Transport in Porous Solids

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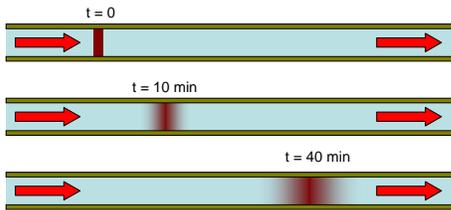

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Mass Transport Modes

1. Convective transport (due to directed bulk flow)
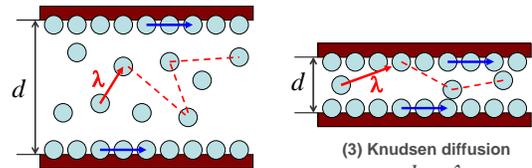2. Diffusive transport (due to random molecular motion).

t = 0

t = 10 min

t = 40 min

Convective pick displacement: $L = vt$
Diffusive pick broadening: $W = (Dt)^{1/2}$

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Diffusion Mechanisms in Porous Solids
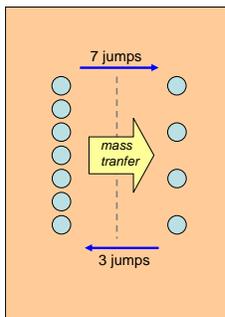
(1) surface diffusion (film flow)

d λ

d λ

(3) Knudsen diffusion
$$d \ll \lambda$$

(2) bulk diffusion (gas or liquid)
$$d \gg \lambda$$

The mean free path $= \dfrac{\text{velocity}}{\text{collision frequency}} \approx \dfrac{v}{r^2 \times v \times \dfrac{N}{V}} = \dfrac{kT}{r^2 p} \approx$ 50 to 100 nm

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Fick Law
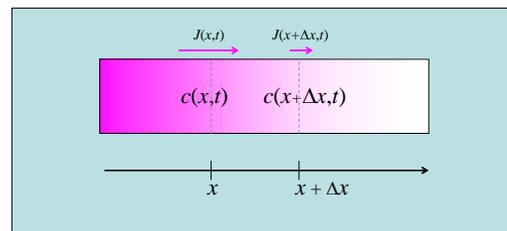
Flux of the *i*-th component

7 jumps

mass tranfer

3 jumps

$$\mathbf{J}_i = n_i(\mathbf{u}_i - \mathbf{u}) = -D_i \nabla n_i$$

Molar flux of the same with respect to a fixed reference:

$$\mathbf{N}_i = n_i \mathbf{u}_i = -D_i \nabla n_i + n_i \mathbf{u}$$

$$= -D_i \nabla n_i + n_i \frac{\sum_j n_j \mathbf{u}_j}{\sum_j n_j}$$

$$= -D_i \nabla n_i + x_i \sum_j \mathbf{N}_j$$

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The Diffusion Equation

$J(x,t)$ $J(x+\Delta x,t)$

$c(x,t)$ $c(x+\Delta x,t)$

x $x + \Delta x$

$$[J(x,t) - J(x+\Delta x,t)]\Delta t = [c(x,t+\Delta t) - c(x,t)]\Delta x$$

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial t^2}$$

An Example of Diffusion Problems
Silicon Release from River Beds

water $c(t)$
L
Si(OH)$_4$
sand sediment
x

SiO$_2$ (*solid*) $\rightarrow$ Si(OH)$_4$ (*solution*)

From: B.V. Zhmud, W.A. House, F.H. Denison, J. Chem. Soc., Faraday Trans. 93 (1997) 3473.

$$\varepsilon \frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2} + kp[c_{sat} - c(x,t)]$$
$$c(x,0) = c_{ini}; \quad c(0,t) = \xi(t)$$
$$c(x,t) = c_{sat} - (c_{sat} - c_{ini})\exp(-kt) + u(x,t)$$
$$u(x,t) = \int_0^t \frac{\partial G}{\partial x}\{[\xi(t-t') - c_{sat}]\exp(-kt') + (c_{sat} - c_{ini})\exp(-kt)\}dt'$$
$$L\xi(t) = p\int_0^\infty \left\{c_{ini} + k\int_0^t [c_{sat} - c(x,t')]dt' - c(x,t)\right\}dx$$

The Richards Equation

flow

Degree of saturation, S,

$$S = \frac{\text{volume of liquid in pores}}{\text{volume of pores}}$$

$$\mathbf{v} = \frac{K}{\eta} B(S)[\rho \mathbf{g} - \nabla p]$$

$$\varepsilon \frac{\partial S}{\partial t} + \nabla \cdot \mathbf{v} = 0$$

$B(S)$ – relative permeability
ε – porosity
p – pressure
η – viscosity
ρ – density

$$\frac{\partial S}{\partial t} = \frac{K}{\varepsilon \eta}\left\{ B(S)\nabla^2 p - [\rho \mathbf{g} - \nabla p]\cdot \nabla B(S) \right\}$$

Relationship between B(S) and p

Higher vapor pressure $\Rightarrow$ More capillary condensate $\Rightarrow$ Lower pore permeability

$$B(S) = B(S(p))$$

saturation depends on vapour pressure

$$\nabla B(S) = \frac{dB}{dS}\frac{dS}{dp}\nabla p$$

permeability depends on saturation

$$\frac{\partial S}{\partial t} = \frac{dS}{dp}\frac{\partial p}{\partial t}$$

$$\frac{\partial p}{\partial t} = F_1(p)\nabla^2 p + F_2(p)(\nabla p)^2$$

Instant equilibration between vapor and condensate is implied!

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Condensation of Liquid in Pores

$$V_{tot} = n(r_1)V(r_1) + n(r_2)V(r_2) + \ldots + n(r_N)V(r_N)$$
$$= \int d(nV)] = \int \frac{d(nV)}{dr}dr = \int_{r_{min}}^{r_{max}} \Omega(r)dr$$

$$W = \underbrace{\frac{2\gamma}{r}}_{\substack{\text{pressure}}} \times \underbrace{S}_{\substack{\text{cross-}\\ \text{section}}} \times \underbrace{\frac{V_M}{S}}_{\substack{\text{distance}}} = \frac{2\gamma V_M}{r}$$

p — capillary force — r

$$W = \int p\,dV = -\int V\,dp$$
$$= -RT\int_{p_0}^p \frac{dp}{p} = -RT\ln\frac{p}{p_0}$$

$$r = \frac{2\gamma V_M}{RT\ln(p_0/p)}$$

$\Omega(r)$
$r(p)$

Diffusion in a Ternary Gas Mixture

CO$_2$

bulb 1
N$_2$ and CO$_2$

bulb 2
H$_2$ and N$_2$

H$_2$

H$_2$ (Duncan and Toor, 1962)
bulb 2
bulb 1

N$_2$ (Duncan and Toor, 1962)
bulb 2
bulb 1

The Maxwell-Stefan Formalism

The main lesson learnt from the Duncan & Toor experiment:
The transfer of nitrogen occurs even though there's no concentation gradient.

bulb 2   bulb 1

As H$_2$ diffuses faster than CO$_2$, pressure builds up in bulb 1, forcing N$_2$ out:

$$V_{N_2}\frac{dp_{N_2}}{dx} = \frac{n_{N_2}RT}{p_{N_2}}\frac{dp_{N_2}}{dx} = n_{N_2}\frac{d\mu_{N_2}}{dx}$$

The flows of H$_2$ and CO$_2$ "push" N$_2$ molecules, e.g.

$$F_{by\,H_2} = \frac{RT}{D_{N_2\ldots H_2}}n_{N_2}n_{H_2}(u_{H_2} - u_{N_2})$$

$$-\frac{d\mu_{N_2}}{dx} = RT \times \left\{ \frac{n_{H_2}(u_{N_2} - u_{H_2})}{D_{N_2\ldots H_2}} + \frac{n_{CO_2}(u_{N_2} - u_{CO_2})}{D_{N_2\ldots CO_2}} \right\}$$

The Maxwell-Stefan Formalism
Multicomponent Mixtures

$$-\frac{d\mu_i}{dx} = \sum_{j\neq i} \frac{RT}{D_{ij}} n_j(u_i - u_j), \quad (i=1,2,...,N)$$

$$-n_i\frac{d\mu_i}{dx} = RT\sum_{j\neq i}\frac{n_i n_j(u_i - u_j)}{D_{ij}} = RT\sum_{j\neq i}\frac{n_j J_i - n_i J_j}{D_{ij}}$$

$$\boxed{-\frac{n_i}{RT}\nabla\mu_i = \sum_{j\neq i}\frac{n_j \mathbf{J}_i - n_i \mathbf{J}_j}{D_{ij}}}$$

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Generalization of the Fick Law

$$-\frac{n_i}{RT}\nabla\mu_i = -\frac{n_i}{RT}\nabla(RT\ln n_i) = -\nabla n_i$$

$$\begin{pmatrix}\mathbf{J}_1\\ \mathbf{J}_2\\ .\\ .\\ \mathbf{J}_N\end{pmatrix} = -\begin{pmatrix}D_{11} & D_{12} & ... & D_{1N}\\ D_{21} & D_{22} & ... & D_{2N}\\ . & . & ... & .\\ . & . & ... & .\\ D_{N1} & D_{N2} & ... & D_{NN}\end{pmatrix}\begin{pmatrix}\nabla n_1\\ \nabla n_2\\ .\\ .\\ \nabla n_N\end{pmatrix}$$

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The Dusty Gas Model

Interactions involved:

$u_3 = 0$

$$-\frac{1}{RT}\nabla p_i = \sum_j \frac{x_j\mathbf{N}_i - x_i\mathbf{N}_j}{D_{ij}^{eff}} + \frac{\mathbf{N}_i}{D_i^K}$$

(underbrace: interactions with other gas molecules) (underbrace: interaction with "dust")

The effective binary pair diffusion coefficients:

$$D_{ij}^{eff} \approx \varphi D_{ij}$$

The Knudsen diffusion coefficients

$$D_i^K \approx \varphi\frac{2r}{3}\left(\frac{8RT}{\pi M_i}\right)^{1/2}$$

The porous matrix is considered as a gigant immobile macromolecule (dust).

One More Generalization

$$\underbrace{-\frac{c_i}{RT}(\nabla\mu_i + V_i\nabla p)}_{\substack{\text{diffusive flow due to differences}\\\text{in chemical potentials}}} \quad \underbrace{-\alpha_i c_i\frac{B}{\eta D_i}\nabla p}_{\substack{\text{viscous flow}\\\text{due to pressure gradient}}} \quad \underbrace{-c_i z_i\frac{F}{RT}\nabla\psi}_{\substack{\text{electroosmotic flow}\\\text{due to potential difference}}}$$

DRIVING FORCES

$$= \underbrace{\sum_j\frac{x_j\mathbf{N}_i - x_i\mathbf{N}_j}{D_{ij}^{eff}}}_{\substack{\text{"friction" between}\\\text{individual fluxes}}} \quad + \quad \underbrace{\frac{\mathbf{N}_i}{D_i^{eff}}}_{\substack{\text{friction with}\\\text{porous matrix}}}$$

RESISTING FORCES

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The Principle of Chromatography

Adsorption-desorption processes:

flow

$t = t_0$
$t = t_1$
$t = t_2$
$t = t_3$

c
x
flow

"Blue" species have lower adsorptivity, hence they stay more time in solution, moving downstream faster.

"Red" species have higher adsorptivity, hence they spend more time fixed to the surface, lagging behind the "blue" species in their downstream motion.

Eddy Diffusion

$$\frac{\partial c(\mathbf{r},t)}{\partial t} + \underbrace{\mathbf{v}\cdot\nabla c(\mathbf{r},t)}_{\text{convection}} = \underbrace{D\nabla^2 c(\mathbf{r},t)}_{\text{diffusion}} + \underbrace{s(\mathbf{r},t)}_{\text{source}}$$

$t = t_0$
$t = t_1$
$t = t_2$
$t = t_3$

c
x
flow

$t = t_0$
$t = t_1$
$t = t_2$
$t = t_3$

c
x
flow

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3

Surfactant - Induced Percolation
Rise Of Surfactant Solution in Hydrophobic Capillaries

The governing equations:

$$\begin{cases} \rho[zz''+(z')^2] = \dfrac{2}{r}f(t) - \dfrac{8}{r^2}\eta zz' - \rho g z \\[2mm] \dfrac{\partial c}{\partial t} = D\dfrac{\partial^2 c}{\partial \zeta^2} - z'\dfrac{\partial c}{\partial \zeta} \quad (0<\zeta<z) \end{cases}$$

η - viscosity
ρ - density
g - acceleration of gravity
$f(t)$ - capillary force

Plus the boundary and initial conditions, e.g.

$$z(0) = 0$$
$$c(0,t) = c_b$$
$$c(z,t) = F^{-1} \circ \Gamma_{lv}(t) \quad \text{etc.}$$

Surfactant - Induced Percolation
Diffusion-Limited Imbibition of Surfactant Solutions

The surfactant concentration gradient near the *lv* interface:

$$\left. \frac{\partial c}{\partial \zeta}\right|_{\zeta=z(t)} \cong -\frac{c_b}{\sqrt{Dt}}$$

Mass conservation:

$$\underbrace{2\pi r \Gamma_{ls}^m dz}_{\substack{\text{amount} \\ \text{adsorbed} \\ \text{to the wall}}} = \underbrace{\pi r^2 D \frac{c_b}{\sqrt{Dt}} dt}_{\substack{\text{amount transported} \\ \text{to the lv interface}}}$$

$$z(t) \cong \frac{r c_b}{\Gamma_{ls}^m}\sqrt{Dt}$$

(F. Tiberg, B. Zhmud, K. Hallstensson, M. von Bahr, Phys. Chem. Chem. Phys., 2 (2000) 5189)

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Fractal Approach to Percolation

percolation clusters

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Percolation Limit

$p = 0.40$ $p = 0.60$ $p = 0.80$

- Connectivity increases with increasing the fraction of filled sites.
- There is a critical site density needed for an interconnected network known as the spanning cluster to form (p_c = 0.5928, D = 1.89)
- Permeability is related to connectivity and density of "pore space".

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Gradient Percolation

low occupancy zone ($p < p_c$) the majority of pores are empty

advancing liquid front ($p = p_c$)

high occupancy zone ($p > p_c$) the majority of pores are filled by liquid

For N random jumps (length a) over the nodes of a square lattice,

$$\langle x^2(N)\rangle = a^2 N = 2Dt_N$$

$$p(x,t) = 1 - \frac{2}{\sqrt{\pi}}\int_0^{x/\sqrt{4Dt}} \exp(-u^2)\,du$$

$p(x,t) = p_c$ defines the front dynamics

Percolation with Displacement

Percolation resulting in displacement of white fluid by black fluid on a 100x200 cell lattice. (J. Fader, Fractals, Plenum, NY, 1988).

- The regular diffusion theory allows some water to penetrate to the right border at an infinite speed.
- The percolation theory limits the penetration speed to the propagation of the "critical probability" front. Each cell is either empty (0) or filled (1), it cannot be filled by, say, 10 or 90%. There remain a number of "white islands".
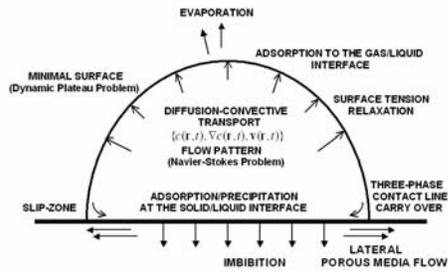
Enhanced Oil Recovery
(Displacement of Oil by Gas)
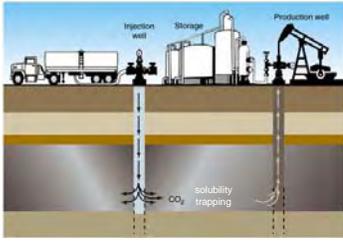
- CO_2 is mixed with oil, and, once dissolved, causes the oil to swell. Thereby, reservoir pressure is restored and oil is rendered less viscous.
- 5 to 20% more oil can be recovered.
- In the USA, during 1998 alone, a total of 43 million tons CO_2 were injected at over 65 EOR sites.

Claus Process
For Sulfur Recovery after Catalytic Desulfurization Process
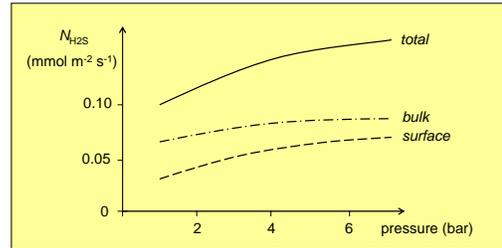
Transport Processes Occurring
while Drying an Inkjet Ink Drop on Paper

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