Dyfuzja w układach wieloskładnikowych

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Dyfuzja chemiczna

I prawo Ficka

$$J = -D\frac{\partial c}{\partial x}$$

Równanie Nernsta-Plancka

$$\boxed{J_i = -\frac{D_i^*}{RT}c_i\frac{\partial \mu_i}{\partial x}} \qquad \mu_i = \mu_i^\circ + RT\ln(a_i) = \mu_i^\circ + RT\ln(f_i \cdot c_i)$$

Dla układu jednofazowego

$$J_i = -\frac{D_i^*}{RT}c_i RT\frac{\partial \ln(f_i \cdot c_i)}{\partial x} = -D_i^* \cdot c_i\frac{1}{f_i \cdot c_i}\frac{\partial (f_i \cdot c_i)}{\partial x} = -D_i^*\frac{1}{f_i}\left[c_i\frac{\partial f_i}{\partial x} + f_i\frac{\partial c_i}{\partial x}\right]$$

$$J_i = -D_i^*\frac{1}{f_i}f_i\frac{\partial c_i}{\partial x}\left[1 + \frac{c_i}{f_i}\frac{\partial f_i}{\partial c_i}\right] = -D_i^*\frac{\partial c_i}{\partial x}\left[1 + \frac{\partial \ln(f_i)}{\partial \ln(c_i)}\right] = -\widetilde{D}_i\frac{\partial c_i}{\partial x}$$

$$\boxed{\widetilde{D}_i = D_i^*\left[1 + \frac{c_i}{f_i}\frac{\partial f_i}{\partial c_i}\right]}$$

Współczynnik dyfuzji chemicznej

$$\boxed{W_i = 1 + \frac{\partial \ln(f_i)}{\partial \ln(c_i)}}$$

Czynnik termo-dynamiczny

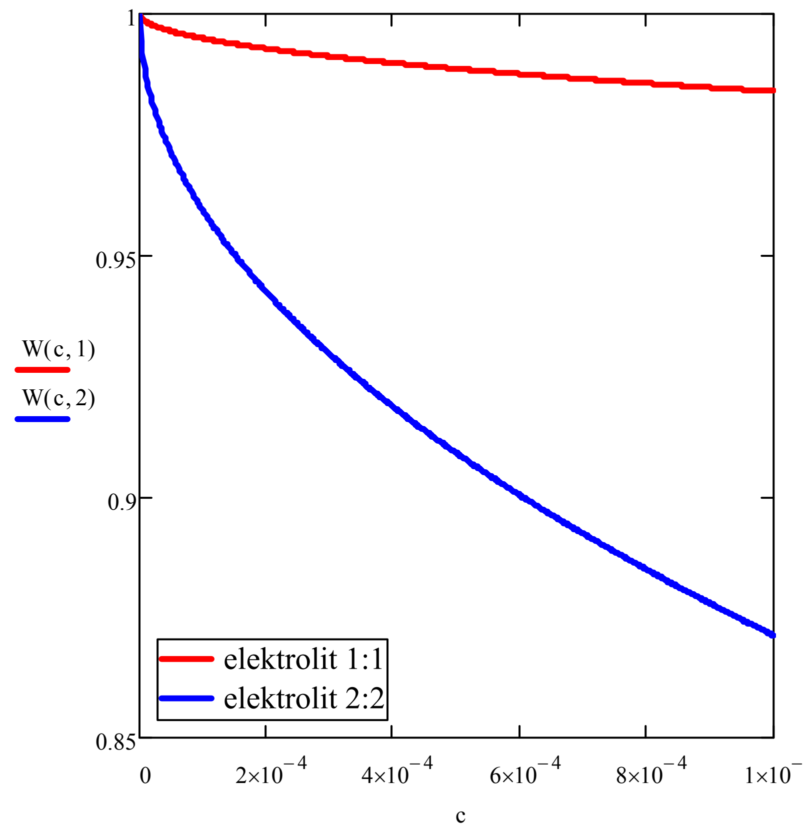
Dyfuzja chemiczna, przykłady

Prawo graniczne Debye'a-Hueckla (rozcieńczone elektrolity)

$$\log(f) = -0.509|z_+ z_-|\sqrt{0.5\left(z_+^2 c_+ + z_-^2 c_-\right)}$$

$$z_+ = z_- = z$$

$$\log(f) = -0.509 z^3 \sqrt{c}$$



Czynnik termodynamiczny

$$\boxed{W = 1 + \frac{\partial \ln(f)}{\partial \ln(c)}}$$

$$W = 1 + c\frac{1}{\log(e)}\frac{\partial \log(f)}{\partial c} = 1 + 2.303 \cdot c\left(\frac{-0.509 z^3}{2\sqrt{c}}\right)$$

$$W = 1 - 0.59 z^3 \sqrt{c}$$

Dyfuzja chemiczna, przykłady

Entalpia swobodna (roztwór dwuskładnikowy)

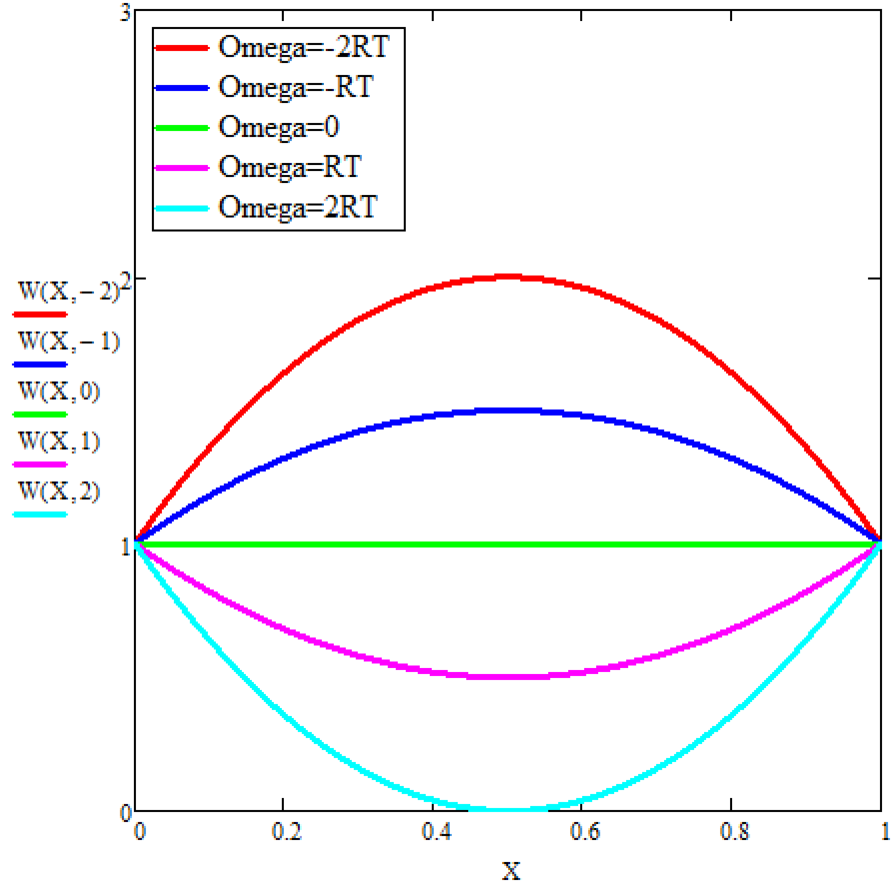
$$G_{mix} = RT\left[X\ln(X) + (1-X)\ln(1-X)\right] + X(1-X)\Omega$$

$$\mu = \mu_i^\circ + G_{mix} + (1-X)\frac{\mathrm{d}G_{mix}}{\mathrm{d}X}$$

$$\mu = \mu_i^\circ + RT\ln(X) + (1-X)^2\Omega$$

$$\mu = \mu_i^\circ + RT\ln(f\cdot X) = RT\left[\ln(f) + \ln(X)\right]$$

$$\ln(f) = \frac{(1-X)^2\Omega}{RT}$$



Czynnik termodynamiczny

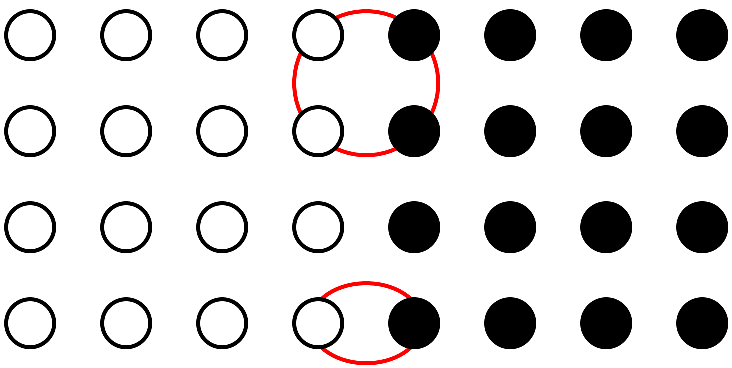
$$\boxed{W = 1 + \frac{\partial\ln(f)}{\partial\ln(X)}}$$

$$W = 1 + X\frac{\partial\ln(f)}{\partial X} = 1 - 2\cdot X(1-X)\frac{\Omega}{RT}$$

W- taki sam dla obu składników

Dyfuzja wzajemna

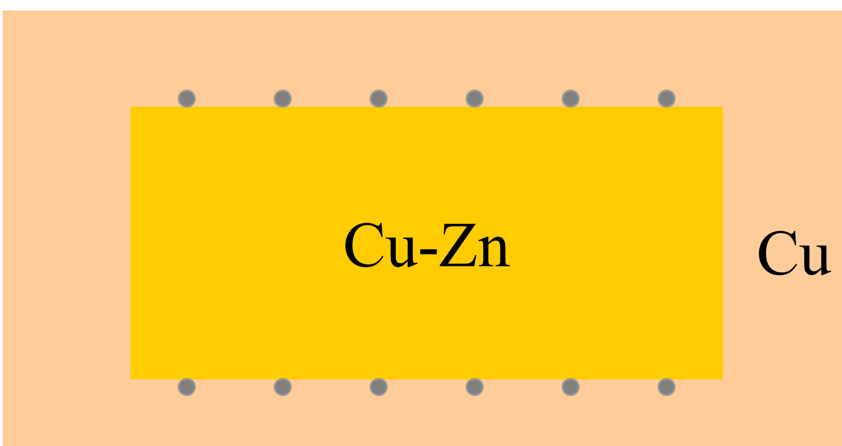
Stan wiedzy do 1947



$$D_A = D_B$$

Stan wiedzy po 1947

Eksperyment Kirkendalla



Efekt Kirkendalla:
ruch obojętnych markerów

$$D_{Cu} \neq D_{Zn}$$

Dyfuzja wzajemna, model Darkena

I prawo Ficka

$$J = -D\frac{\partial c}{\partial x}$$

Darken (1948)

$$J_i = -D_i\frac{\partial c_i}{\partial x} + c_i v$$

oraz

$$\sum_i c_i = const$$

$$\Downarrow$$

$$\sum_i \frac{\partial c_i}{\partial t} = 0$$

$\Downarrow$ z równ. ciągłości

$$\sum_i \frac{\partial J_i}{\partial x} = 0$$

$$\Downarrow$$

$$\sum_i J_i = const$$

$\Downarrow$ dla układu zamkniętego

$$\sum_i J_i = 0$$

$$\Downarrow$$

$$\boxed{v = \frac{\sum_i D_i \frac{\partial c_i}{\partial x}}{\sum_i c_i} = \sum_i D_i \frac{\partial X_i}{\partial x}}$$

Dyfuzja wzajemna, model Darkena

Układ wieloskładnikowy

$$\boxed{J_i = -D_i \frac{\partial c_i}{\partial x} + c_i v} \qquad \boxed{v = \sum_i D_i \frac{\partial X_i}{\partial x}}$$

Układ dwuskładnikowy (A-B)

$$J_A = -D_A \frac{\partial c_A}{\partial x} + c_A v \qquad v = D_A \frac{\partial X_A}{\partial x} + D_B \frac{\partial X_B}{\partial x} = (D_A - D_B)\frac{\partial X_A}{\partial x}$$

$$J_A = -D_A \frac{\partial c_A}{\partial x} + c_A (D_A - D_B)\frac{\partial X_A}{\partial x} = -D_A \frac{\partial c_A}{\partial x} + X_A (D_A - D_B)\frac{\partial c_A}{\partial x} = -(D_A - X_A D_A + X_A D_B)\frac{\partial c_A}{\partial x}$$

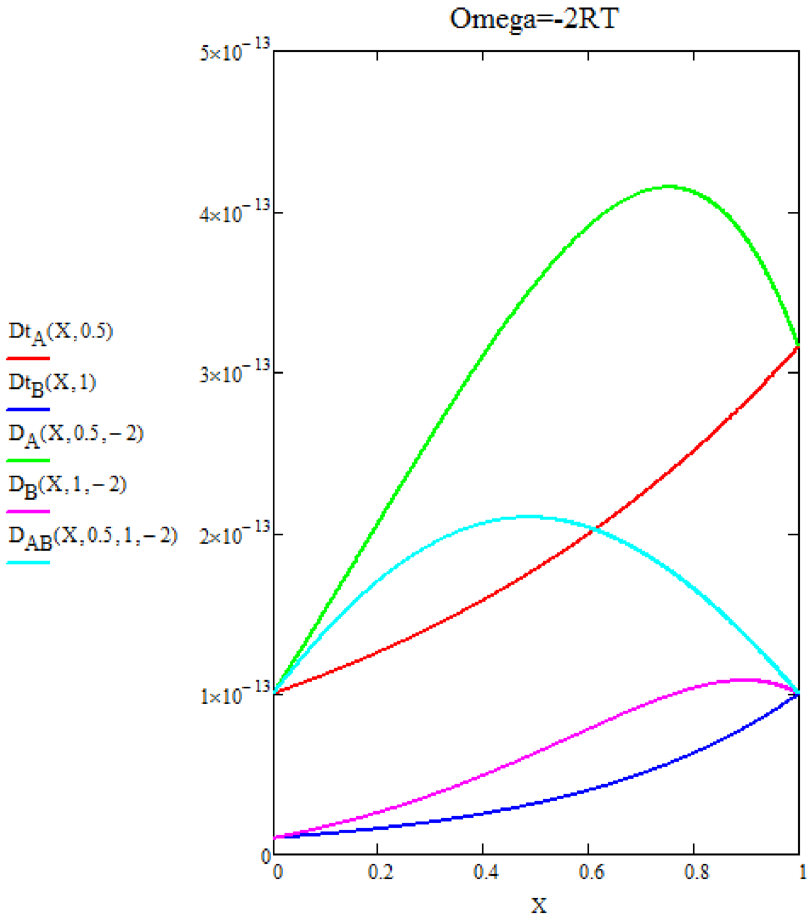
$$J_A = -(X_B D_A + X_A D_B)\frac{\partial c_A}{\partial x} = -D_{AB} \frac{\partial c_A}{\partial x}$$

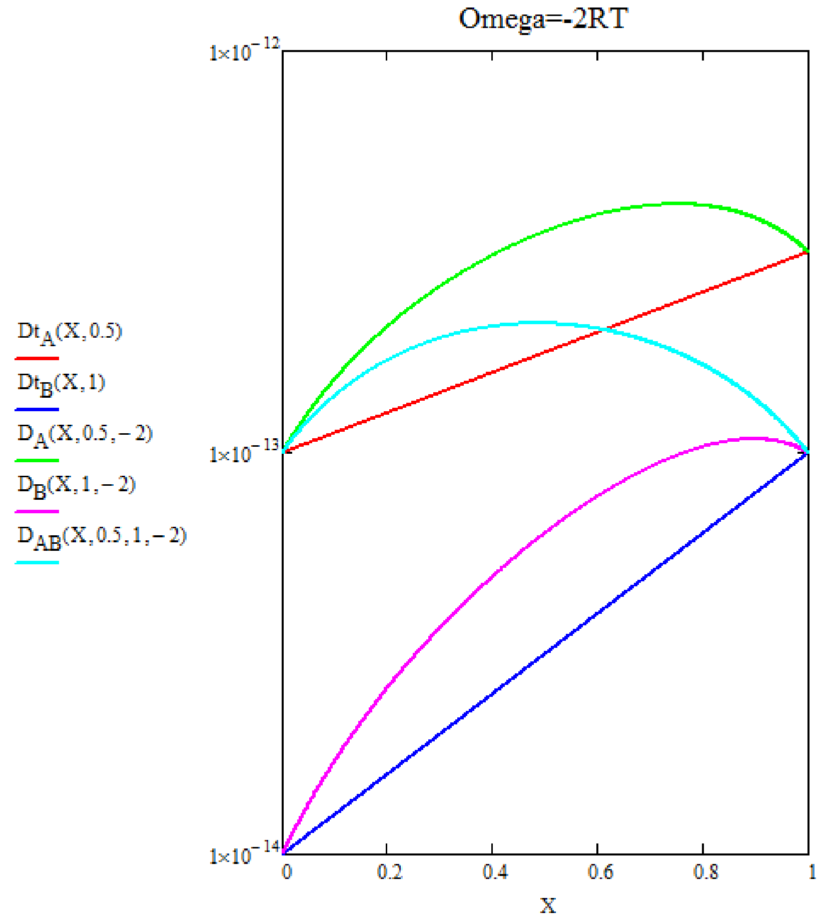
$$D_{AB} = X_B D_A + X_A D_B$$

W ogólnym przypadku dla roztworów rzeczywistych

$$\boxed{J_A = -\widetilde{D}_{AB} \frac{\partial c_A}{\partial x}} \qquad \boxed{\widetilde{D}_{AB} = X_B \widetilde{D}_A + X_A \widetilde{D}_B}$$

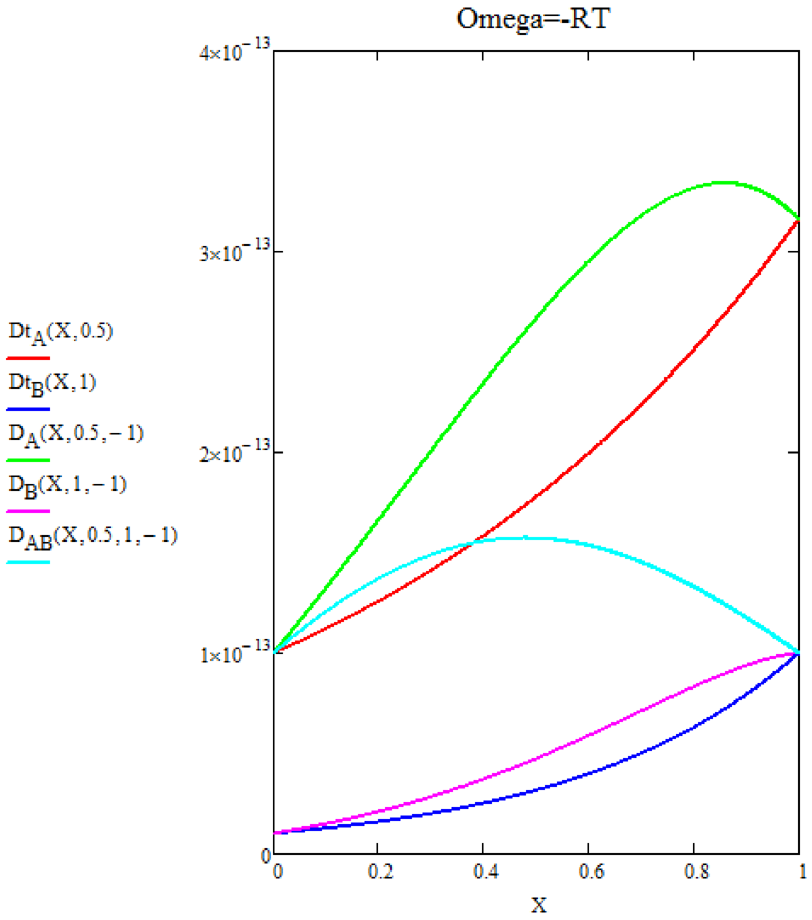
Model Darkena, przykłady

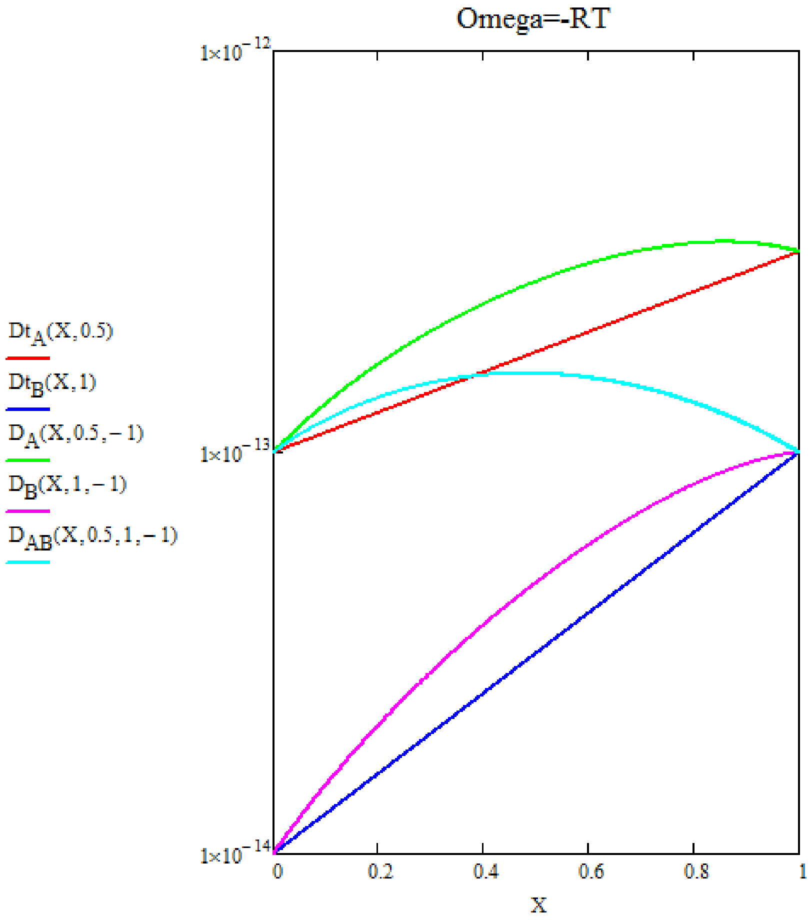




Różne wsp. dyfuzji: Dt_A- trasera, D_A- „intrinsic”, D_{AB}- wzajemnej

Model Darkena, przykłady





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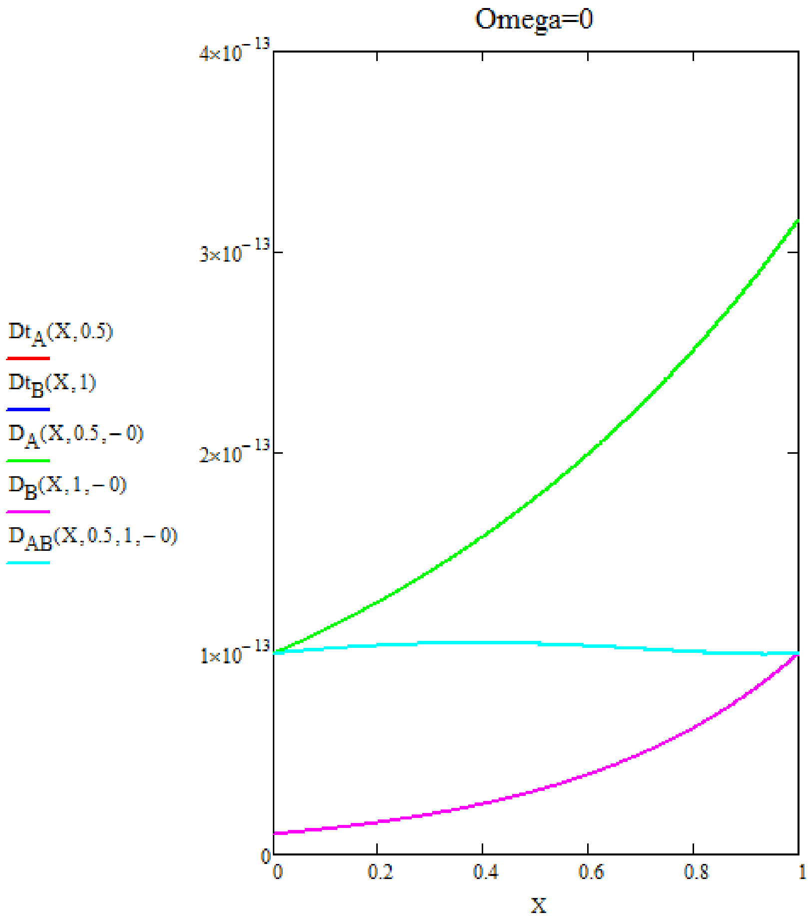
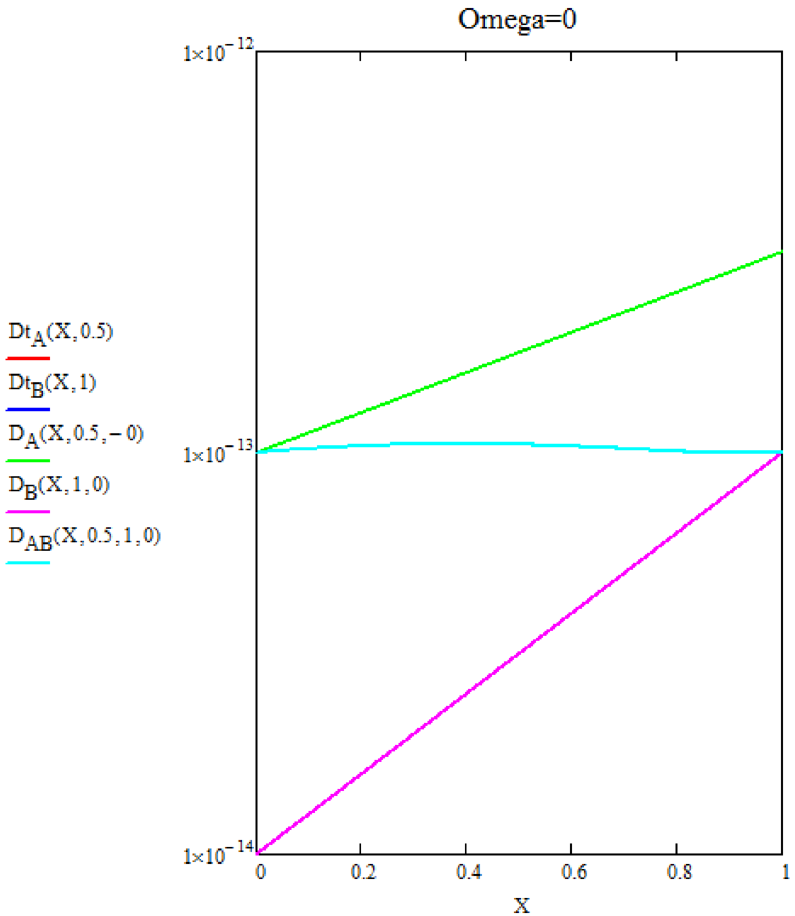
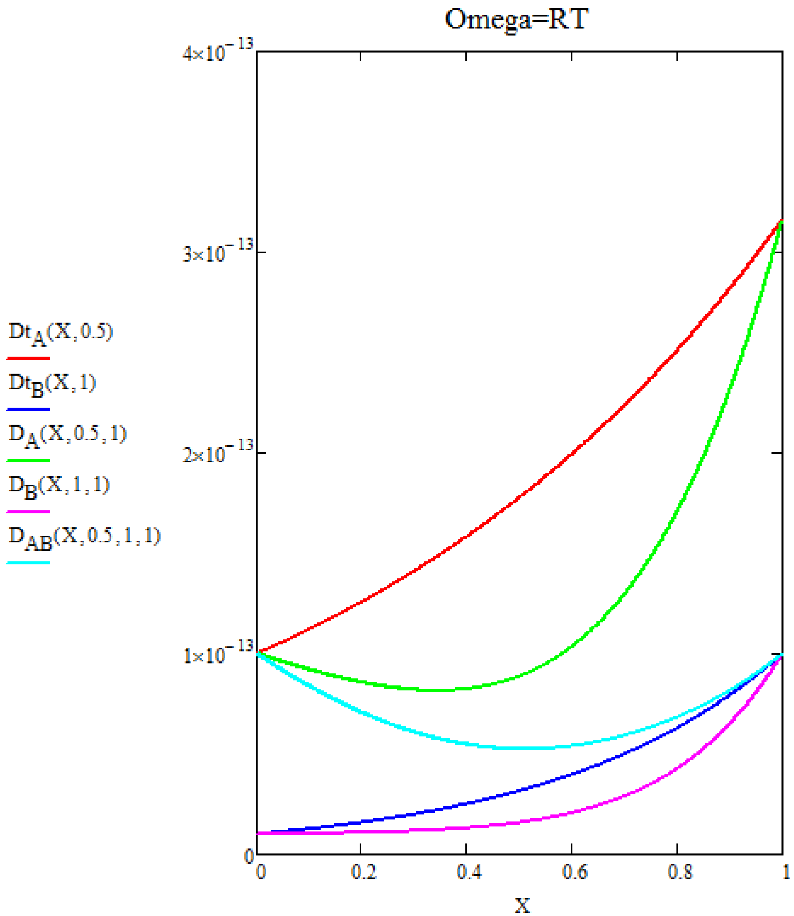
Model Darkena, przykłady

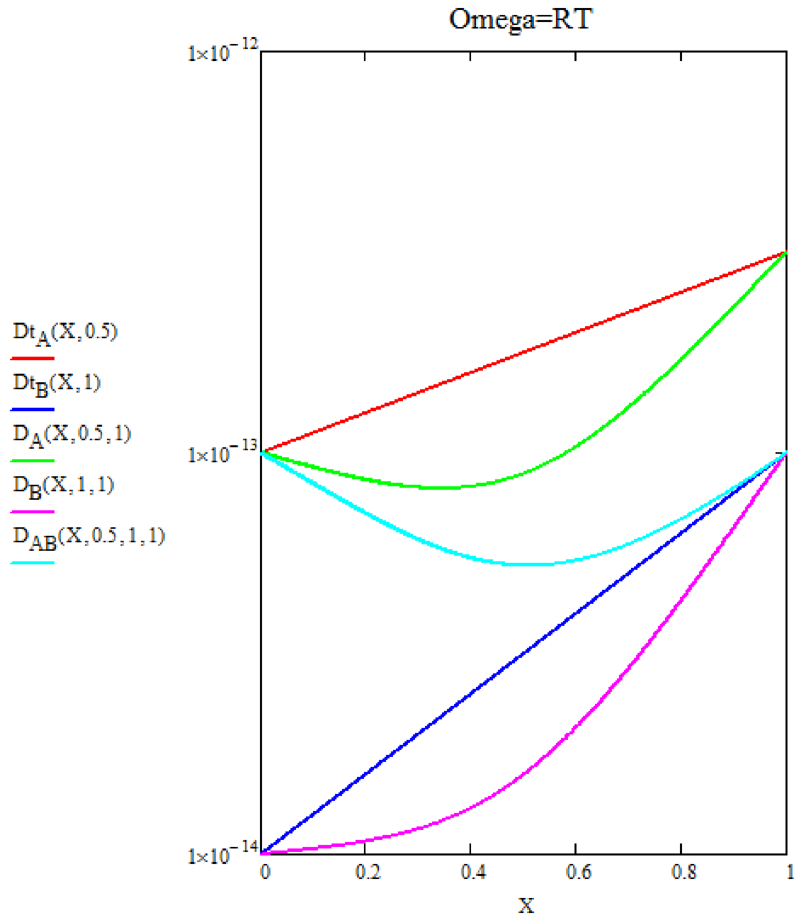




Różne wsp. dyfuzji: Dt_A- trasera, D_A- „intrinsic”, D_{AB}- wzajemnej

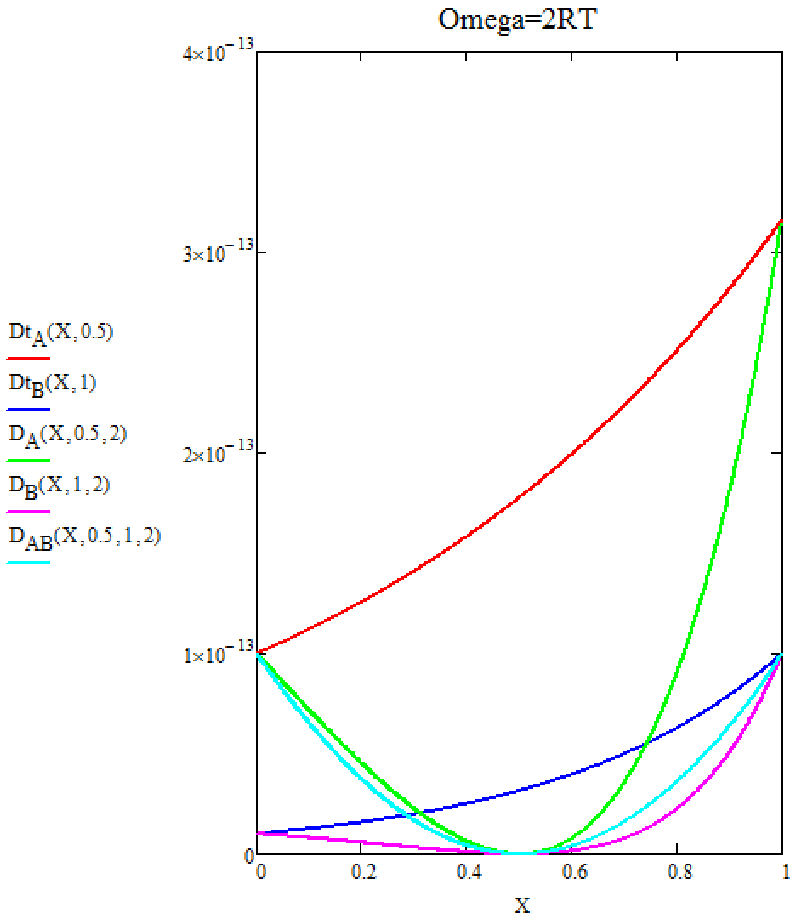
Model Darkena, przykłady

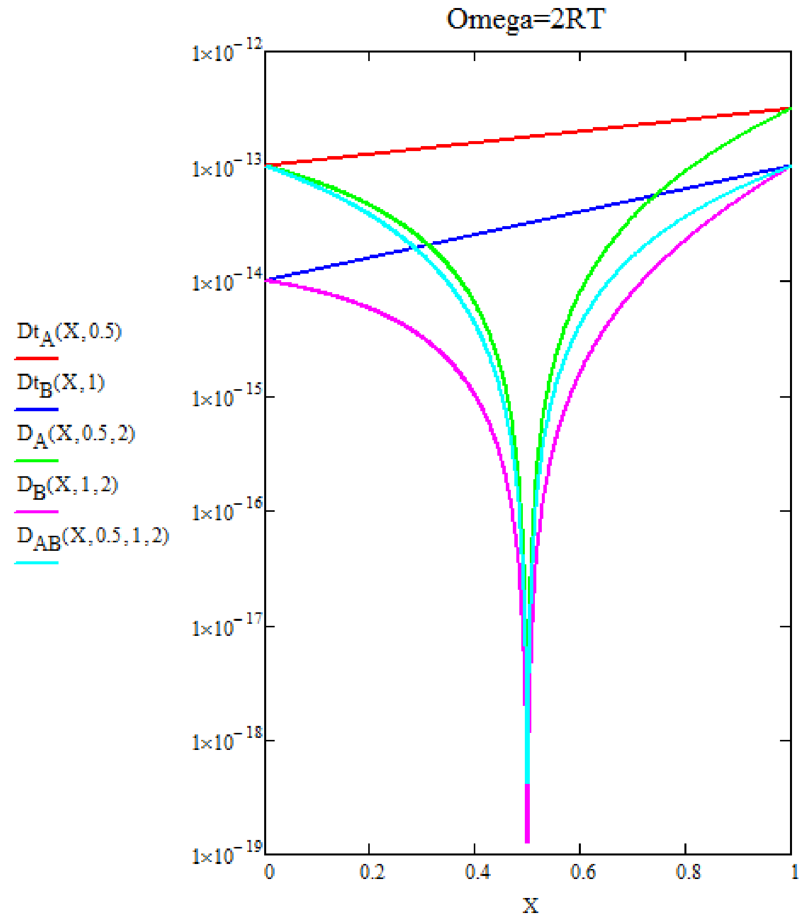




Różne wsp. dyfuzji: Dt_A- trasera, D_A- „intrinsic", D_{AB}- wzajemnej

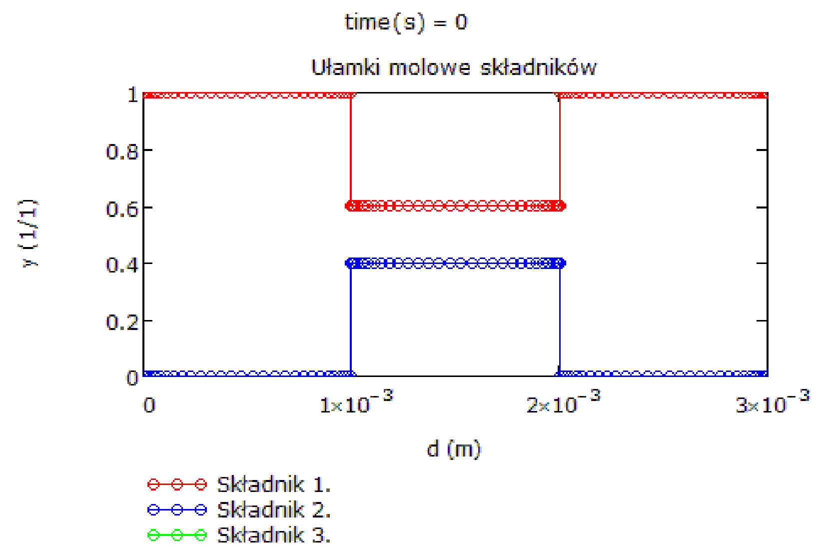
Model Darkena, przykłady

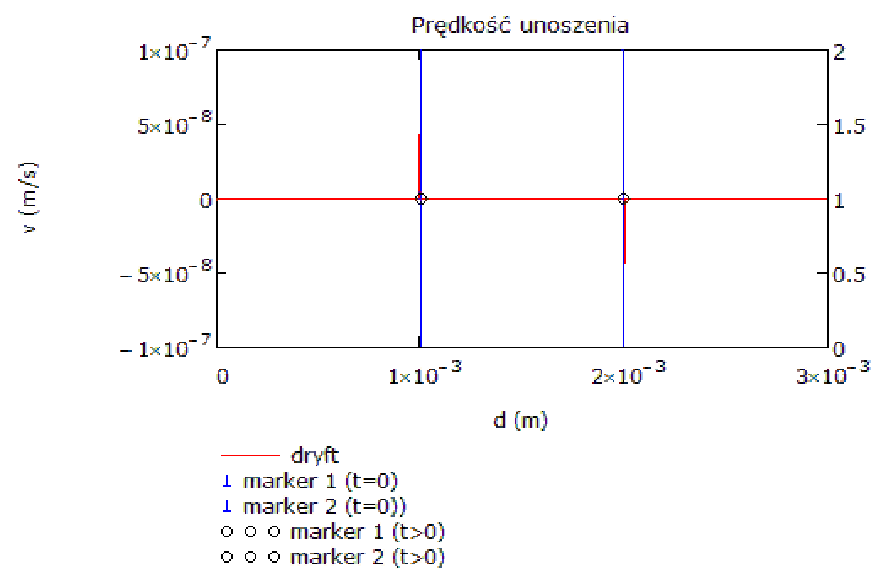




Różne wsp. dyfuzji: Dt_A- trasera, D_A- „intrinsic”, D_{AB}- wzajemnej

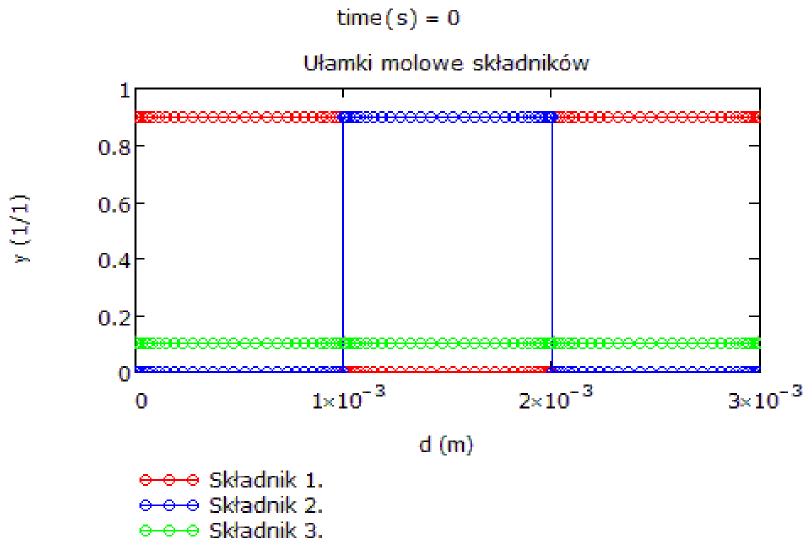
Dyfuzja wzajemna

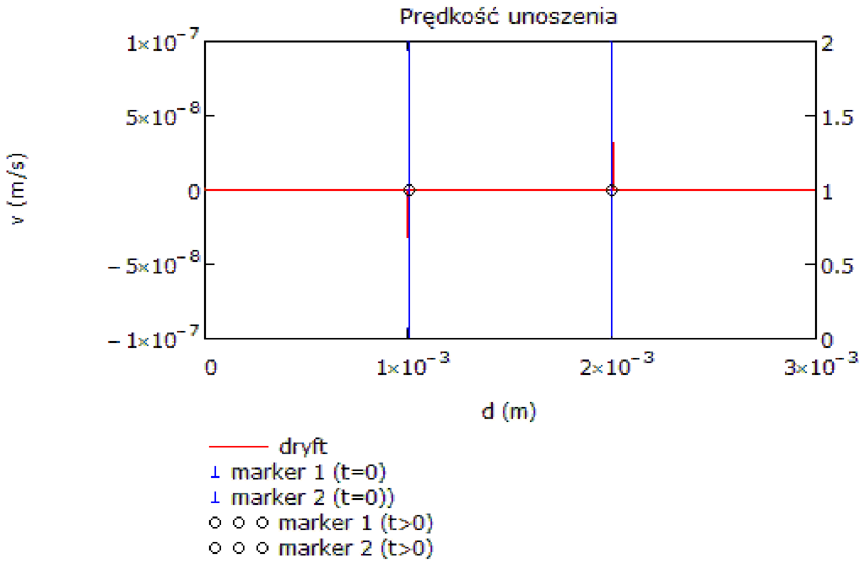




symulacje

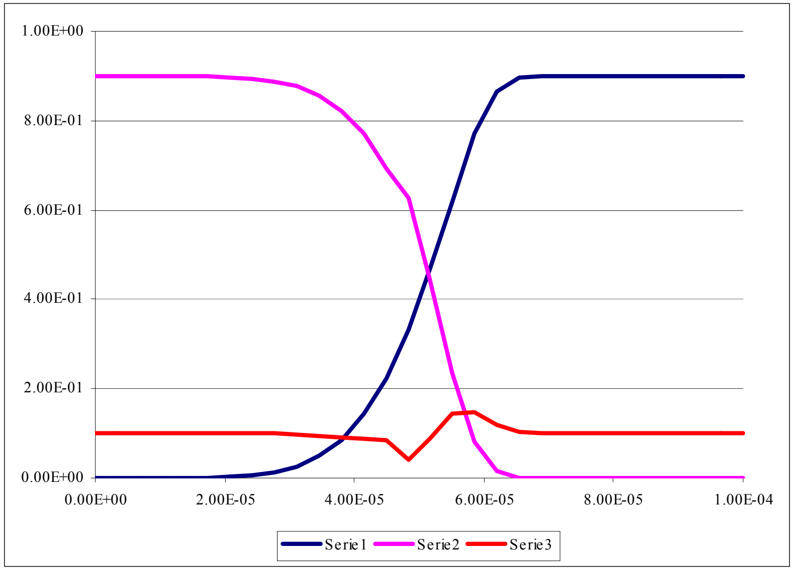
Dyfuzja wzajemna

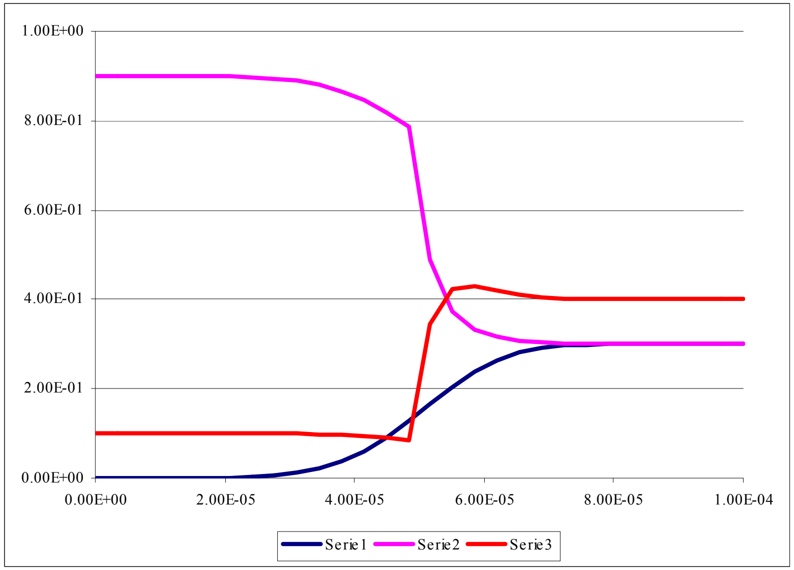


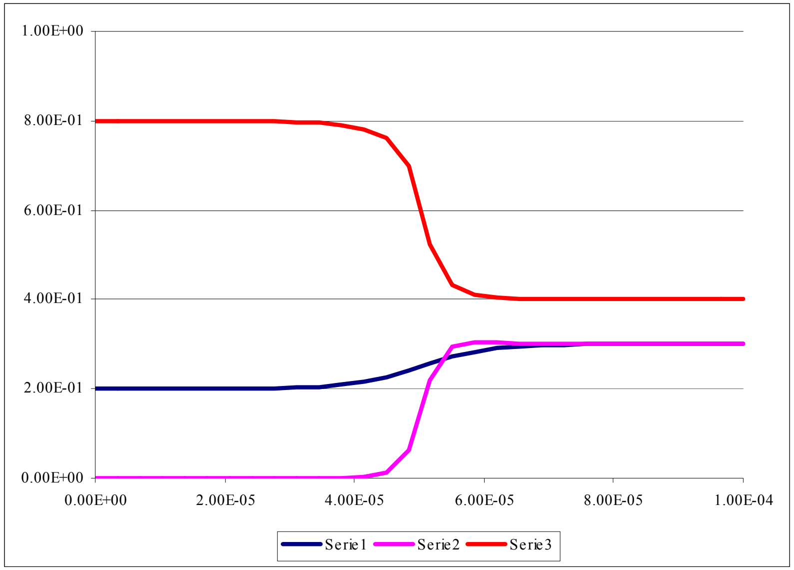


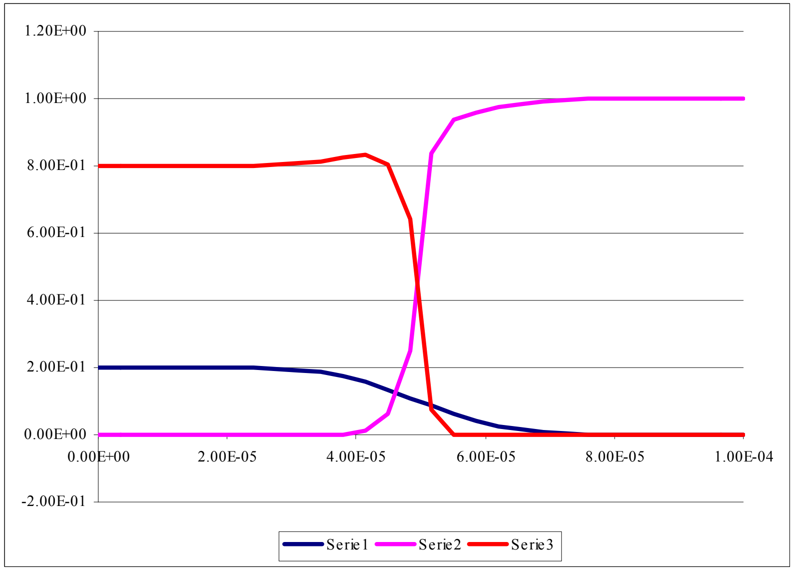
symulacje

Met. Eulera: aneks do wykładu

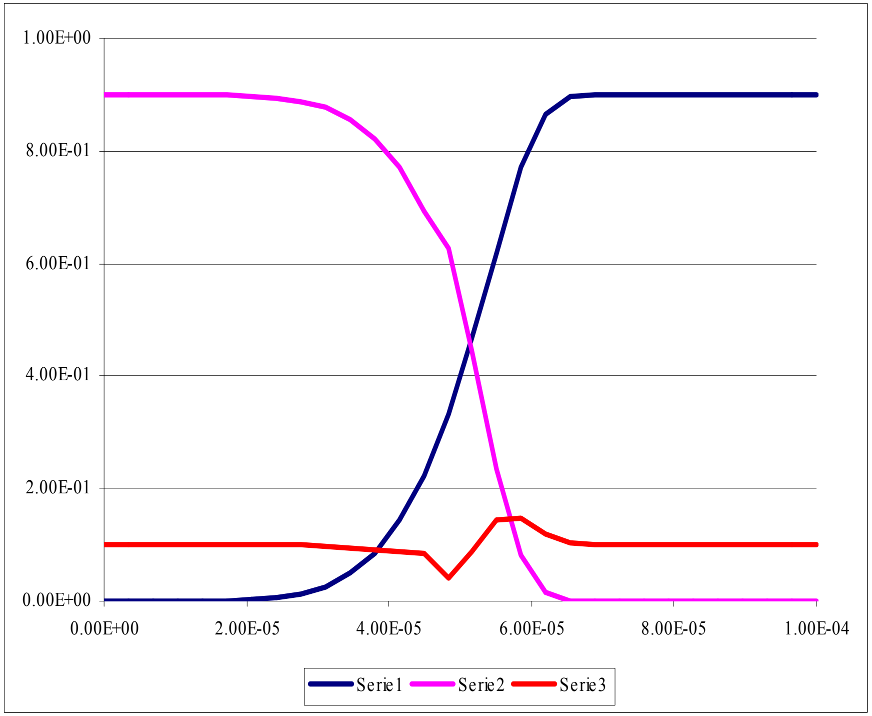








Dyfuzja wzajemna, efekt „up-hill”



i (składnik)	znak J_i	znak $\dfrac{\partial c_i}{\partial x}$
1	–	+
2	+	–
3	+	+

Dyfuzja up-hill

zachodzi wtedy, gdy przynajmniej dla jednego ze składników strumień i gradient stężenia mają ten sam znak