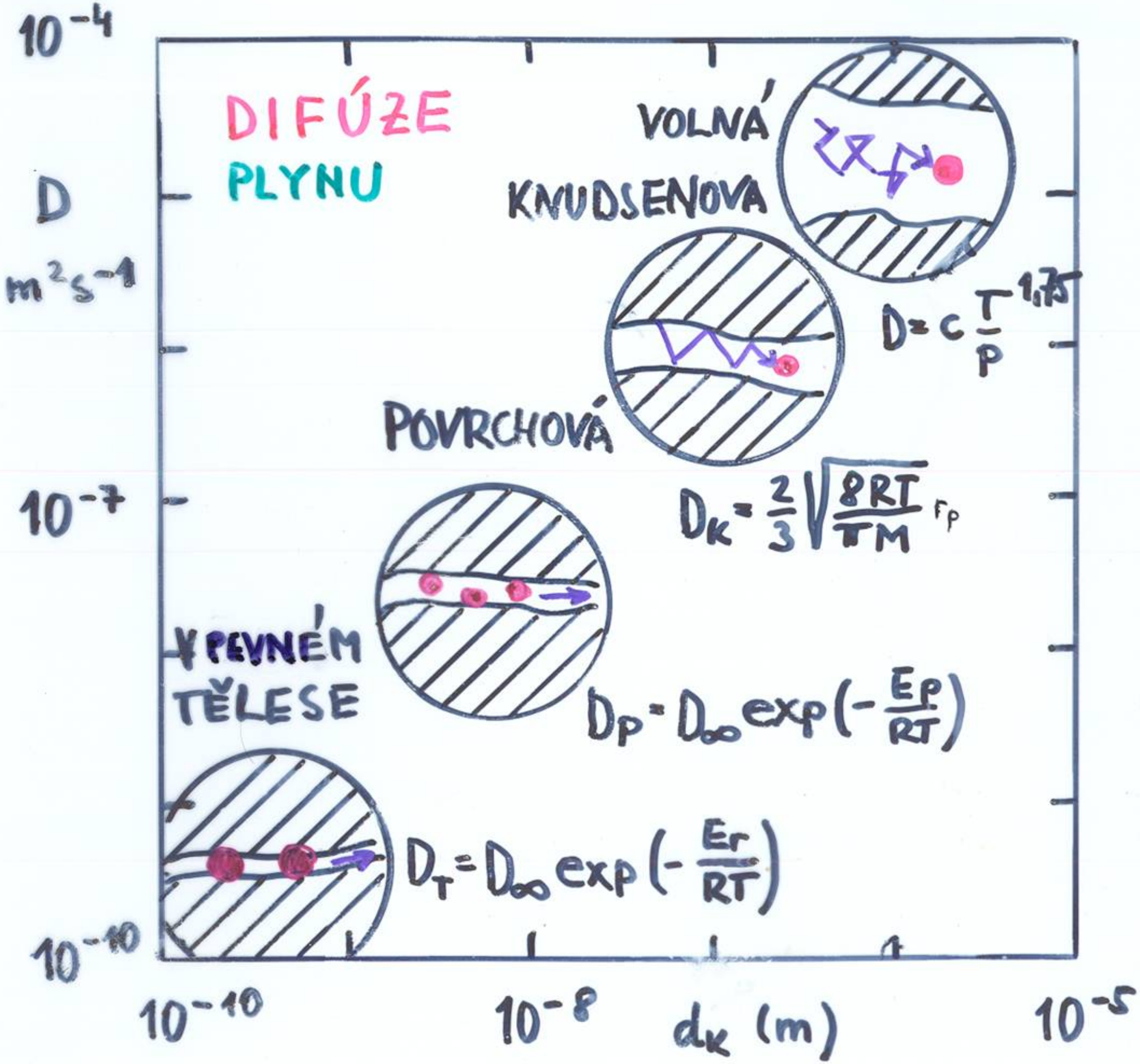
$$J_a^n = -c\, D_{ab}\frac{dx_a}{dz}$$

$$\alpha_{cT} = 1 + \frac{\partial \ln \gamma_a}{\partial \ln x_a}$$

$$\frac{1}{RT}\frac{d\mu_a}{dz} = \frac{\partial \ln a_a}{\partial c_a}\frac{dc_a}{dz} = \frac{1}{\gamma_a x_a}\frac{\partial(\gamma_a x_a)}{\partial(c x_a)}\frac{dc_a}{\partial z} = \frac{1}{c x_a}\left(1 + \frac{x_a}{\gamma_a}\frac{\partial \gamma_a}{\partial x_a}\right)\frac{dc_a}{dz} =$$

$$= \frac{1}{c_a}\left(1 + \frac{\partial \ln \gamma_a}{\partial \ln x_a}\right)\frac{dc_a}{dz}$$

$$\mathcal{D}_{ab} = \frac{RT}{c\, f_{ab}}$$

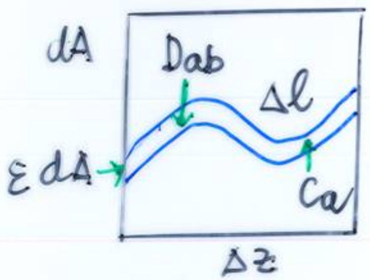

DIFÚZE
PLYNU
D
$m^2 s^{-1}$
10^{-4}
10^{-7}
10^{-10}
VOLNÁ
KNUDSENOVA
POVRCHOVÁ
V PEVNÉM TĚLESE
$D = c \frac{T^{1,75}}{p}$
$D_K = \frac{2}{3} \sqrt{\frac{8RT}{\pi M}} r_p$
$D_P = D_\infty \exp\left(-\frac{E_P}{RT}\right)$
$D_T = D_\infty \exp\left(-\frac{E_T}{RT}\right)$
10^{-10}
10^{-8}
d_K (m)
10^{-5}

S: **HOMOG.** KOVY, IONT. SL.
POLYMERY (DIF. g, l)

$$\vec{J}_a^{s} = -D_{as} \nabla c_a, \quad \nabla c_s = 0, \quad \vec{v}_r = \vec{v}_s = 0$$

D_{as}: $10^{-10} - 10^{-25}$ $m^2 s^{-1}$

PORÉZNÍ



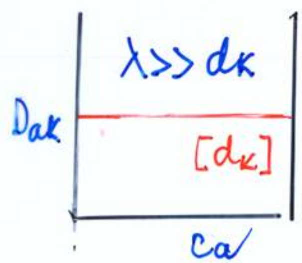
$$J_{az}^{v} = -D_{ab} \frac{dc_a}{dz} \qquad \left(J_{az}^{v} = \frac{dn_a}{\varepsilon dA} \right)$$

EFEKT. $$J_{az}^{s} = -\tilde{D}_{ab} \frac{dc_a}{dz} \qquad \left(J_{az}^{s} = \frac{dn_a}{dA} \right)$$

$$\tilde{D}_a = \frac{D_{ab}\,\varepsilon}{\theta}$$

θ: $\Delta l / \Delta z$

KNUDSEN
(g)



$$\tilde{D}_{aK} = \frac{\bar{D}_{aK}\,\varepsilon}{\theta}$$

PRO $\bar{d}_K$

POVRCH.

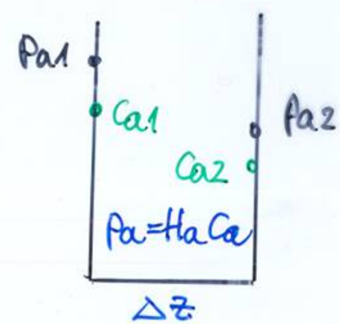
c_{sa} ($mol\,m^{-2}$)

$$J_{az} = -D_{as} \frac{d(c_{sa} a_m \rho_m)}{dz}$$

a_m ($m^2 kg^{-1}$), ρ_m ($kg\,m^{-3}$)

MEMBR.
PERMEABILITA

$$J_{az} = P_a \frac{p_{a1} - p_{a2}}{\Delta z} = D_a \frac{(c_{a1} - c_{a2})}{\Delta z}$$



ROVNICE KONTINUITY (BILANCE)

$$\dot n_{iA} = \int_A \vec j_i \cdot d\vec A = \int_V \nabla\cdot \vec j_i \, dV$$ GAUSS-OSTROGRADSKIJ

$$\int_V \left(\frac{\partial c_i}{\partial \tau} + \nabla\cdot\vec j_i - \sigma_i\right) dV = 0 \xrightarrow{V\to 0} \frac{\partial c_i}{\partial\tau} + \nabla\cdot \vec j_i - \sigma_i = 0$$

$$\vec j_i = \vec j_i^{\,r} + \vec J_i^{\,n}$$

2.FICK : a, b

1. FICK

$$\frac{\partial c_a}{\partial\tau} + \nabla\cdot(c_a \vec v_v) = \nabla\cdot(D_{ab}\nabla c_a) + \sigma_a$$

∅ ch. r, $v_v = 0$, D_{ab} = konst : $\frac{\partial c_a}{\partial \tau} = D_{ab}\nabla^2 c_a$ (2. FICK)

$$\frac{\partial c_a}{\partial\tau} + \frac{\partial (c_a v_x)}{\partial x} + \frac{\partial (c_a v_y)}{\partial y} + \frac{\partial (c_a v_z)}{\partial z} = D_{ab}\left(\frac{\partial^2 c_a}{\partial x^2} + \frac{\partial^2 c_a}{\partial y^2} + \frac{\partial^2 c_a}{\partial z^2}\right) + \sigma_a$$

KART.

SOUŘADNICE (1 SMĚR)

$$\frac{\partial c_a}{\partial\tau} = \frac{1}{r^m}\frac{\partial}{\partial r}\left(r^m D_{ab}\frac{\partial c_a}{\partial r}\right) = D_{ab}\left(\frac{\partial^2 c_a}{\partial r^2} + \frac{m}{r}\frac{\partial c_a}{\partial r}\right)$$

$m = 0$ KART.

$m = 1$ CYLINDR

$m = 2$ SFÉR.

3 SLOŽKY:

SM

$$-\frac{1}{RT}\frac{d\mu_1}{dz} = x_2\frac{v_1 - v_2}{Đ_{12}} + x_3\frac{v_1 - v_3}{Đ_{13}}$$

$$-\frac{1}{RT}\frac{d\mu_2}{dz} = x_1\frac{v_2 - v_1}{Đ_{12}} + x_3\frac{v_2 - v_3}{Đ_{23}}$$

BINÁR. KOEF.

$(Đ_{21} = Đ_{12})$

F

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

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

KOEF. ZÁV. NA SLOŽ.

PŘEP.

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

$D'_{21} = x_2 D_{13}(D_{23} - D_{12})/Z$ $\qquad D'_{22} = D_{23}\left[x_2 D_{13} + (x_1 + x_3) D_{12}\right]/Z$

$Z = x_1 D_{23} + x_2 D_{13} + x_3 D_{12}$ $\qquad [\alpha_{cr} = 1,\ v_v = v_n,\ D_{12} = D_{21}]$

$$\frac{1}{RT}\frac{d\mu_i}{dz} = \frac{1}{x_i}\frac{dx_i}{dz}$$

$J_i = (v_i - v_n) c x_i$

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

PSEUDOBINÁR

$$J_1 = -cD_1\frac{dx_1}{dz}$$

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

$[\alpha_{cr} = 1]$

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

$$cD_{12}\frac{dx_1}{dz} = x_1 j_2 + x_1 j_3 - (1 - x_1) j_1 = x_1 j - j_1 = -J_1$$

2. $x_1 \to 0$: binár 1 - 2+3

BLANC

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

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

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

DIFÚZE V ROZTOCÍCH ELEKTROLYTŮ

NERNST - PLANCK
$$\vec{J}_i^{\,0} = -\underbrace{D_i \nabla c_i}_{\text{ROZP.}} - \underbrace{c_i u_i}_{\text{EL. POHYB.}} \underbrace{\nabla \varphi}_{\text{EL. POT.}}$$

EINSTEIN
$$u_i = \frac{z_i D_i F}{RT}$$
NÁBOJ (z_i), FARADAYOVA KONST. (F)

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

FORMA STEFAN-MAXWELL $(v_0 = 0,\ c_0 \to c)$
$$\nabla c_i + \frac{F}{RT} z_i c_i \nabla \varphi = -\frac{\vec{J}_i}{Đ_{i0}} \left(- \sum_{j \neq i,0} \frac{c_j \vec{J}_i - c_i \vec{J}_j}{c Đ_{ij}} \right)$$

FARADAY
$$\vec{i} = F \sum z_j \vec{J}_j^{\,0}$$
INT. EL. PROUDU
$$= -F \sum z_j D_j \nabla c_j - \underbrace{\frac{F^2}{RT} \sum z_j^2 c_j D_j}_{\varkappa} \nabla \varphi$$
$\varkappa$ SPEC. VODIVOST ELLYTU

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

NULOVÝ PROUD
$$\frac{F}{RT} \nabla \varphi = -\frac{\sum z_j D_j \nabla c_j}{\sum z_j^2 D_j \nabla c_j} \Leftarrow \sum z_j \vec{J}_j^{\,0} = 0$$

ELEKTRONEUTRALITA
$$\sum z_j c_j = 0 \Rightarrow \sum z_j \nabla c_j = 0$$
$$z_c c_c = -\sum_{j \neq c} z_j c_j\ , \quad z_c \nabla c_c = -\sum_{j \neq c} z_j \nabla c_j$$

$\boxed{a-b}$

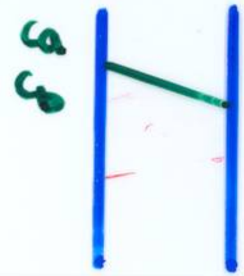
(H^+, Cl^-)

el. pot. zpomaluje H^+
urychluje Cl^-

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

N-P : $J_a = -D_a \nabla c_a - c_a D_a G \nabla \varphi$ $\quad G = \frac{F}{RT}$

$J_b = -D_b \nabla c_b + c_b D_b G \nabla \varphi$ $\quad \sim 40\, V^{-1}$



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

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

$\nabla c_a - \nabla c_b = 0$

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

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

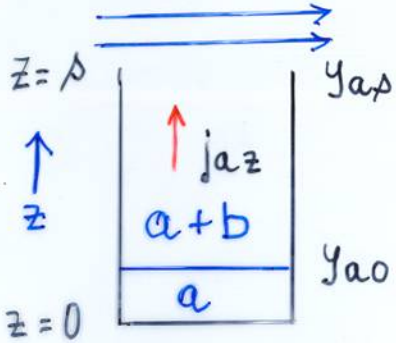
$$J_a = -D_a \left(1 - \frac{D_a - D_b}{D_a + D_b}\right) \nabla c_a = -\frac{2 D_a D_b}{D_a + D_b} \nabla c_a = -\frac{2}{\frac{1}{D_a} + \frac{1}{D_b}} \nabla c_a$$

D

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

$\boxed{\text{USTÁL. DIF.}}$

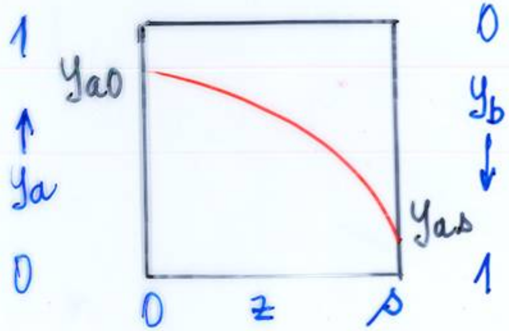
(1 SMĚR, θ CH.R.)



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

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

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



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

$$\boxed{\frac{j_z}{cD_{ab}}\,z = \ln\frac{1-y_a}{1-y_{a0}}} \qquad \frac{1-y_a}{1-y_{a0}} = \exp\left[\frac{j_z z}{cD_{ab}}\right]$$

$$z = \delta,\ y_a = y_{a\delta} \qquad 1 - y_a = y_b$$

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

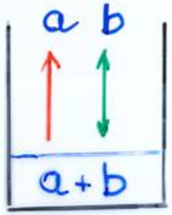
$$\boxed{j_{az} = j_z = \frac{cD_{ab}}{\delta}\ln\frac{1-y_{a\delta}}{1-y_{a0}} = \frac{cD_{ab}}{\delta}\cdot\frac{y_{a0}-y_{a\delta}}{(1-y_a)_{ls}}}$$

$$y_{bls} = (1-y_a)_{ls} = \frac{(1-y_{a\delta})-(1-y_{a0})}{\ln\frac{1-y_{a\delta}}{1-y_{a0}}} = \frac{y_{a0}-y_{a\delta}}{\ln\frac{1-y_{a\delta}}{1-y_{a0}}}$$

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

STEFAN

OBEC.



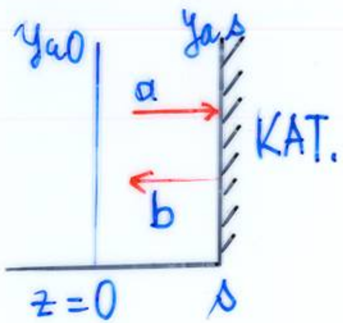
$$j_{az} = y_a j_z - c D_{ab} \frac{dy_a}{dz}$$

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

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

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

+ HET. REAKCE



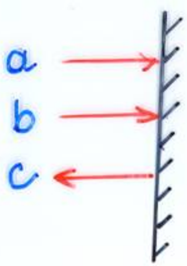
$$n_a a \longrightarrow b \qquad \text{(POLYM.)}$$

$$j_{bz} = -\frac{1}{n_a} j_{az} \qquad (n_a < 0)$$

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

$$j_{a\delta} = k_\delta c^m y_{a\delta}^m \qquad y_{a\delta} = \frac{1}{c} \left(\frac{j_{az}}{k_\delta} \right)^{\frac{1}{m}}$$

OKAMŽ. $y_{a\delta} = 0$



$$n_a a + n_b b = n_c c$$

$$j_i = \frac{n_i}{n_a} j_a \Rightarrow g_i = \frac{j_i}{|\vec{j}_a + \vec{j}_b + \vec{j}_c|} = \frac{n_i}{n_a + n_b + n_c} \qquad n_{reakt.} < 0, \quad n_{produk.} > 0$$

$$j_a = k_\delta c^{m+n} y_{a\delta}^m y_{b\delta}^n$$

PSEUDOBIN. $x_b \to 1$ OKAMŽ. $y_{a\delta} = 0$