Difúze v roztocích elektrolytů

Nernst-Planckova r.: $\overrightarrow{J_i^0} = -D_i \nabla c_i - c_i u_i \nabla \varphi$

pro zředěné roztoky

Nernst-Einsteinova r.: $u_i = \dfrac{z_i D_i F}{RT}$

elektrická pohyblivot iontu

$$\overrightarrow{J_i^0} = -D_i \nabla c_i - c_i \frac{z_i D_i F}{RT} \nabla \varphi$$

Faradayův z. (součet proudů) : $\vec{\imath} = F \sum z_n \overrightarrow{J_n^0}$

$$\vec{\imath} = -F \sum z_n D_n \nabla c_n - \underbrace{\frac{F^2}{RT} \sum z_n^2 \; D_n c_n}_{\varkappa} \nabla \varphi$$

specifická vodivost ellytu

Ohmův z.: $\nabla c_i = 0 \Rightarrow \vec{\imath} = -\varkappa \nabla \varphi$

Nulový proud $\left(\sum z_n \overrightarrow{J_n^0} = 0\right)$: $\dfrac{F}{RT} \nabla \varphi = -\dfrac{\sum z_n D_n \nabla c_n}{\sum z_n^2 \; D_n c_n}$

převodové číslo iontu

$$t_i = \frac{z_i D_i c_i}{\sum z_n^2 \; D_n c_n}$$

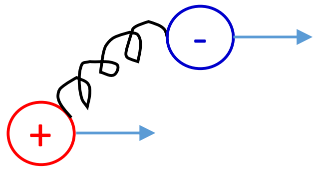
Elektroneutralita: $\sum z_n c_n = 0 \Rightarrow \sum z_n \nabla c_n = 0$

$$z_i c_i = -\sum_{n \neq i} z_n c_n \Longrightarrow z_i \nabla c_i = -\sum_{n \neq i} z_n \nabla c_n$$

Difúze v roztocích elektrolytů

i-k

$z_i=1;\ z_k=-1;\ c_i=c_k$



např. HCl: zpomalení H^+, urychlení Cl^-

N-P:

$$J_i = -D_i \nabla c_i - c_i D_i \frac{F}{RT} \nabla \varphi$$

$$J_k = -D_k \nabla c_k + c_k D_k \frac{F}{RT} \nabla \varphi$$

elektroneutralita: $c_i - c_k = 0$ $\left(\sum z_n c_n = 0\right)$

$$\nabla c_i - \nabla c_k = 0$$

nulový proud: $J_i - J_k = 0$ $\left(\sum z_n J_n = 0\right)$

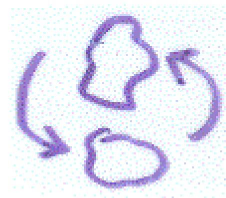
$$0 = -\left(D_i - D_k\right)\nabla c_i - c_i\left(D_i + D_k\right)\frac{F}{RT}\nabla\varphi \rightarrow -\frac{D_i - D_k}{D_i + D_k}\frac{\nabla c_i}{c_i} = \frac{F}{RT}\nabla\varphi$$

$$J_i = -D_i\left(1 - \frac{D_i - D_k}{D_i + D_k}\right)\nabla c_i = \frac{2D_i D_k}{D_i + D_k}\nabla c_i = \frac{2}{\frac{1}{D_i} + \frac{1}{D_k}}\nabla c_i$$

$\boxed{D}$

$$\boxed{D = \frac{\frac{1}{|z_i|} + \frac{1}{|z_k|}}{\frac{1}{|z_i| D_i} + \frac{1}{|z_k| D_k}} = \frac{\frac{1}{|z_i|} + \frac{1}{|z_k|}}{\frac{1}{\lambda_i} + \frac{1}{\lambda_k}} \cdot \frac{RT}{F^2}}$$

Turbulentní difúze



rychlost $\quad \upsilon = \bar{\upsilon} + \upsilon'$

v určitém místě

koncentrace $\quad c_i = \bar{c}_i + c_i'$

průměrná hodnota $\quad$ fluktuační složka

zprůměrnění v čase

$$\bar{\upsilon} = \bar{\bar{\upsilon}} + \overline{\upsilon'}$$

$$\bar{\upsilon} = \bar{\upsilon} + 0$$

$$\bar{c}_i = \bar{\bar{c}}_i + \overline{c_i'}$$

$$\bar{c}_i = \bar{c}_i + 0$$

vektor rychlosti

$$\vec{\upsilon} \Leftrightarrow \upsilon$$

co zprůměrněním neeliminujeme?

Rovnice kontinuity složky

$$\frac{\partial(\bar{c}_i + c_i')}{\partial\tau} + \nabla[(\bar{c}_i + c_i')(\bar{\upsilon} + \upsilon')] - D_i\nabla^2(\bar{c}_i + c_i') = -k(\bar{c}_i + c_i') \quad \text{1.ř}$$

$$\frac{\partial(\bar{c}_i + \underbrace{\overline{c_i'}}_{=0})}{\partial\tau} + \nabla[(\bar{c}_i + c_i')(\bar{\upsilon} + \upsilon')] - \underbrace{D_i\nabla^2(\bar{c}_i}_{\nabla J_{i,Dif}} + \underbrace{\overline{c_i'}}_{=0}) = -k(\bar{c}_i + c_i')^2 \quad \text{2.ř}$$

CHR

$$\nabla[\underbrace{\bar{c}_i\bar{\upsilon}}_{\nabla j_i^r} + \underbrace{\overline{c_i'}\bar{\upsilon}}_{=0} + \underbrace{\bar{c}_i\overline{\upsilon'}}_{=0} + \underbrace{c_i'\upsilon'}_{\nabla J_{i,Turb}}]$$

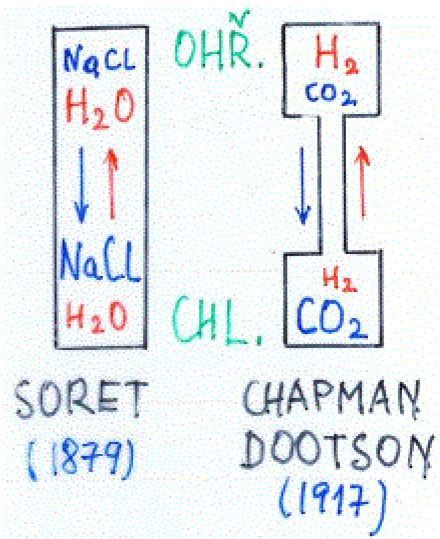
$$-k(\underbrace{\bar{c}_i^2}_{\sigma_i} + \underbrace{2\overline{c_i'}\bar{c}_i}_{=0} + \underbrace{c_i'^2}_{\sigma_{Turb,i}})$$

$$J_{i,Turb} = -D_{Turb}\nabla\bar{c}_i$$

$$J_i^r = -(D_i + D_{Turb})\nabla\bar{c}_i$$

$$\frac{D_{Turb}}{D_i} \approx 10^2(G); 10^5(L)$$

termodifuze



Fourier Difour

$$-\vec{J}_e = \lambda \nabla T + c D_i^{\mathrm{D}} \nabla x_i$$

$$-\vec{J}_i = \frac{D_i^{\mathrm{T}}}{T}\nabla T + c D_{ik} \nabla x_i$$

Soret Fick

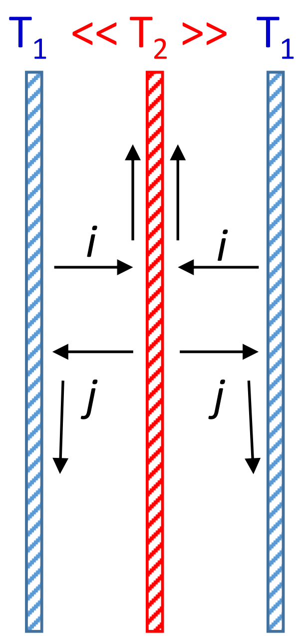
$$-\vec{J}_i = c D_{ik}\left(\nabla x_i + \underbrace{\frac{D_i^{\mathrm{T}}}{c D_{ik}}}_{k_{ik}^{T}} \cdot \frac{\nabla T}{T}\right)$$

T-D poměr

T-D faktor(G)

Soret(L)

$$k_{ik}^T = \alpha_{ik}^T x_i x_k = \sigma_{ik} T x_i x_k$$



$$\alpha_{ik}^T < 0$$
$$\alpha_{ki}^T > 0$$

G:

$$-J_i^n = c D_{ik}\left(\nabla x_i + \alpha_{ik}^T x_i x_k \frac{\nabla T}{T}\right) = 0$$

ustál. stav

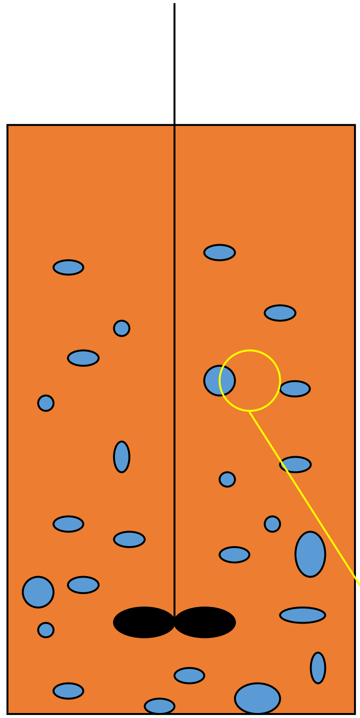
$$\int_{x_{1i}}^{x_{2i}} \frac{dx_i}{x_i(1-x_i)} = -\alpha_{ik}^T \int_{T_1}^{T_2} \frac{dT}{T}$$

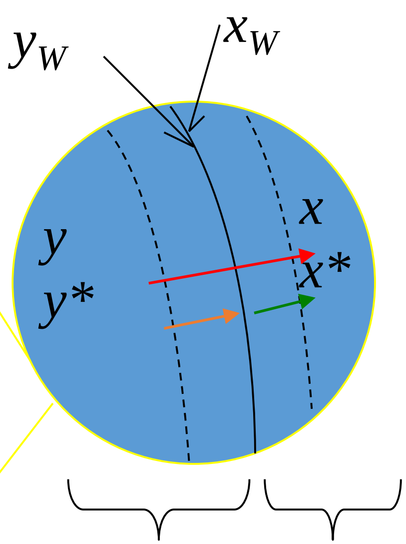
$$\ln \frac{x_{2i}/x_{2k}}{x_{1i}/x_{1k}} = \alpha_{ik}^T \ln \frac{T_1}{T_2}$$

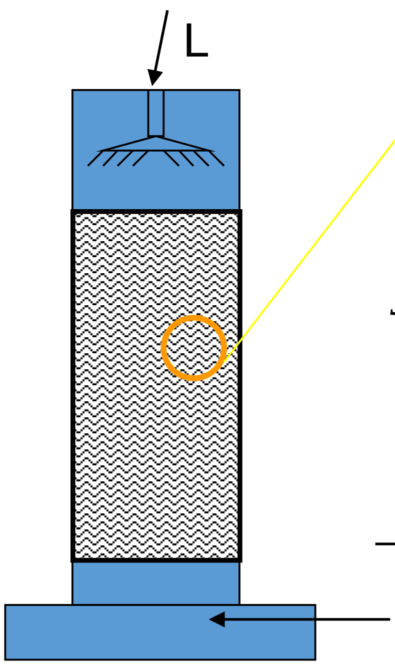
pro střední *T*

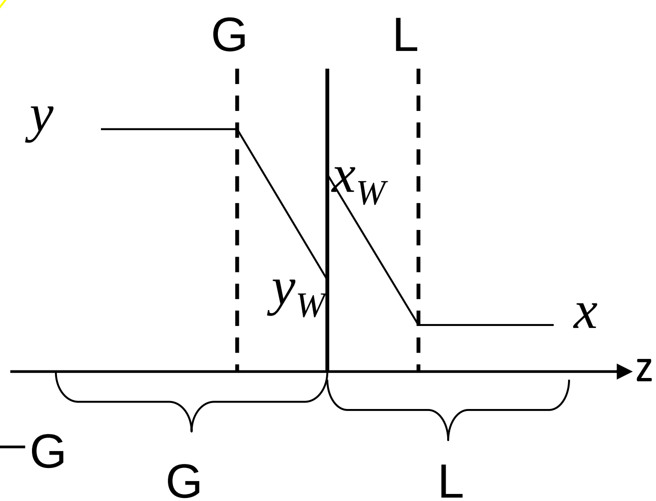
Sdílení hmoty

mezi dvěma fázemi (prostup hmoty)









$$y_w = \Psi x_w$$

$$y^* = \Psi x$$

$$x^* = y/\Psi$$

$$J_{\cancel{z}} \equiv J$$

$$J = K_x(x^* - x) = K_y(y - y^*)$$

$$J = k_x(x_W - x) = k_x/\Psi\,(y_W - y^*)$$

$$J = k_y(y - y_W) = \Psi\, k_y\,(x^* - x_W)$$

$$J\,[1/k_x + 1/(\Psi\, k_y)] = (x^* - \cancel{x_W} + \cancel{x_W} - x)$$

$$1/K_x = 1/k_x + 1/\Psi k_y$$

$$J\,[\Psi/k_x + 1/k_y] = (y - \cancel{y_W} + \cancel{y_W} - y^*)$$

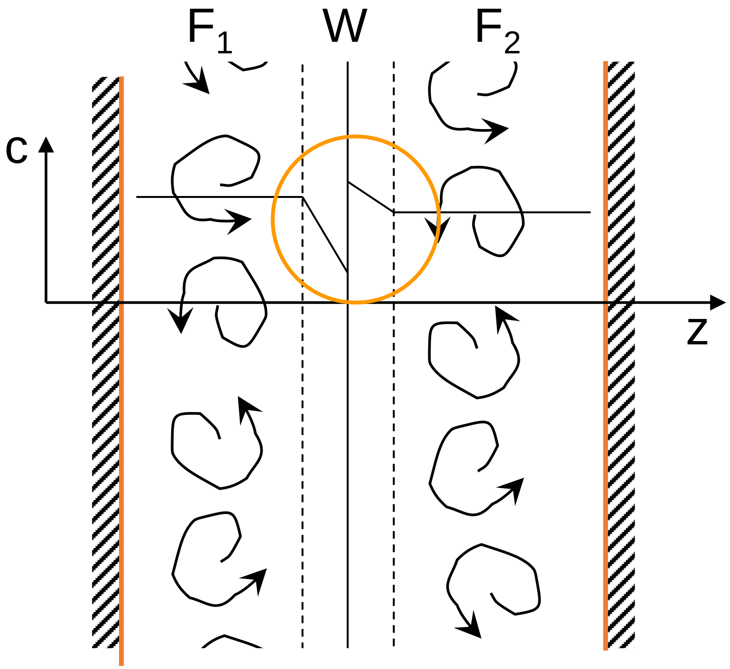
$$1/K_y = \Psi/k_x + 1/k_y$$

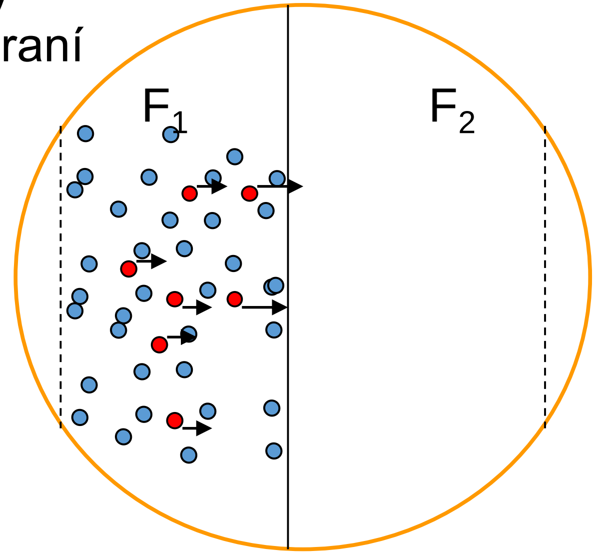
$$K_x = \Psi\, K_y$$

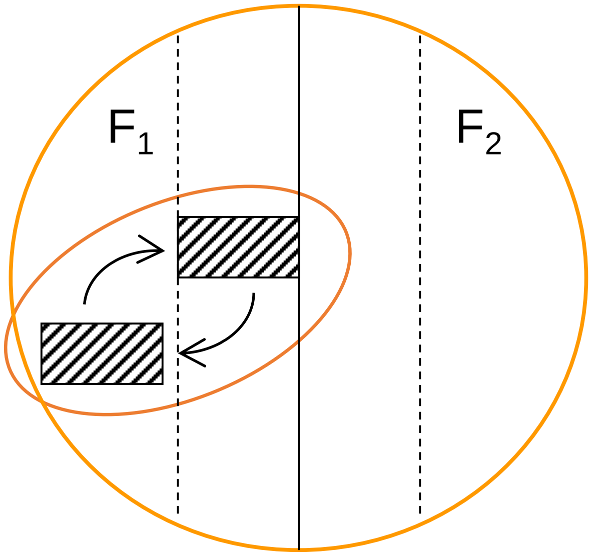
$\boxed{\text{dvoufilmová teorie}}$

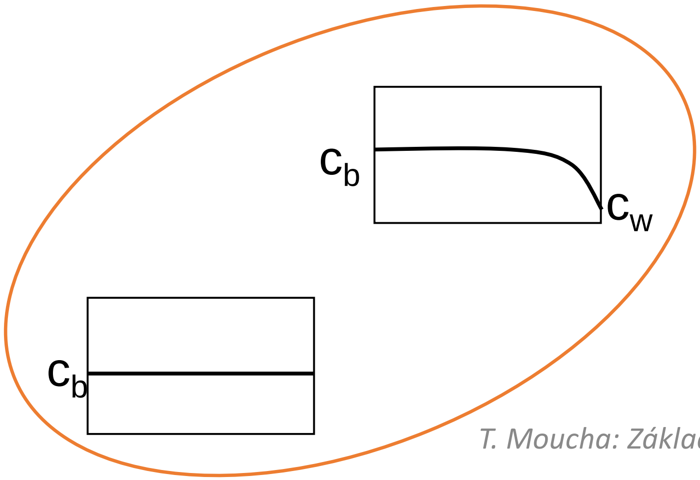
Sdílení hmoty

transport k fázovému rozhraní
(přestup hmoty)





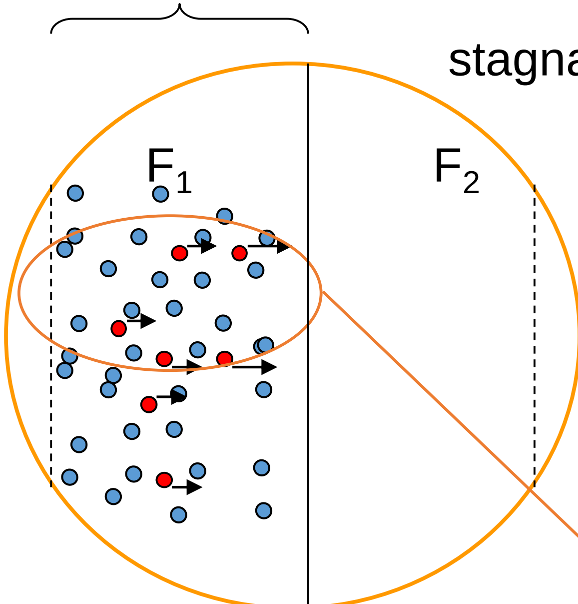


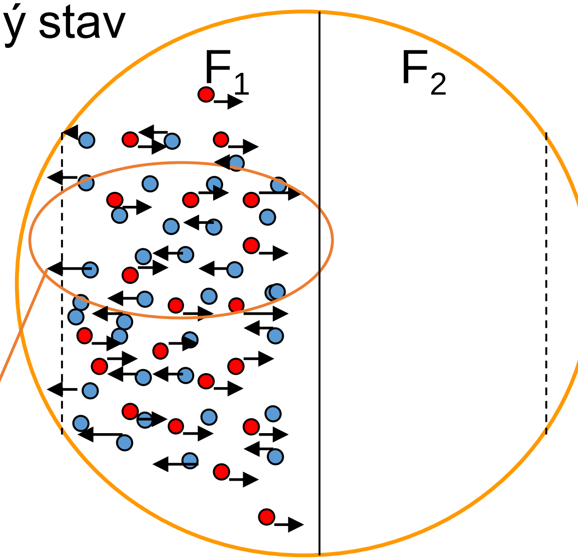


Sdílení hmoty

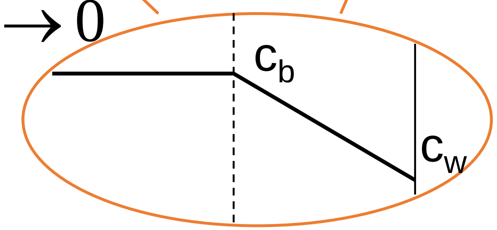
transport k fázovému rozhraní (přestup hmoty)

stagnantní film, ustálený stav





$$x_i << 1 \wedge J_{kz} \doteq 0 \quad \Rightarrow \quad \upsilon_z \to 0$$



$$J_{iz} \doteq -J_{kz} \quad \Rightarrow \quad \upsilon_z \to 0$$

$$j_{iz} \equiv J_{iz}$$

$$\boxed{J_{iz} = -D_{ik}\frac{dc_i}{dz}}$$

1. Fickův zákon

$$J_{iz} = \frac{D_{ik}}{s}(c_{ib} - c_{iw})$$

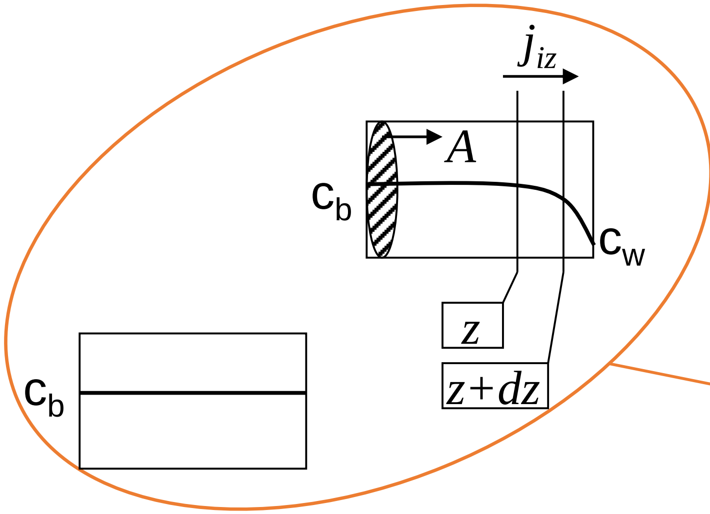
k_{F_1} koeficient přestupu hmoty

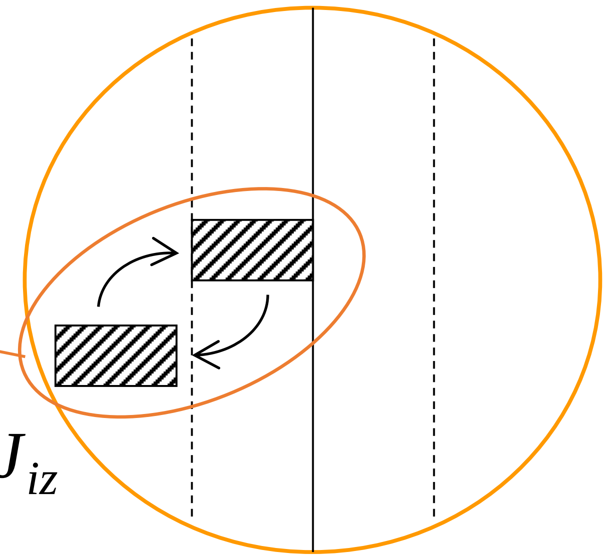
Filmová teorie

Sdílení hmoty

transport k fázovému rozhraní (přestup hmoty)

periodické obměňování elementů u fázového rozhraní





$x_i << 1$ nebo $j_{iz} = -j_{kz}$

$$j_{iz} \equiv J_{iz}$$

$$-\frac{\partial c_i}{\partial \tau} = \cancel{\frac{\partial (c_i \upsilon_z)}{\partial z}} - D_{ik}\frac{\partial^2 c_i}{\partial z^2}$$

$$\boxed{\frac{\partial c_i}{\partial \tau} = D_{ik}\frac{\partial^2 c_i}{\partial z^2}}$$

2. Fickův zákon

Penetrační teorie (Higbie)

$$J_{iz} = 2 \cdot \sqrt{\frac{D_{ik}}{\pi \overline{\tau}}}\,(c_{ib} - c_{iw})$$

k_{F_1}