Diffusion in solids

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Steady Systems

1^{st} Fick's Law

Fick Law

$$J = -D\frac{dC}{dz}$$

Mass transfer

$$N_A = -D_A \frac{dC_A}{dz}$$

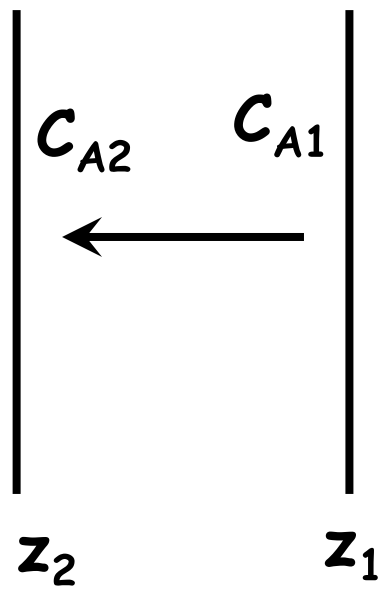
- One axis
- Steady system
- No chemical reaction

Mass transfer

$$N_A = -D_A \frac{dC_A}{dz}$$

Mass transfer through parallell walls

$$N_A = \frac{D_A}{z}\left[C_{A1} - C_{A2}\right]$$



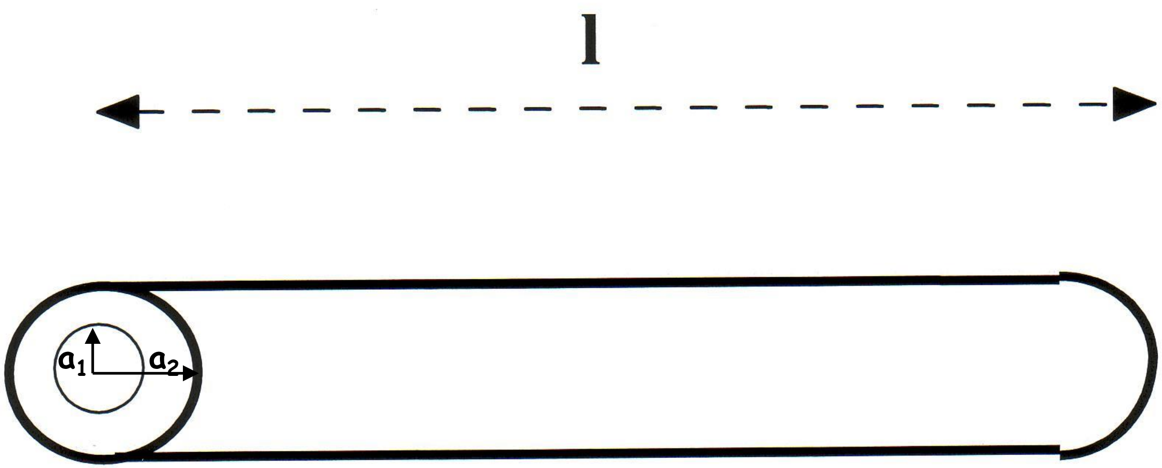
Examples of different solids

Transfer rate

$$W = N_a S_a$$

$$W = \frac{D_A S_a}{z}\left[C_{A1} - C_{A2}\right]$$

Example 1 : cylinder – pipe

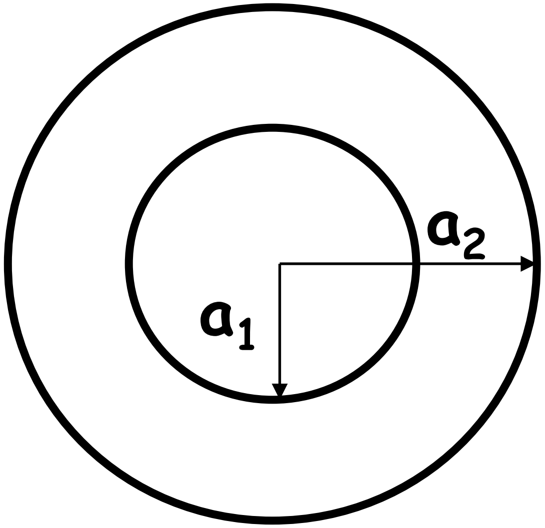


$$S_a = \frac{2\pi l(a_2 - a_1)}{\mathrm{Ln}\, {}^{a_2}\!/_{a_1}}$$

$$z = a_2 - a_1$$

$$W = \frac{D_A S_a}{z}\left[C_{A1} - C_{A2}\right]$$

Example 2 : empty sphere
Gas storage



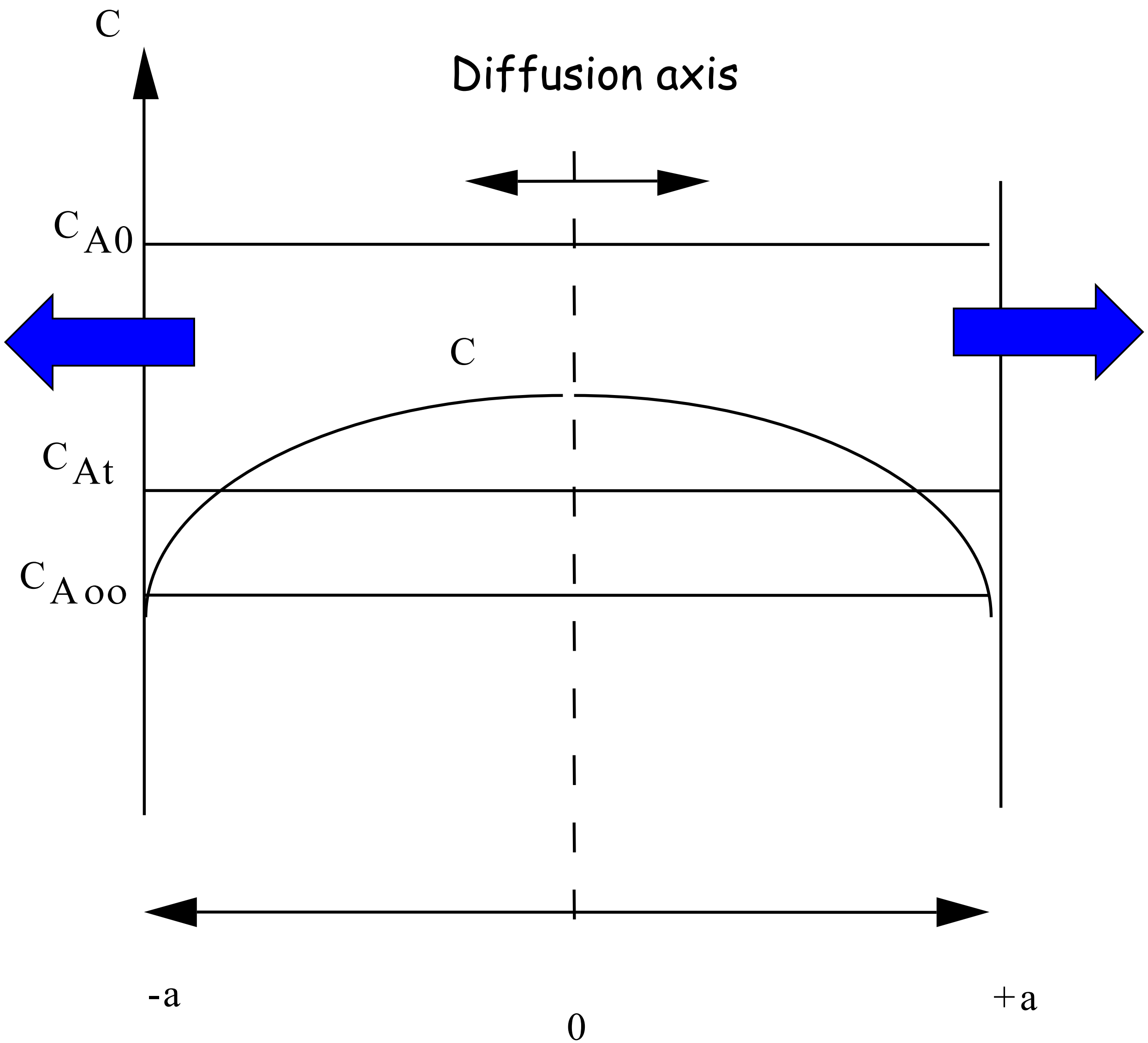
$$W = \frac{D_A S_a}{z}\left[C_{A1} - C_{A2}\right]$$

$$S_a = 4\pi a_1 a_2$$

$$z = a_2 - a_1$$

Non-Steady Systems

2nd Fick's Law


C
Diffusion axis
C A0
C
C At
C Aoo
-a
0
+a

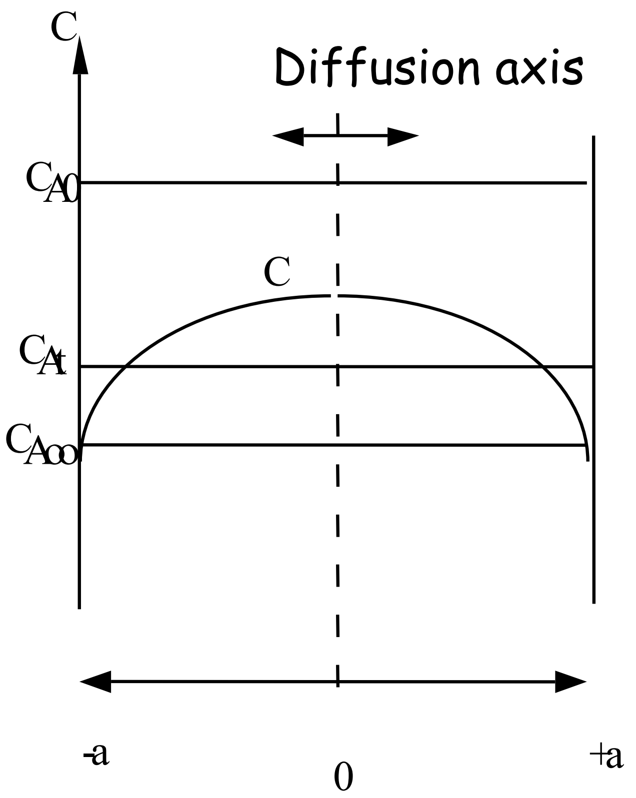
2nd Fick's Law

$$\frac{\partial C_A}{\partial t} = D_{AB}\left[\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right]$$

- Non-steady system
- Evolution as a function of time
- No chemical reaction

Non-Removed Fraction

$$E = \frac{C_{At} - C_{A\infty}}{C_{A0} - C_{A\infty}}$$



$$E = \frac{C_{At} - C_{A\infty}}{C_{A0} - C_{A\infty}}$$

$$\frac{\partial C_A}{\partial t} = D_{AB}\left[\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right]$$

$$E = \frac{8}{\pi^2}\left[e^{-Dt\pi^2/4a^2} + \frac{1}{9}e^{-9Dt\pi^2/4a^2} + \frac{1}{25}e^{-25Dt\pi^2/4a^2} + \ldots\right]$$

Example 1
Sheet – one contact wall (a)

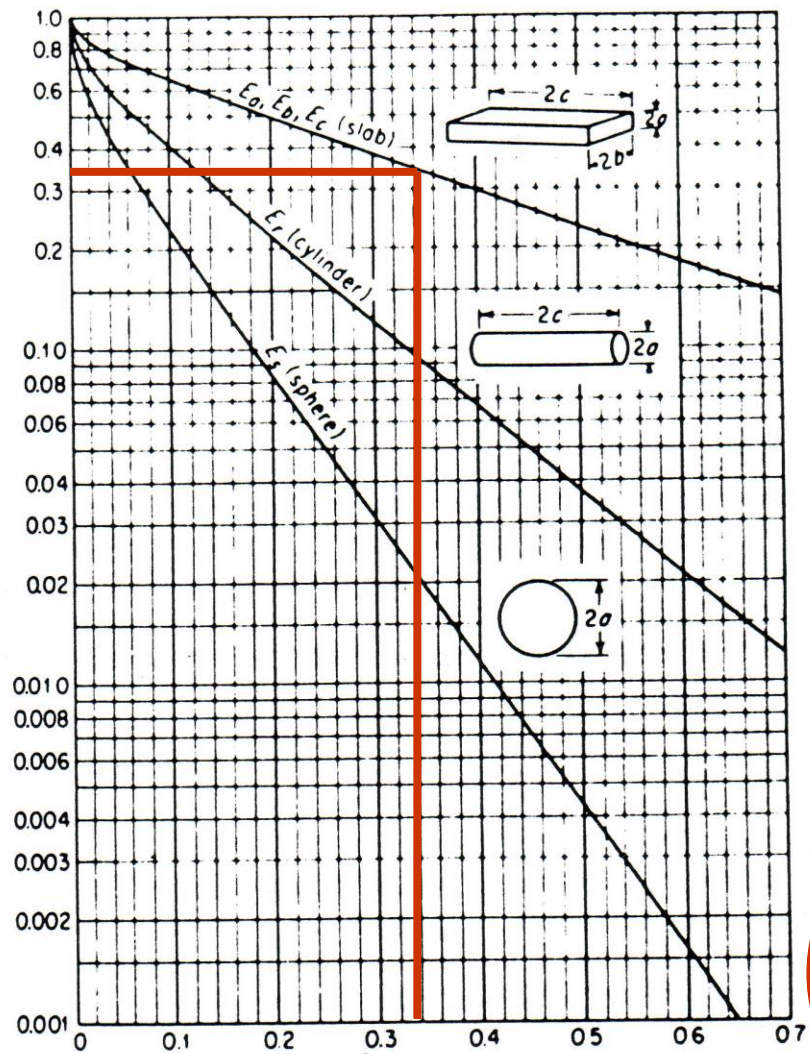
Diagram determination

$$E = \frac{C_{At} - C_{A\infty}}{C_{A0} - C_{A\infty}} = f\left(\frac{Dt}{a^2}\right) = E_a$$

Numerical approach

$$E = \frac{8}{\pi^2}\left[e^{-Dt\pi^2/4a^2} + \frac{1}{9}e^{-9Dt\pi^2/4a^2} + \frac{1}{25}e^{-25Dt\pi^2/4a^2} + \ldots\right]$$

Ea, Eb, Ec, Er, Es



$$\frac{Dt}{a^2}, \frac{Dt}{b^2}, \frac{Dt}{c^2}$$

Example 2
Plate – Two contact walls (a, b)

Diagram determination

$$E = \frac{C_{At} - C_{A\infty}}{C_{A0} - C_{A\infty}} = f\left(\frac{Dt}{a^2}\right) f\left(\frac{Dt}{b^2}\right) = E_a E_b$$

Example 3
Bar – (a, b, c)

Diagram determination

$$E = \frac{C_{At} - C_{A\infty}}{C_{A0} - C_{A\infty}} = f\left(\frac{Dt}{a^2}\right) f\left(\frac{Dt}{b^2}\right) f\left(\frac{Dt}{c^2}\right) = E_a E_b E_c$$

Example 4
Sphere

Diagram determination

$$r = a$$

$$E = \frac{C_{At} - C_{A\infty}}{C_{A0} - C_{A\infty}} = f'\left(\frac{Dt}{a^2}\right) = E_s$$

Example 5
Cylinder without faces

Diagram determination

$$r = a$$

$$E = \frac{C_{At} - C_{A\infty}}{C_{A0} - C_{A\infty}} = f''\left(\frac{Dt}{a^2}\right) = E_r$$

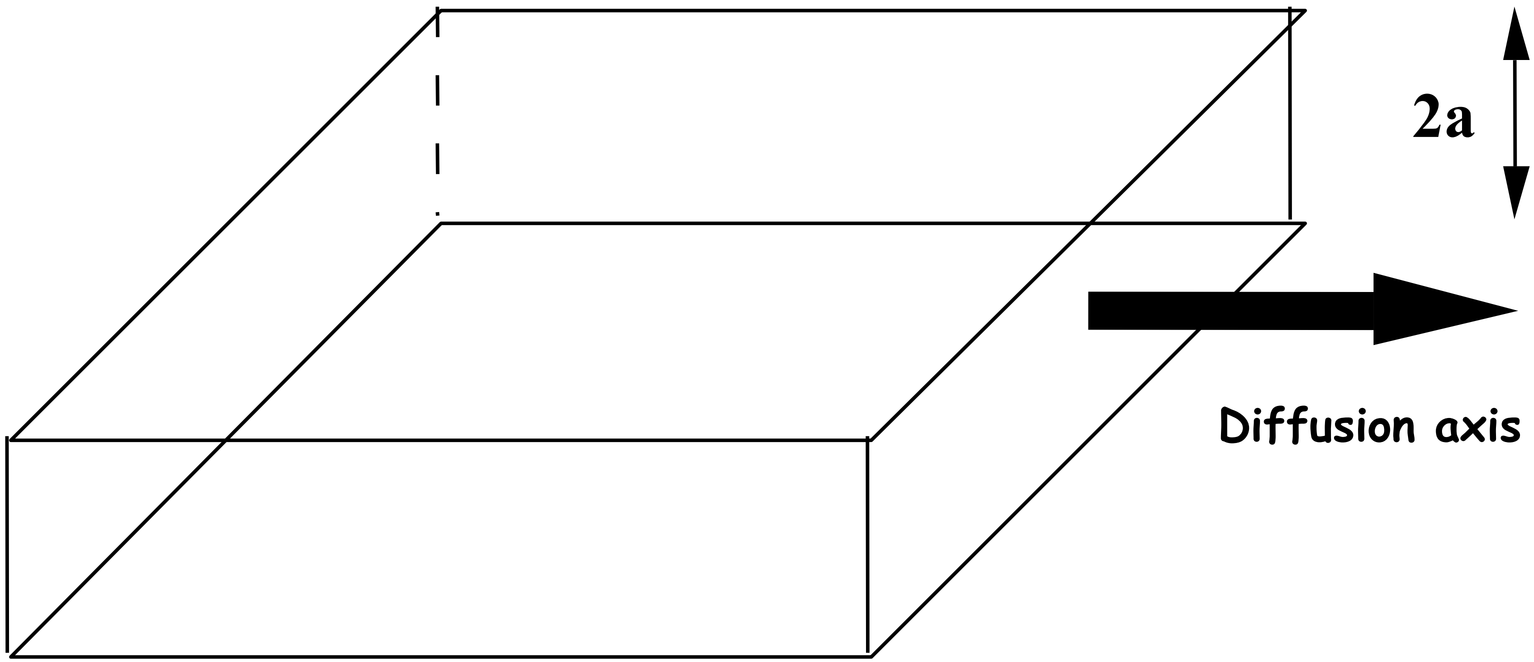
Example 6
Cylinder with faces

Diagram determination

$$r = a$$
$$r' = c$$

$$E = \frac{C_{At} - C_{A\infty}}{C_{A0} - C_{A\infty}} = f\left(\frac{Dt}{c^2}\right) f''\left(\frac{Dt}{a^2}\right) = E_c E_r$$

Specific case

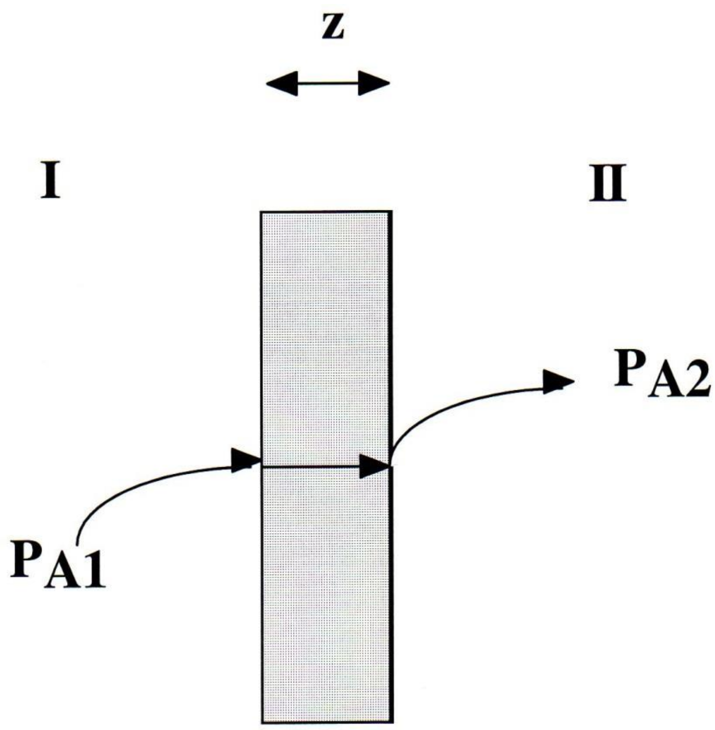


Diffusion

Through a polymer

Diffusion through a polymer

Volumic flow

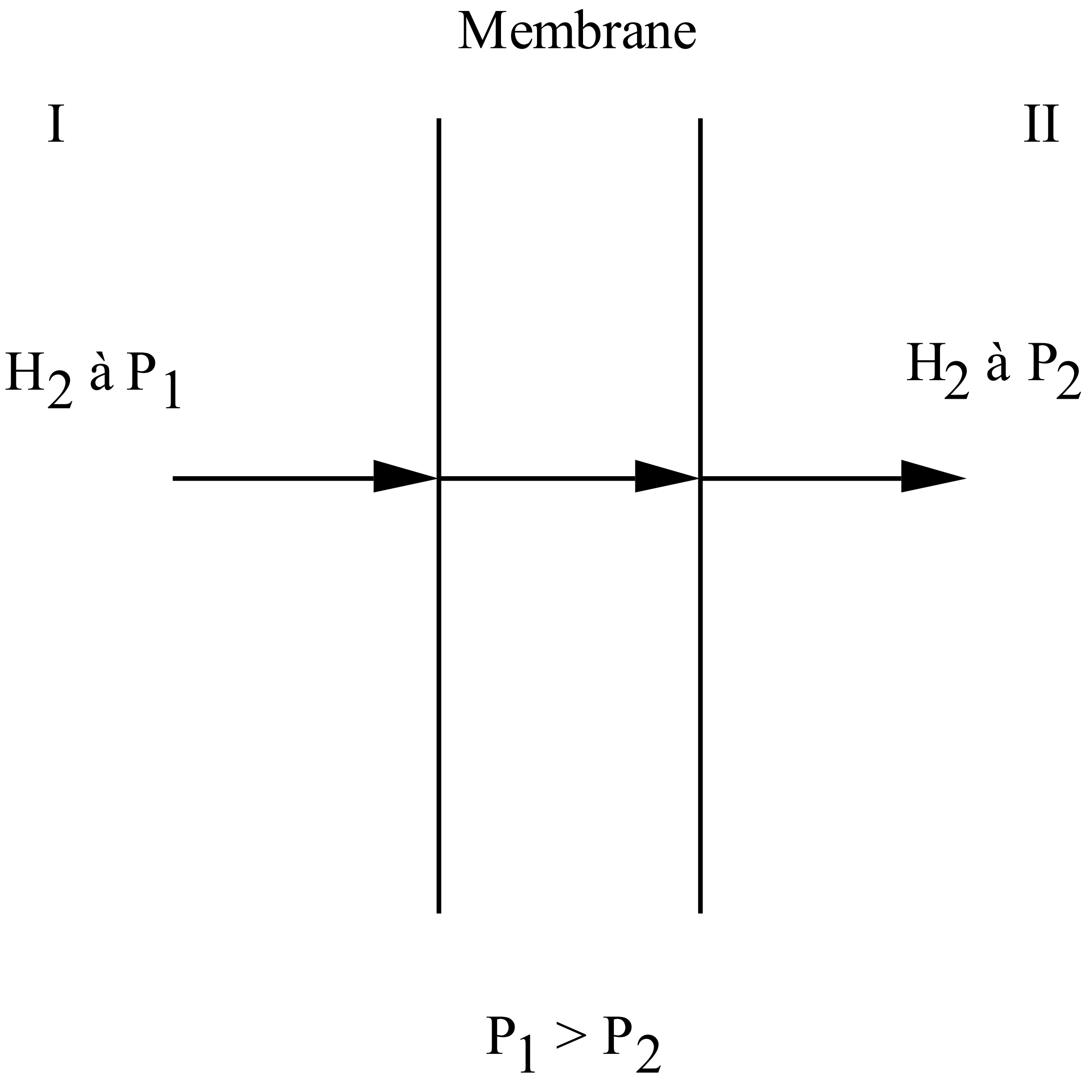


$$P_{A1} > P_{A2}$$

$$W_A = \frac{D_A S_A (P_{A1} - P_{A2})}{z}$$

Permeability :

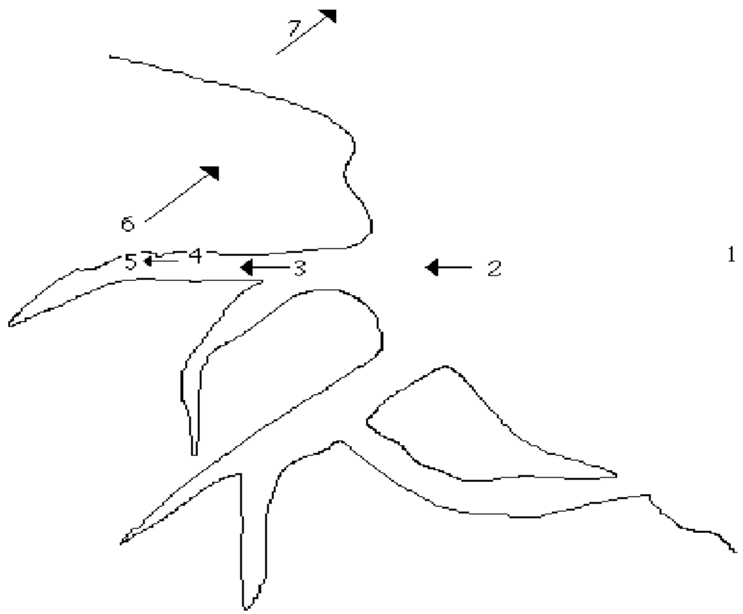
$$P = D_A S_A$$


Membrane
I
II
H_2 à P_1
H_2 à P_2
$P_1 > P_2$

Diffusion

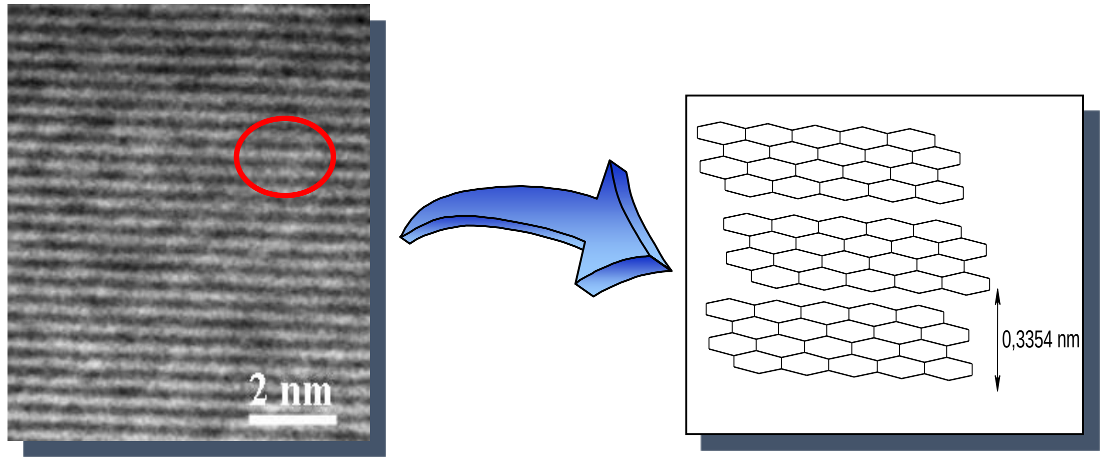
in a porous solid

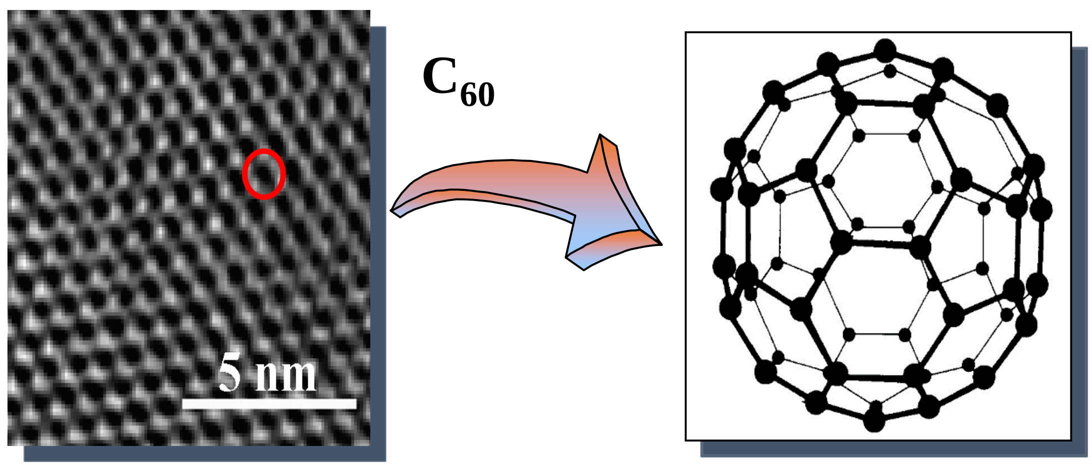
Principe de l'adsorption



Pure carbon crystals

High Resolution Transmission Electron Microscopy Image Analysis => **Direct imaging of the structure**





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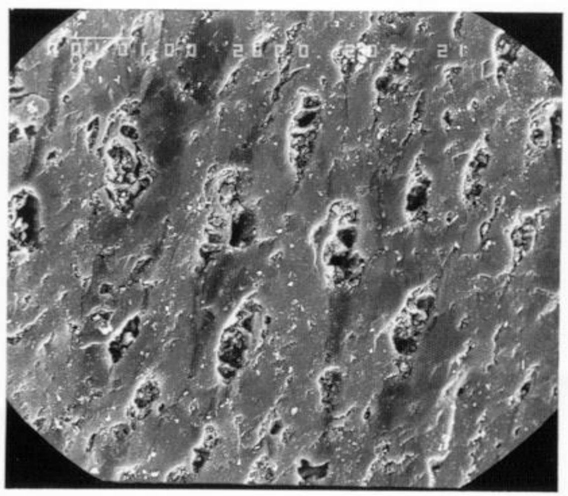
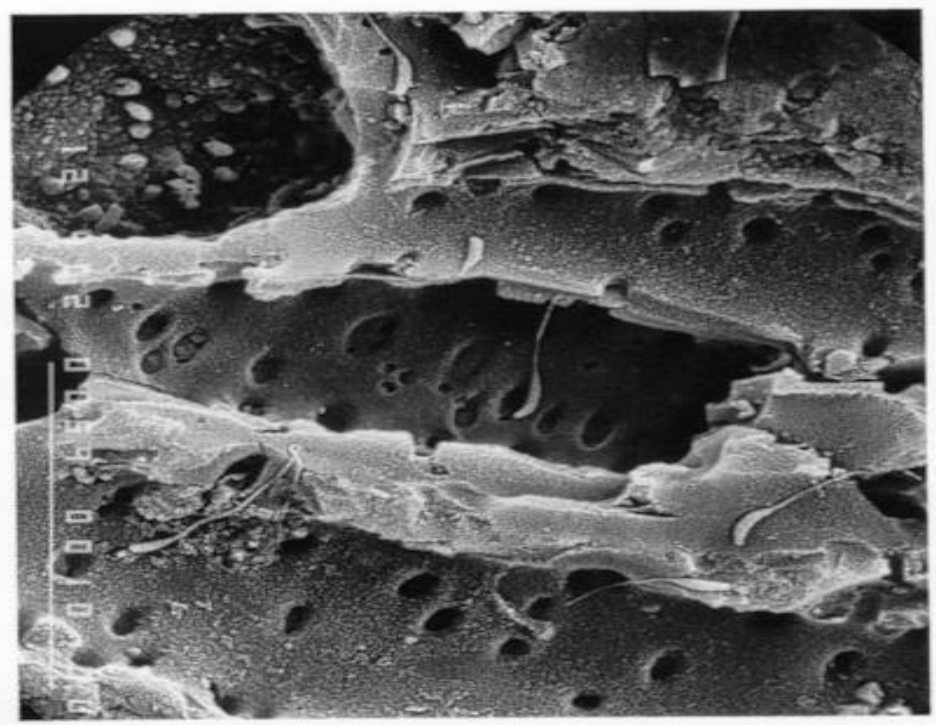
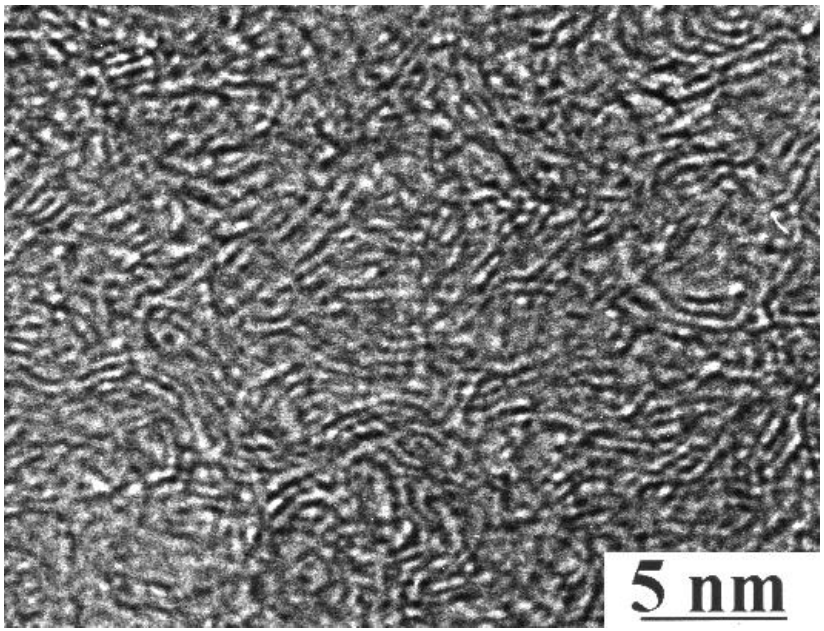
Activated carbon



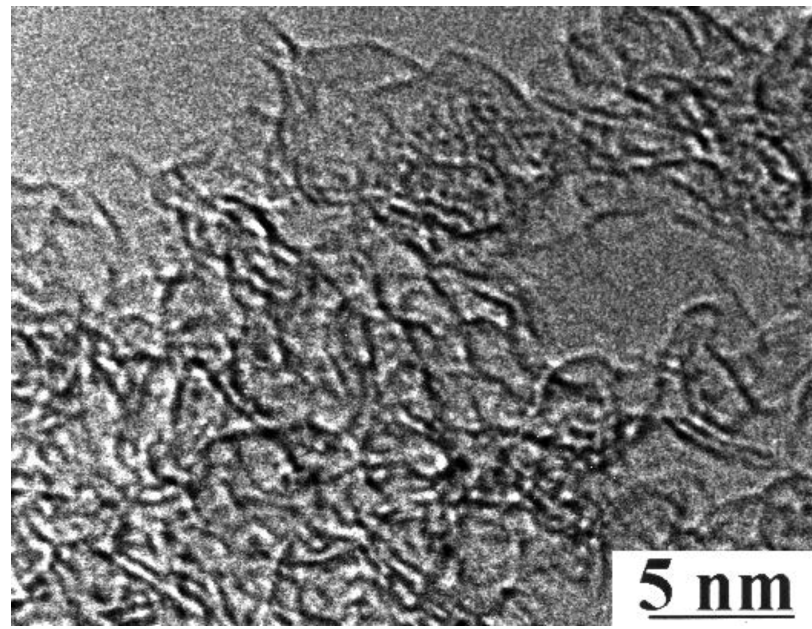


Saccharose-based Adsorbent Carbons
High Resolution TEM characterisation

Before activation

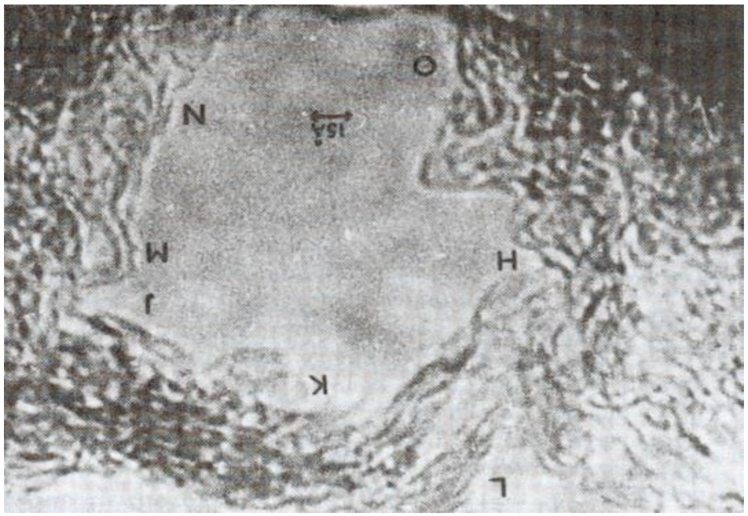


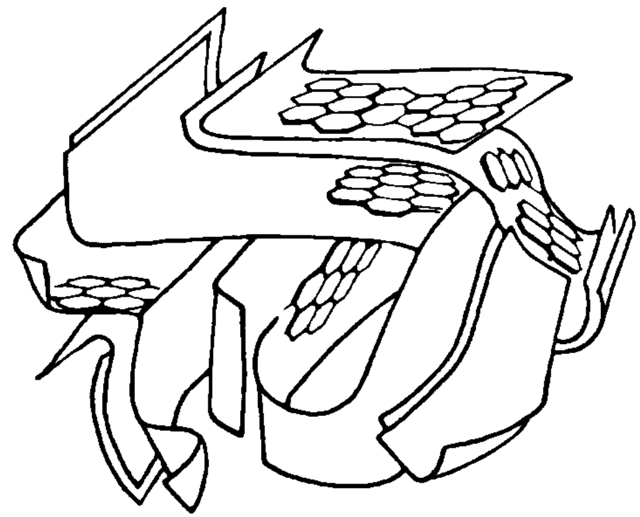
Some strongly activated areas



Duber et al, Fuel Proces. Technol
77-78 (2002), 221-227

Activated carbon surface





Bansal et al., 1988, Active Carbon, Marcel Dekker Inc

Activated carbon characteristics

Internal Porosity

Pore diameter	**nm**	**dp**	
- Macropores			**> 50**
- Mesopores			**2 < d < 50**
- Micropores			**< 2**
Porous volume	**cm^3/g**	**Vp**	**0.3 – 0.7**
Specific surface area (BET)	**m^2/g**	**S_{BET}**	
- non activated			**2 - 20**
- activated			**500 - 2000**

Diffusion in porous media

Specific case : gas
P_T = constant

$$N_A = \frac{N_A}{N_A + N_B} \frac{D_{AB} P_T}{RTz} Ln \left[\frac{\left(N_A / N_A + N_B \right) P_T - P_{A2}}{\left(N_A / N_A + N_B \right) P_T - P_{A1}} \right]$$

or

$$N_A = \frac{N_A}{N_A + N_B} \frac{D_{AB} P_T}{RTz} Ln \left[\frac{\left(N_A / N_A + N_B \right) - y_2}{\left(N_A / N_A + N_B \right) - y_1} \right]$$

Diffusion in porous media

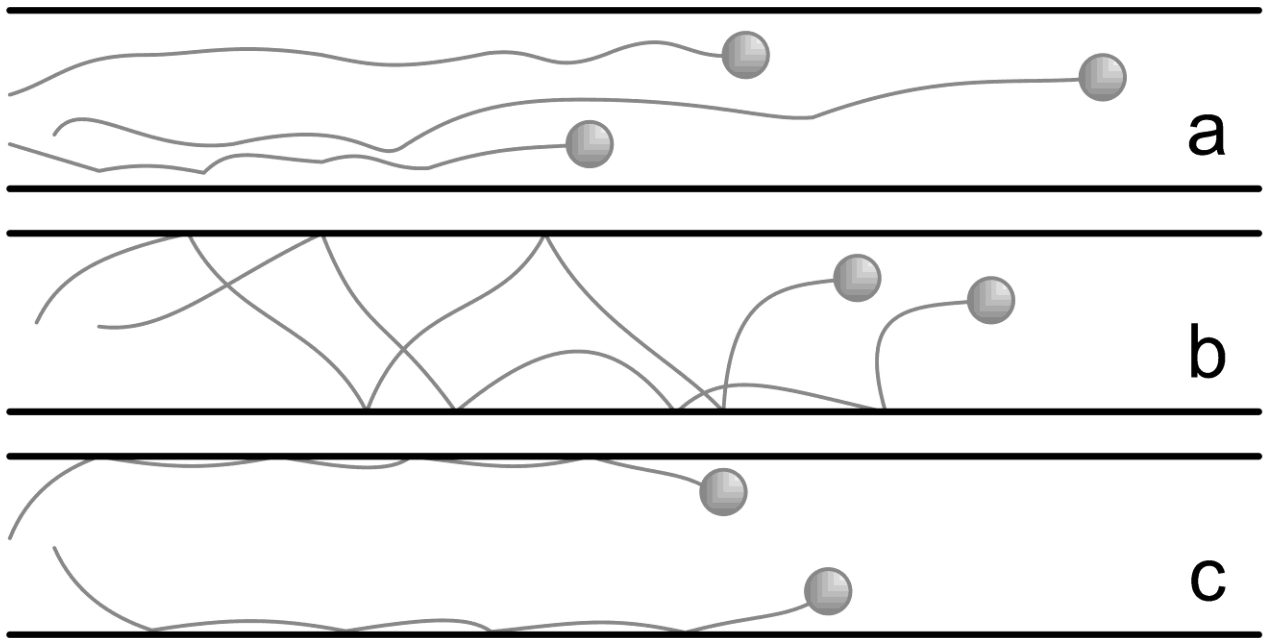
$$N_A = \frac{N_A}{N_A + N_B} \frac{D_{AB} P_T}{RTz} \mathrm{Ln}\left[\frac{\left(N_A / N_A + N_B\right) - y_2}{\left(N_A / N_A + N_B\right) - y_1}\right]$$

D_{AB} is not known
Then for a similar processus :

$$\frac{D_{AB}}{(D_{AB})_{eff}} = cste$$

$$N_A = \frac{N_A}{N_A + N_B} \frac{(D_{AB})_{eff} P_T}{RTz} \mathrm{Ln}\left[\frac{\left(N_A / N_A + N_B\right) - y_2}{\left(N_A / N_A + N_B\right) - y_1}\right]$$

Diffusion in porous media



a. Diffusion in a pore
b. Knudsen diffusion
c. Surface diffusion

Knudsen approach (1)

Specific case for gas

P_T = constant

Criteria

$$\frac{d}{\lambda} \geq 20$$

With

$$\lambda = \frac{3.2\mu}{P_T}\left[\frac{RT}{2\pi M_A}\right]^{0.5}$$

$$N_A = \frac{N_A}{N_A + N_B}\frac{(D_{AB})_{eff} P_T}{RTz} \mathrm{Ln}\left[\frac{\left(N_A / N_A + N_B\right) - y_2}{\left(N_A / N_A + N_B\right) - y_1}\right]$$

Knudsen approach (2)

Specific case for gas

P_T = constant

Criteria

$$\frac{d}{\lambda} \leq 0.2$$

With

$$\lambda = \frac{3.2\mu}{P_T}\left[\frac{RT}{2\pi M_A}\right]^{0.5}$$

Knudsen law

$$N_A = \frac{d\overline{U_A}}{3RTl}\left[P_{A1} - P_{A2}\right]$$

$$\overline{U_A} = \left[\frac{8RT}{\pi M_A}\right]^{0.5}$$

Knudsen approach (3)

Knudsen law

$$N_A = \frac{d\overline{U}_A}{3RTl}\left[P_{A1} - P_{A2}\right] \qquad \overline{U}_A = \left[\frac{8RT}{\pi M_A}\right]^{0.5}$$

$$N_A = \frac{d}{3RTl}\left[\frac{8RT}{\pi M_A}\right]^{0.5}\left[P_{A1} - P_{A2}\right]$$

$$\boxed{N_A = \frac{D_{KA}}{RTl}\left[P_{A1} - P_{A2}\right]}$$

Knudsen coefficient $$D_{kA} = \frac{d}{3}\left[\frac{8RT}{\pi M_A}\right]^{0.5}$$

$$N_A = \frac{D_{KA}}{RTl}\left[P_{A1} - P_{A2}\right]$$

- l is not known then l→z with z a diameter, a length…

$$D_{kA} \rightarrow \left(D_{kA}\right)_{eff}$$

- $$\left(D_{kA}\right)_{eff} = f\left[\left(\frac{T}{M}\right)^{0.5}\right]$$

- $\left(D_{kA}\right)_{eff}$ is independant of P

$$N_A = \frac{D_{KA}}{RTl}\left[P_{A1} - P_{A2}\right]$$

- For binary mixture…

$$\frac{N_A}{N_B} = -\left[\frac{M_A}{M_B}\right]^{0.5}$$

- For a specific solid

$$\frac{\left(D_{kB}\right)_{eff}}{\left(D_{kA}\right)_{eff}} = \frac{D_{kB}}{D_{kA}}$$

Knudsen approach (4)

Specific case for gas

P_T = constant

Criteria

$$0.2 \leq \frac{d}{\lambda} \leq 20$$

With

$$\lambda = \frac{3.2\mu}{P_T}\left[\frac{RT}{2\pi M_A}\right]^{0.5}$$

Knudsen's law + Diffusivity

$$N_A = \frac{N_A}{N_A + N_B}\frac{(D_{AB})_{eff} P_T}{RTz} \mathrm{Ln}\left[\frac{\left(N_A / N_A + N_B\right)\left(1 + \frac{D_{ABeff}}{D_{kAeff}}\right) - y_2}{\left(N_A / N_A + N_B\right)\left(1 + \frac{D_{ABeff}}{D_{kAeff}}\right) - y_1}\right]$$

abstract

Specific case for gas
P_T = constant

$$\lambda = \frac{3.2\mu}{P_T}\left[\frac{RT}{2\pi M_A}\right]^{0.5}$$

Diffusivity

$$\frac{d}{\lambda} \geq 20$$

$$N_A = \frac{N_A}{N_A+N_B}\frac{(D_{AB})_{eff}P_T}{RTz}\mathrm{Ln}\left[\frac{\left(N_A / N_A+N_B\right)-y_2}{\left(N_A / N_A+N_B\right)-y_1}\right]$$

Knudsen's law

$$\frac{d}{\lambda} \leq 0.2$$

$$N_A = \frac{D_{KA}}{RTl}\left[P_{A1}-P_{A2}\right]$$

Knudsen's law + Diffusivity

$$0.2 \leq \frac{d}{\lambda} \leq 20$$

$$N_A = \frac{N_A}{N_A+N_B}\frac{(D_{AB})_{eff}P_T}{RTz}\mathrm{Ln}\left[\frac{\left(N_A / N_A+N_B\right)\left(1+\frac{D_{ABeff}}{D_{kAeff}}\right)-y_2}{\left(N_A / N_A+N_B\right)\left(1+\frac{D_{ABeff}}{D_{kAeff}}\right)-y_1}\right]$$