Gas transport in porous solids

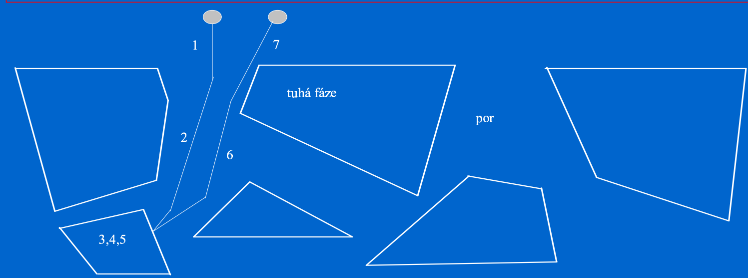
Texture of porous solids

Gas transport in pores

- diffusion
- permeation
- combined

Gas transport in porous solids

Processes in porous solids
(catalysts, adsorbents, reaction components)



Texture of porous solids

pore volume/porosity

surface area

pore-size distribution (PSD)

pore shape

pore connectivity

etc.

Texture of porous solids

why?

“an sich” (e.g. zeolites)

description/simulation of processes in pores (frequent)

Texture of porous solids

Standard methods

Model independent

pore volume / porosity
- true (helium density)
- apparent (mercury) density

specific surface
- physical adsorption (nitrogen, argon) + BET
  (caution: micropores !!)

Texture of porous solids

Model dependent

pore-size distribution (PSD)

physical adsorption (nitrogen, argon)
- cylindrical pores, slits

mercury porosimetry
- cylindrical pores

Texture of porous solids

Methods related to transport of fluids

philosophy:

pore structure characteristics suitable for description/simulation of mass transport (mean pore radius, tortuosity, etc.) obtained from simple transport processes

Gas transport in pores

- simple pore model & description
- experiments with simple transport process
- evaluation of pore structure characteristics

Petr Schneider, ICPF CAS

Transport processes

Transport processes:

Steady-state

- binary countercurrent diffusion
- permeation of simple gases
- simple reaction (p-hydrogen→o-hydrogen)

Unsteady-state

- chromatography
- combined diffusion/permeation

Transport parameters

Transport parameters

material constants of the porous solid

- independent of temperature
  pressure
  gas composition
- suitable for prediction of the process (rate) inside pores (**multicomponent)**

optimisation of pore structure (but no recipes for production !)

Gas diffusion

Diffusion

driving force: composition (mole fraction) gradient

multicomponent gas mixture

transition between Knudsen and bulk regions

Knudsen diffusion: collisions A-wall, B-wall, ...

bulk diffusion: collisions A-B, A-C, B-C, ...

Bulk diffusion

Diffusion

isothermal, isobaric mixing of species

In a pore: collisions A-A, B-B, A-B, A-wall, B-wall

Infinite gas (only collisions A-A, B-B, A-B)

BULK DIFFUSION

Constant p and T (activity a_i, mole fraction y_i)

Driving force for A (Newton per mole of A)

$$F_A = -\frac{d\mu_A}{dz} = -R_g T \frac{d\ln(a_A)}{dz} = -\frac{R_g T}{y_A}\frac{dy_A}{dz}$$

Bulk diffusion

Driving force of A is compensated by friction force of B exerted on A

$$F_A = \xi_{AB} y_B (v_A - v_B)$$

v_A, v_B linear velocities of diffusion in the diffusion direction (cm/s)

c total molar concentration (mol/cm^3)

Bulk diffusion

$$-\frac{R_g T}{y_A}\frac{dy_A}{dz} = \xi_{AB} y_B (v_A - v_B) \qquad v_A \; (=) \; \text{cm/s}$$

$$-c\frac{dy_A}{dz} = \frac{\xi_{AB}}{R_g T} c y_A y_B (v_A - v_B)$$

$$\mathcal{N}_A = v_A c y_A \qquad \mathcal{N}_B = v_B c y_B \qquad \mathcal{N}_A (=) \; \text{mol/cm}^2\text{s}$$

diffusion flux density

Bulk diffusion

$$\mathcal{D}_{AB}^{m} \equiv \frac{R_g T}{\xi_{AB} c}$$

binary bulk

diffusion coefficient

$$\mathcal{D}_{AB}^{m} \approx \frac{1}{c} \approx \frac{1}{p}$$

Bulk diffusion

$$-c\frac{dy_A}{dz} = \frac{y_B c v_A y_A - y_A c v_B y_B}{\mathcal{D}_{AB}^{m}}$$

$$-c\frac{dy_A}{dz} = \frac{y_B \mathcal{N}_A - y_A \mathcal{N}_B}{\mathcal{D}_{AB}^{m}}$$

Stefan-Maxwell diffusion equation

for binary diffusion A-B

Bulk diffusion

multicomponent case (A, B, C, D, ...)

$$-c\frac{dy_A}{dz} = \frac{y_B\mathcal{N}_A - y_A\mathcal{N}_B}{\mathcal{D}^m_{AB}} + \frac{y_C\mathcal{N}_A - y_A\mathcal{N}_C}{\mathcal{D}^m_{AC}} + \frac{y_D\mathcal{N}_A - y_A\mathcal{N}_D}{\mathcal{D}^m_{AD}} \dots$$

multicomponent case (i=1, 2, ..., n)

$$-c\frac{dy_i}{dz} = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{y_j\mathcal{N}_i - y_i\mathcal{N}_j}{\mathcal{D}^m_{ij}}$$

Knudsen diffusion

At cylinder (pore) wall (collisions A-wall, B-wall; Knudsen region)

KNUDSEN DIFFUSION IN CYLINDRICAL PORE

$$\mathcal{N}_A = r\frac{2}{3}\bar{v}_A\left(-c\frac{dy_A}{dz}\right) = \mathcal{D}^k_A\left(-c\frac{dy_A}{dz}\right)$$

$\bar{v}_A$....mean molecular thermal velocity

r....pore radius

$$v_A = \sqrt{\frac{8R_gT}{\pi M_A}}$$

$\mathcal{D}^k_A$....Knudsen diffusivity

Transition region

TRANSITION DIFFUSION REGION
(combination of bulk and Knudsen diffusion)

z-Momentum balance

$$-c\frac{dy_i}{dz} = \left(-c\frac{dy_i}{dz}\right)_{i-wall} + \sum_{\substack{j=1\\j\neq i}}^{n}\left(-c\frac{dy_i}{dz}\right)_{i-j}$$

$$-\left(c\frac{dy_i}{dz}\right)_{i-wall} = \frac{\mathcal{N}_i}{\mathcal{D}_i^k} \qquad \sum_{\substack{j=1\\j\neq i}}^{n} -\left(c\frac{dy_i}{dz}\right)_{i-j} = \sum_{\substack{j=1\\j\neq i}}^{n} \frac{y_j\mathcal{N}_i - y_i\mathcal{N}_j}{\mathcal{D}_{ij}^m}$$

$$-c\frac{dy_i}{dz} = \frac{\mathcal{N}_i}{\mathcal{D}_i^k} + \sum_{\substack{j=1\\j\neq i}}^{n} \frac{y_j\mathcal{N}_i - y_i\mathcal{N}_j}{\mathcal{D}_{ij}^m}$$

Models

Mean Transport-Pore Model
(MTPM)

Only some pores responsible for gas transport

Cylindrical pores <r>, <r^2>

Porosity ε_t, tortuosity q; parameter $\psi = \varepsilon_t/q$

Three parameters: <r>ψ, <r^2>ψ, ψ

Material parameters (to be determined experimentally)

simple apparatus, simple conditions, inert gases (single, binaries)

Models

Dusty-Gas Model

(DGM)

n+1 component gas mixture

- n gas components
- giant (dust) particles

kinetic theory of gases + force for keeping dust immovable

three model parameters: ψ, $\langle r \rangle$, B ($=\langle r^2 \rangle \psi/8$)

Material parameters (to be determined experimentally)

Gas diffusion in pores

POROUS SOLID

Only part of the cross-section is available for diffusion - ε

The diffusion path z is longer than x. Tortuosity $q = z/x$

Combination $\psi = \varepsilon/q$

Mean pore radius $\langle r \rangle$

Replacements $\mathcal{N} \rightarrow N^d$, $z \rightarrow x$, $\mathcal{D}^m \rightarrow D^m$, $\mathcal{D}^k \rightarrow D^k$

Gas diffusion in pores

(Modified) Stefan-Maxwell diffusion equation

$$-c\frac{dy_i}{dx}=\frac{N^d_i}{D^k_i}+\sum_{\substack{j=1\\j\neq i}}^{n}\frac{y_jN^d_i-y_iN^d_j}{D^m_{ij}}$$

N^d_i	component diffusion flux density (mol/$cm^2_{por.s.}$s)
c	total molar concentration
y_i	mole fraction
D^m_{ij}	effective bulk diffusion coefficient (cm^2/s)
D^k_i	effective Knudsen diffusion coefficient

Effective diffusivities

Effective diffusion coefficients
(MTPM and DGM)

include transport parameters: ψ, <r>
gas properties:
M_i molecular weight of i

Effective **bulk diffusion** coefficient:

$$D^m_{ij} = \psi\,\mathscr{D}^m_{ij}$$

Effective **Knudsen diffusion** coefficient:

$$D^k_i = \langle r\rangle\psi(2/3)(8R_gT/\pi M_i)^{1/2}$$

Graham's law

(Modified) Stefan-Maxwell diffusion equation for binary case A-B

$$-c\frac{dy_A}{dx}=\frac{N_A^d}{D_A^k}+\frac{y_B N_A^d - y_A N_B^d}{D_{AB}^m}$$

$$-c\frac{dy_B}{dx}=\frac{N_B^d}{D_B^k}+\frac{y_A N_B^d - y_B N_A^d}{D_{AB}^m}$$

Graham's law

$$-c\frac{dy_A}{dx}=\frac{N_A^d}{D_A^k}+\frac{y_B N_A^d - y_A N_B^d}{D_{AB}^m}$$

$$-c\frac{dy_B}{dx}=\frac{N_B^d}{D_B^k}+\frac{y_A N_B^d - y_B N_A^d}{D_{AB}^m}$$

$$-c\frac{d(y_A+y_B)}{dx}=\frac{N_A^d}{D_A^k}+\frac{N_B^d}{D_B^k}+0 \qquad -c\frac{d(1)}{dx}=\frac{N_A^d}{D_A^k}+\frac{N_B^d}{D_B^k}+0$$

$$\frac{N_A^d}{D_A^k}+\frac{N_B^d}{D_B^k}=0$$

Graham's law

$$\frac{N^d_A}{D^k_A} + \frac{N^d_B}{D^k_B} = 0 \qquad D^k_A = \langle r \rangle \psi (2/3) \sqrt{(8 R_g T / \pi M_A)}$$

$$N^d_A \sqrt{M_A} + N^d_B \sqrt{M_B} = 0$$

Graham's law

$$\frac{N^d_A}{N^d_B} = -\sqrt{\frac{M_B}{M_A}}$$

e.g. $N^d(H_2)/N^d(N_2) = (28/2)^{1/2} = 3.7$

Generalised Graham law

condition for **isobaric** gas diffusion

(true diffusion)

$$\sum_{i=1}^{n} N_i \sqrt{M_i} = 0$$

Binary gas diffusion

Binary case

$$-c\frac{dy_1}{dx} = \frac{N_1^d}{D_1^k} + \frac{y_2 N_1^d - y_1 N_2^d}{D_{12}^m} =$$

$$= \frac{N_1^d}{D_1^k} + \frac{(1-y_1)N_1^d - y_1\left(N_1^d\left(-\sqrt{\frac{M_1}{M_2}}\right)\right)}{D_{12}^m} =$$

$$= \frac{N_1^d}{D_1^k} + N_1^d \frac{1-y_1\left(1-\sqrt{\frac{M_1}{M_2}}\right)}{D_{12}^m}$$

=

$$-c\frac{dy_1}{dx} = N_1^d\left[\frac{1}{D_1^k} + \frac{1-\alpha_{12}y_1}{D_{12}^m}\right]$$

$$\alpha_{12} = \left(1-\sqrt{\frac{M_1}{M_2}}\right)$$

Binary gas diffusion

$$-c\frac{dy_1}{dx} = N_1^d\left[\frac{1}{D_1^k} + \frac{1-\alpha_{12}y_1}{D_{12}^m}\right]$$

$$N_1^d = \frac{1}{\left[\frac{1}{D_1^k} + \frac{1-\alpha_{12}y_1}{D_{12}^m}\right]}\left(-c\frac{dy_1}{dx}\right)$$

Fick's law form;

Flux = Diffusivity *(- composition gradient)

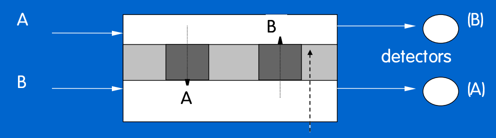
concentration dependent diffusivity !!! ONLY FOR A BINARY

Wicke-Kallenbach

Steady-state countercurrent diffusion in binary gas mixtures

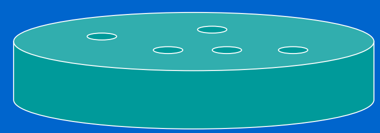
Wicke-Kallenbach diffusion cell (1944)

INERT GASES (no surface transport contribution)



Diffusion cell

metallic disc with holes for porous pellets
tightening: silicon rubber tubing
glue



Diffusion cell

measurements with different inert gases A, B

(hydrogen, helium, nitrogen, argon,..)

at different temperature

at different (total) pressures

$\Rightarrow$ $\langle r \rangle$, ψ

The Graham cell

$$N_B^d = -N_A^d \sqrt{\frac{M_B}{M_A}}$$

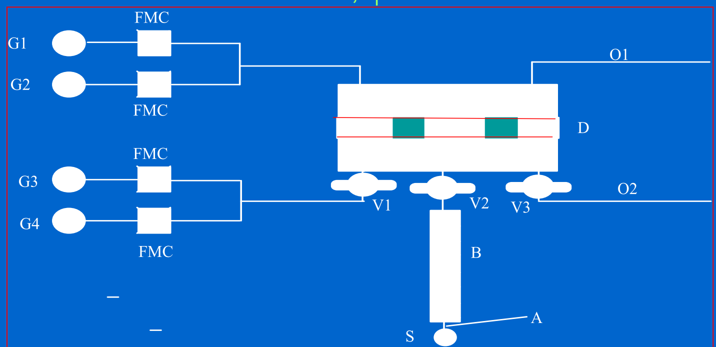
$$N_{total} = N_A^d + N_B^d = N_A^d \left(1 - \sqrt{\frac{M_B}{M_A}}\right)$$

e.g. H_2 (A) versus N_2 (B)

$N_{total} = 0.73\ N^d(H_2)$

The Graham cell

Graham diffusion cell
($M_A \neq M_B$):
hydrogen, helium, nitrogen, argon
$\langle r \rangle$, ψ



The Graham cell

Modified Stefan-Maxwell equation for countercurrent diffusion of a binary A-B

$$N_A^d = \frac{1}{\frac{1}{D_A^k} + \frac{1 - y_A \alpha_{AB}}{D_{AB}^m}} \left(-c \frac{dy_A}{dx} \right)$$

Integrated form ->

The Graham cell

$$N_A^d = \frac{c_T}{\alpha_{AB} L} D_{AB}^m \ln \frac{1-\alpha_{AB} y_A^L + \left(D_{AB}^m / D_A^k\right)}{1-\alpha_{AB} y_A^U + \left(D_{AB}^m / D_A^k\right)}$$

e.g. $y_A^U = 1 \quad y_A^L = 0$

$$N_A^d = \frac{c_T}{\alpha_{AB} L} D_{AB}^m \ln \frac{1+\left(D_{AB}^m / D_A^k\right)}{1-\alpha_{AB}\left(D_{AB}^m / D_A^k\right)}$$

The Graham cell

$$N^d = N_A^d + N_B^d = N_A^d \left(1-\sqrt{\frac{M_A}{M_B}}\right) = N_A^d \alpha_{AB} \quad \Rightarrow$$

$$\boxed{N^d = \frac{c}{L} \psi \mathcal{D}_{AB}^m \ln \frac{1+\left(\mathcal{D}_{AB}^m / \langle r \rangle K_A\right)}{1-\alpha_{AB}+\left(\mathcal{D}_{AB}^m / \langle r \rangle K_A\right)}}$$

The Graham cell

measurements with different inert gases A, B

(hydrogen, helium, nitrogen, argon,..)

$\Rightarrow$ $\langle r \rangle$, ψ

Gas transport in pores

Graham law violation:

- fluxes fixed by reaction stoichiometry (ss)
- dynamic process (us)
- etc.

pressure gradient develops $\Rightarrow$ additional transport mechanism (permeation)

Gas permeation

Inert gases: helium, hydrogen, nitrogen, argon,…

Single gas permeation

driving force: pressure gradient (total molar concentration)

Darcy law:

$$N^p = B\left(-\frac{dc}{dx}\right)$$

N^p	molar **p**ermeation flux density (mol/cm^{2}s)
B	effective permeability coeff. (cm$^{2/}$s)
c	total molar concentration (mol/cm^3)

$B = f(p, \mu, \langle r^2\rangle, \psi)$

Gas permeation

Multicomponent permeation

generalization of single component case

driving force: pressure gradient (total molar concentration)

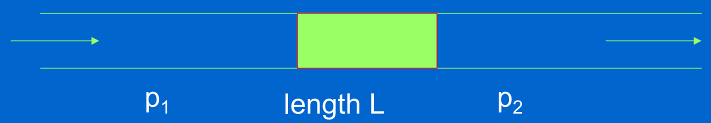
$$N_i^p = B_i y_i\left(-\frac{dc}{dx}\right)$$

N^p_i	molar **p**ermeation flux density (mol/cm^{2}s)
B_i	effective permeability coeff. (cm^{2}s)
c	total molar concentration (mol/cm^3)

$B_i = f(p, \mu, \langle r^2\rangle, \psi)$

Gas permeation

Permeation



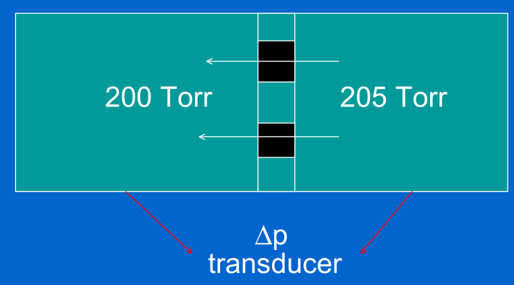
pressure difference Δp

$\frac{\text{Flowrate}}{\Delta p/L}$ = Effective permeability coefficient (B) at $\bar{p}$

Measurement at different mean pressures
Complicated flowrate regulation at subatmospheric pressures

Gas permeation

Pseudostationary permeation cell



Gas permeation

with equal volumes: end pressure 202.5 Torr

exponential pressure decline ⇒ $B(p_{end})$

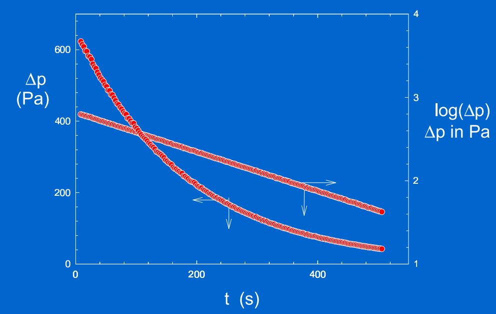
measurements at different pressures (10 - 1000 Torr)

measurements at higher pressures possible

measurements with different simple gases:

hydrogen, helium, nitrogen, argon

Gas permeation



p^o=2000 Pa, Δp^o=622 Pa, p(mean)=2311 Pa

Gas permeation

$$\frac{d\Delta p}{dt} = -\frac{SNR_gT}{V}$$

at $t=0_-$ $p_{left} = p_{right} = p^o$

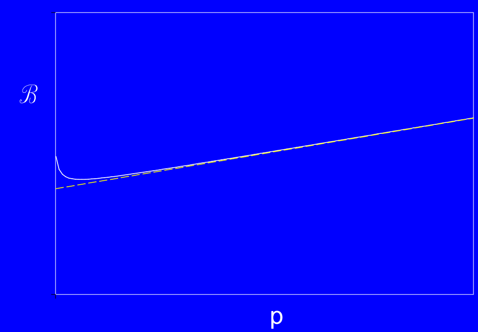
at $t=0_+$ $p_{left} = p^o + \Delta p^o$

$$\Delta p = \Delta p^o \exp\left(\frac{S}{L}\frac{2}{V}\bar{B}t\right)$$

$\bar{B} = B(\bar{p})$ $\bar{p} = p^o + \Delta p^o/2$

Capillary

Knudsen 1913



Weber equation

$$\mathscr{B} = \frac{2}{3} r \sqrt{\frac{8R_gT}{\pi M}} \frac{Kn}{1+Kn} + \frac{2}{3} r \sqrt{\frac{8R_gT}{\pi M}} \frac{\omega}{1+Kn} + \frac{r^2 p}{8\mu}$$

Knudsen flow — slip flow — viscous flow

$$\mathscr{B} = \frac{2}{3} r \sqrt{\frac{8R_gT}{\pi M}} \frac{\omega + Kn}{1+Kn} + \frac{r^2 p}{8\mu}$$

ω — 0.4, $3\pi/16$, 1, ...

Kn — Knudsen number = $\lambda/2r$ — Kn(p)

Knudsen number

$Kn = \lambda/2r$

Mean free-path length $\lambda \propto 1/p$

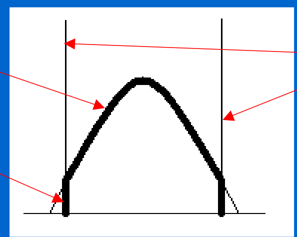
Pressure radius	Mean free-path length	Knudsen number	
low small	high	high	Knudsen flow region
high large	low	low	viscous flow region

Wall slip

Velocity profile in a tube

Replaced by parabola extending beyond the wall

Apparent wall slip (nonzero velocity at the wall)



parabolic velocity profile

wall slip velocity

pore wall

Weber equation

Porous solid - single gas

$\mathscr{B} \rightarrow B$ $r \rightarrow <r>\psi$ $r^2 \rightarrow <r^2>\psi$

$$B = <r> \psi \frac{2}{3}\sqrt{\frac{8R_gT}{\pi M}} \frac{\omega + Kn}{1 + Kn} + \frac{<r^2> \psi p}{8\mu}$$

$$K = \frac{2}{3}\sqrt{\frac{8R_gT}{\pi M}}$$

$$B = <r> \psi K \frac{\omega + Kn}{1 + Kn} + \frac{<r^2> \psi p}{8\mu}$$

Weber equation

Porous solid - single gas

usually linear dependence B vers p

$$B = D^k + \frac{<r^2>\psi}{8\mu} p$$

$$D^k = \psi <r> \frac{2}{3}\sqrt{\frac{8R_gT}{\pi M}}$$

from slope and intercept <r>ψ and <r²>ψ

Weber equation

One straight line for different gases

$$B = <r>\psi K + \frac{<r^2>\psi}{8\mu} p \qquad K = \frac{2}{3}\sqrt{\frac{8R_gT}{\pi M}}$$

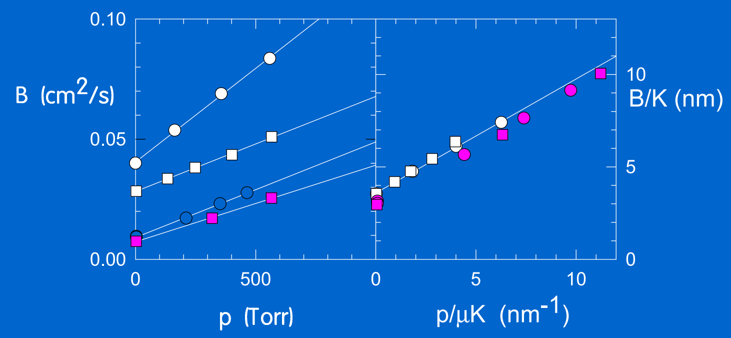
$$\frac{B}{K} = <r>\psi + \frac{<r^2>\psi}{8K\mu} p$$

$$\frac{B}{K} = <r>\psi + \frac{<r^2>\psi}{8}\frac{p}{K\mu} \qquad \frac{B}{K} = \text{intercept} + \text{slope}\frac{p}{K\mu}$$

intercept=<r>ψ

$$\text{slope} = \frac{<r^2>\psi}{8}$$

Effective permeability



Effective permeability

from intercept: $\langle r \rangle \psi$

from slope: $\langle r^2 \rangle \psi$

Combination of diffusion results: $\langle r \rangle \psi$, ψ

with permeation results: **$\langle r \rangle \psi$, $\langle r^2 \rangle \psi$**

$\langle r \rangle$, $\langle r^2 \rangle$, ψ

Chromatographic method

N e u s t á l e n ý t r a n s p o r t p l y n ů

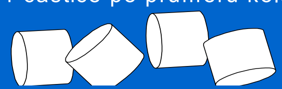
Chromatografická metoda

Dávkovací ventil (stopovací plyn)

alespoň 20 částic po průměru

detektor pro stopovací plyn

válcové / kulové částice
1 částice po průměru kolony (SPSR))

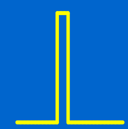


Single **P**ellet-**S**tring **C**olumn

Chromatographic method

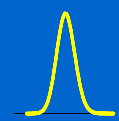
vstupní signál

= impuls



výstupní signál

= peak

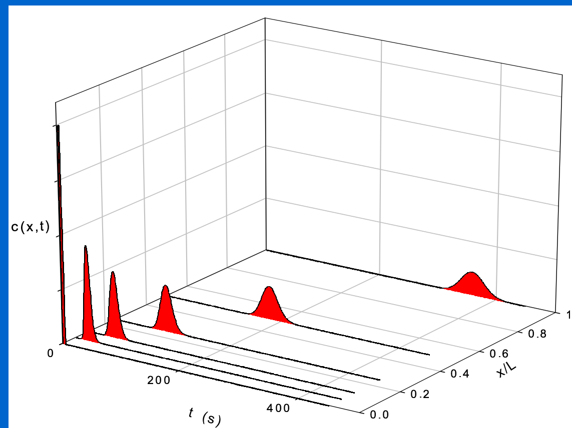


Chromatographic method

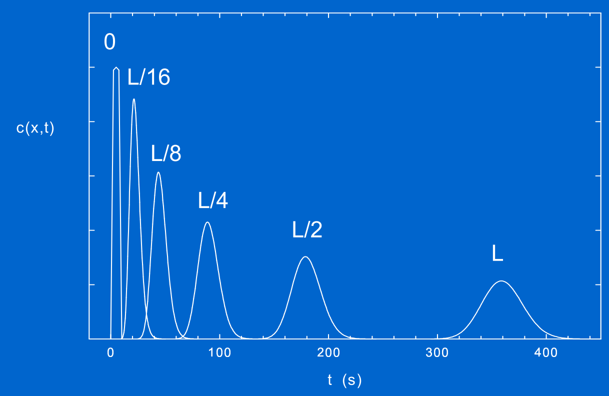
Procesy v koloně:

- **konvekce**
- **axiální disperse**
- **vnější difuse**
- **vnitřní difuse**
- **adsorpce**

Chromatographic method



Chromatographic method



Chromatographic method

Měření

různé rychlosti nosného plynu

různé páry: nosný plyn/ stopovací plyn

Vyhodnocení

momenty odezvových peaků (retenční čas, disperse)

fitování v časové doméně

$<r>\psi$, ψ

Peak moments

$$\mu_1' = \frac{\int_0^\infty tc(t)dt}{\int_0^\infty c(t)dt}$$ first absolute moment

"retention time"

$$\mu_ě = \frac{\int_0^\infty (t-\mu_1')^2 c(t)dt}{\int_0^\infty c(t)dt}$$ second central moment

"variance", σ^2

Peak moments

$$m_0 = \int_0^\infty c(t)dt$$

$$m_1 = \int_0^\infty tc(t)dt$$

$$m_2 = \int_0^\infty t^2c(t)dt$$

$$\mu_1' = \frac{m_1}{m_0} \qquad \mu_2' = \frac{m_2}{m_0} \qquad \mu_2 = \frac{m_2}{m_0} - \left(\frac{m_1}{m_0}\right)^2$$

Peak moments

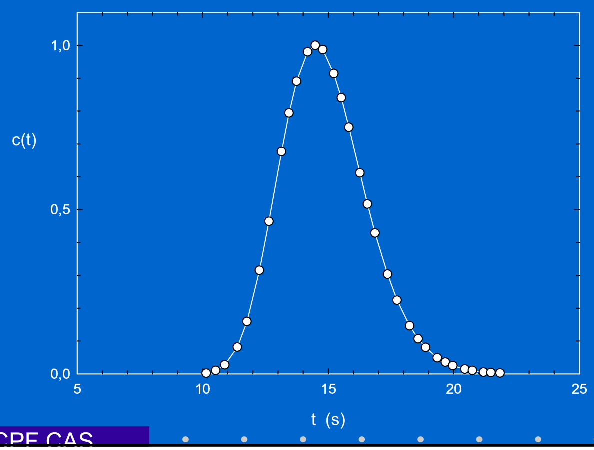
$m_o = 4.16$

$m_1 = 61.92$ (s)

$m_2 = 932.8$ (s^2)

$\mu_1' = 14.87$ (s)

$\mu_2 = 2.88$ (s^2)



Chromatographic method

$$\mu_1' = t_c(1+\delta_o) \qquad \delta_o = \gamma(1+K_T) \qquad t_c = \frac{L}{v}$$

$$\mu_2 = 2t_c\left[\frac{t_c}{Pe}(1+\delta_o)^2 + \delta_1\right] \qquad \delta_1 = \frac{R^2\beta}{D_{TC}}\frac{\delta_0^2}{\gamma}\frac{1}{15}$$

$$\frac{1}{D_{TC}} = \frac{1}{\langle r\rangle\psi\mathcal{K}_T} + \frac{1}{\psi\mathcal{D}_{TC}^m}$$

Momentová metoda
Sypané lože
odezva na impuls

- L délka náplně
- v intersticiální rychlost nosného plynu
- α mezerovitost lože
- β porozita částice
- γ $=(1-\alpha)\beta/\alpha$
- K_T rovnovážná konstanta adsorpce stopovacího plynu
- Pe Pecletovo číslo
- D_{TC} efektivní difuzní koeficient
- $\mathcal{K}_T$ Knudsenův parametr
- $\mathcal{D}_{TC}^m$ bulk difuzní koeficient

Chromatographic method

Axiální disperse

Sypané lože

$Pe = \frac{vL}{E_{TC}}$ Pecletovo číslo

$Bo = \frac{vd}{E_{TC}}$ Bodensteinovo číslo

$Bo = \frac{\gamma}{ReSc} + \frac{\lambda ReSc}{\beta + ReSc}$ $\gamma=0.7;\ \lambda=0.5;\ \beta=20$

$ReSc = \frac{vd\rho}{\mu}\frac{\mu}{\rho\,\mathcal{D}_{TC}^{m}} = \frac{vd}{\mathcal{D}_{TC}^{m}}$

Chromatographic method

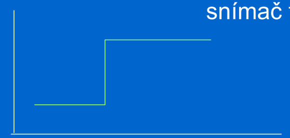
+
- experimentálně snadná
- výsledky průměrované přes mnoho porézních částic
- přesné μ_1' (K_T)

-
- nepřesnost μ_2 (dlouhý ocas peaků)
- více procesů současně (axiální disperse a vnitřní difuse – šířka peaku)
- “mrtvé” objemy; mimokolonové prostory/efekty

Unsteady-state permeation

Neustálená permeace - čistý plyn

tlak v horní cele

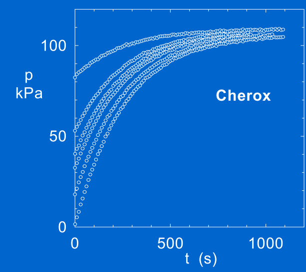


při t = 0 v obou celách stejný tlak (<p_{atmosf})

při t > 0 v horní cele konstantní (atmosferický) tlak

Unsteady-state permeation

Neustálená permeace



řada počátečních tlaků

v horní cele vždy atmosferický tlak

Unsteady-state permeation

Neustálená permeace

Úplné řešení

Látková bilance porézní částice	parc. dif. rov. - c(x,t)
Látková bilance spodní cely	obyč.dif. rov. - p(t)

Unsteady-state permeation

Neustálená permeace

Zjednodušené řešení (zanedbání akumulace v pórech)

Porézní částice	algeb. rov. - $N(t) = f(p_{dolni}(t), p_{horni})$
Látková bilance spodní cely	obyč.dif. rov. - p(t)

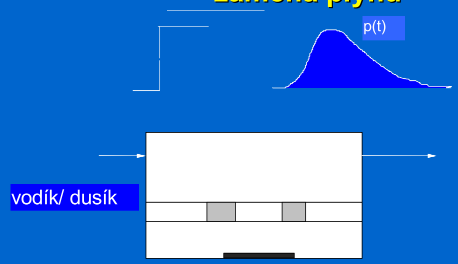
$$N(t)R_g TL = (p_{horni} - p_{dolni}(t))\left[<r> \psi K + \frac{<r^2> \psi}{16\mu}(p_{horni} + p_{dolni}(t)) \right]$$

$$\frac{dp_{dolni}}{dt} = \frac{S}{V_{dolni}} N R_g T$$

Combined transport

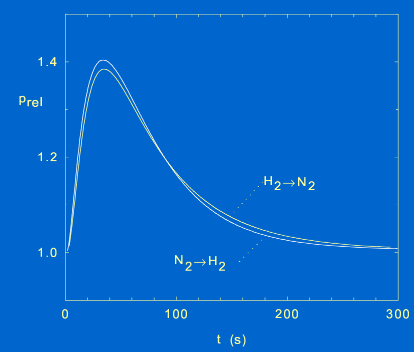
Kombinovaná difuse a permeace

záměna plynu



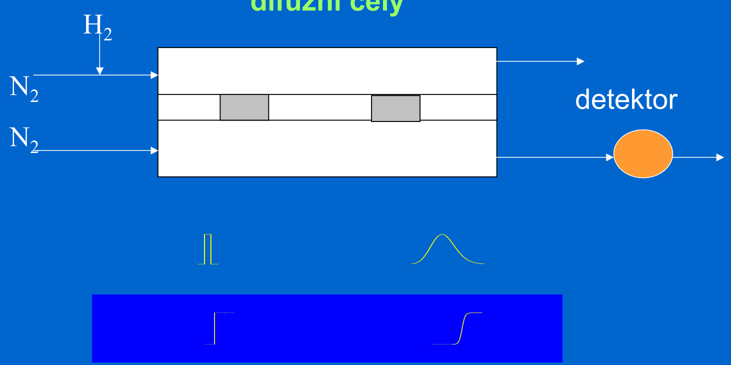
porušení Grahamova zákona, spontání vytvoření gradientu tlaku (přechodný vzrůst/pokles tlaku)

Combined transport



Combined transport

Dynamická modifikace Wicke-Kallenbachovy difuzní cely



Combined transport

měření:
- různé rychlosti průtoku plynů
- různé páry A - B

analýza:
- momenty
- fitování v časové doméně

$\langle r \rangle$, ψ, $\langle r^2 \rangle$

Gas transport in porous solids

END

Chromatographic method