VIII. Fick's law of diffusion

IX. Unsteady and Multivariate diffusion

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Mass Transfer

~~XXI.XXX~~ IX. Unsteady and Multivariate Diffusion

A. Conditions for analogy between unsteady diffusion and unsteady conduction
(cf. BSL Table ~~19~~ 20.0-1)

If:

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... then tabulated solutions unsteady and multivariate heat conduction apply to unsteady diffusion processes

1. **Note**: principles for "extending 1D solutions" apply as well

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Principles for dealing with "complex" problems apply, too.

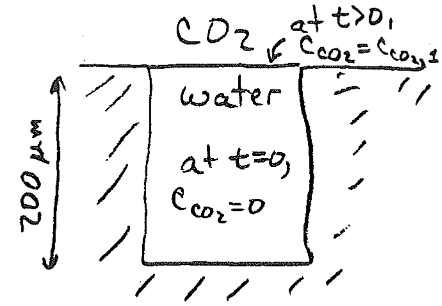
B. correspondence between variables in conduction and diffusion processes

heat conduction	diffusion

C. examples

Examples of Unsteady Diffusion

1\. Diffusion of CO_2 into water-filled pore.



How long until water at wall at far end of pore is 90% saturated with CO_2 (i.e., $C_{CO_2} = 0.9\, C_{CO_2,1}$ at far wall).

Assume CO_2 is "dilute" in aqueous solution. Ignore possible reactions with rock. Assume $\mathcal{D}_{CO_2,H_2O} = \text{const.} \cong 2 \cdot 10^{-10}\ m^2/s$

<u>Solution:</u> no-flux condition at far wall is equivalent to an insulated boundary in heat conduction. Thus the geometry is equivalent to a 400 μm-wide slab exposed to CO_2 on both sides. $b = 200\,\mu m = 2 \cdot 10^{-4}$ m. We want time for

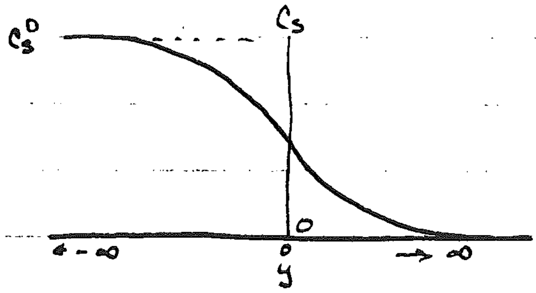
$$\frac{C_{CO_2} - C_{CO_2,0}}{C_{CO_2,1} - C_{CO_2,0}} = \frac{C_{CO_2}}{C_{CO_2,1}} = 0.9 \longleftrightarrow \frac{T - T_0}{T_1 - T_0} = 0.9 \text{ at } y/b = 0.$$

From Fig 12.1-1, $\frac{\alpha t}{b^2} \approx 1.0 \leftrightarrow \frac{\mathcal{D} t}{b^2} = 1.0$

$b = 200$ sec.

2\. Diffusion between semi-infinite blocks.

Identical porous media, one saturated with dilute brine, one with pure water, are brought into contact. There is diffusion of salt, but no bulk flow. Assume $\mathcal{D}_s \approx 5 \cdot 10^{-10}\ m^2/s$.



a) How far into saline block has C_s fallen to $0.9\, C_s^0$ after 1 day?

Want $\frac{C_s - C_{sb}}{C_{sf} - C_{sb}} = \frac{0.9\, C_s^0 - 0}{C_s^0 - 0} = 0.9$. From figure for unsteady conduction between semi-infinite blocks in contact,

$$y/\sqrt{4\alpha t} \leftrightarrow \frac{y}{\sqrt{4\mathcal{D}t}} \cong 0.92 \rightarrow y = (0.92)\left[(4)(5 \cdot 10^{-10})(8.64 \cdot 10^4)\right]^{1/2} = 0.012\ m$$

b) what is molar flux at $y=0$ after 1 day?

(Need value for C_{so}; say $C_S^0 = 0.17$ Kgmole/m^3 (~1% by wt))

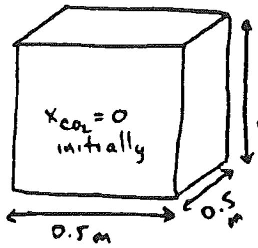
Eq. 12.1-10: $q = \frac{k}{\sqrt{\pi \alpha t}}(T_1 - T_0) \rightarrow \frac{q}{\rho C_p} = \frac{\alpha}{\sqrt{\pi \alpha t}}(T_1 - T_0)$

$\Leftrightarrow N_A = \frac{\mathcal{D}}{\sqrt{\pi \mathcal{D} t}}(C_{s1} - C_{so})$; now here $C_{s1} = C_s$ at surface, while C_{so} is initial concentration; thus $(C_{s1} - C_{so}) = \frac{1}{2} C_S^0$.

$N_A = \frac{\mathcal{D}}{\sqrt{\pi \mathcal{D} t}}(\frac{1}{2} C_S^0) \rightarrow N_A = 3.65 \cdot 10^{-9}$ Kgmol / (m^2 s)

3. A fractured reservoir has matrix blocks, roughly cubical, 0.5 m on each side. CO_2 is injected into the field and quickly fills the fractures. Thus at time t=0 the oil at the surfaces of the fractures absorbs a mole fraction $x_{CO_2}^0$, in equilibrium with the surrounding CO_2, while the mole fraction of CO_2 in the oil within the matrix blocks is initially zero. Assuming simplified Fick's ~~second~~ law applies to the diffusion process and that the diffusion coefficient for CO_2 in oil is 2×10^{-9} m^2/s, estimate the time required for the mole fraction of CO_2 in the oil at the center of the block to reach 75% of $x_{CO_2}^0$.

at $t \geq 0$, $x_{CO_2} = x_{CO_2}^0$ on all surfaces



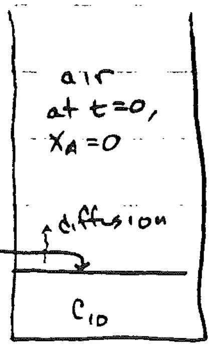
A product-method solution for 3 finite-width slabs; since the sides are equal, $(x_{CO_2}^0 - x_{CO_2})/(x_{CO_2}^0 - 0)$ = the cube of the value for one finite-width slab. Since we want $(x_{CO_2}^0 - x_{CO_2})/(x_{CO_2}^0) = 0.25$ for the block, we seek t for $(x_{CO_2}^0 - x_{CO_2})/(x_{CO_2}^0) = (0.25)^{1/3}$ for a slab. $(0.25)^{1/3} = 0.63$.

From Figure 12.1-1, for $y/b = 0$, $(T_1 - T)/(T_1 - T_0) = 0.63$, $\alpha t/b^2 \Leftrightarrow \mathcal{D}_{AB} t/b^2 \approx$ 0.28. (Reading the chart precisely is difficult.) $(2 \cdot 10^{-9}) t / ((0.25)^2 = 0.28$.

$t = 8.75 \cdot 10^6$ s $= 2{,}430$ hr $= 101$ days.

4. A tall beaker is suddenly partially filled with decane. Predict mole fraction in air above liquid as function of time. Since decane is not volatile, assume $x_A \approx 0$ and simplified Fick's ~~second~~ law applies. This is in essence an unsteady version of BSL Sect. 18.2. For short times (before x_A rises significantly at top of beaker), this problem matches semi-infinite slab. BSL Sect. 20.1 examines case of $x_A >> 0$.

$t > 0$, $x_A = x_A^0$



X. Mass-transfer coefficients

A. review of effects of turbulence

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B. Mass transfer in tubes

1. definition of mass-transfer coefficient $k_{x,ln}$

Methods described here apply only if mass transfer rates are "low" and "simplified Fick's law" applies. In that case, BSL Eq. 22.2-1 (or 22.1-5 or 8)

(cf. eq. 14.1-4 for heat transfer)

Note: C_{A0} is C_A *in fluid next to wall* (typically in equilibrium with solid at wall), not C_A in solid wall itself

2. **mass-conservation equation** (Eq. "IIm")

(similar to "eq. II" in notes on heat transfer in tubes; derivation is similar)

Combine eqs. "Im" and "IIm" to derive Eq. "IIIm"

3. analogy between heat- and mass-transfer coefficients in tubes

For cases in which "simplified Fick's law" applies to mass transfer in tubes, one can use the correlations for heat transfer after making the following substitutions:

heat transfer	mass transfer

(cf. BSL Table ~~21.1-2~~ 22.2-1)

4. using correlations for mass-transfer coefficients in tubes

First question: Are concentration and rate of mass transfer low?
(If no, need microscopic balance.)
If yes, proceed . . .

Second question: What is Re?

Re < 2100

a) Is wall concentration us roughly uniform?
- no - use differential equation for c_A with $k_{x,loc}$
- yes - continue - find $k_{x,ln}$

b) Re Sc D/L >> 10? (Or $[(c_{A02}-c_{Ab2})/(c_{A01}-c_{Ab1})] > 0.2$?)
(in other words, is c_A relatively far from equilibrium at outlet?)
- yes: then can solve in any of 3 ways:
  - use Fig 14.3-2;
  - Eq. 14.3-17 & Eq. "IIIm;"
  - Fig. 14.2-1 "const. wall T (tube)" and Eq. "IIIm"
- no: can use only Fig. 14.2-1 "const. wall T (tube)" & Eq "IIIm"

Re > 2100

Use Fig. 14.3-2 (unless Re > 100,000 and goes off chart)

If Re > 20,000 can also use Eq. 14.3-16 with Eq. "IIIm"

Note: if $c_{A01}=c_{A02}+c_{A0}$, then
$(c_{Ab2}-c_{Ab1})/(c_{A0}-c_{Ab})\ln = \ln[(c_{A0}-c_{Ab1})/(c_{A0}-c_{Ab2})]$

Noncircular Tubes: Use "Hydraulic Radius" Approximation
Substitute $4R_h = 4\ (S/Z)$ for D
Calculate <v> for given tube shape
Calculate $k_{x,ln}$ or c_A as for circular tube
- VALID ONLY FOR TURBULENT FLOW

Note:

$Pr \equiv C_p\mu/k$	$\rightarrow$	$Sc \equiv \mu/\rho D_{AB}$
$Nu_{ln} \equiv h_{ln}D/k$	$\rightarrow$	$Nu_{AB,ln} \equiv k_{x,ln}D/c\mathcal{D}_{AB}$
T, T_o, T_{b1}, etc.	$\rightarrow$	c_A, c_{A0}, c_{Ab1}, etc. (or x_A, x_{A0}, x_{Ab1}, etc. if in dimensionless ratios) (for dilute liquid solutions, $c_A = c\ x_A$)

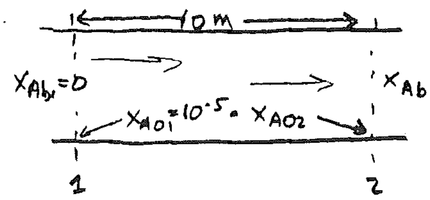
Note: can apply to convective mass transfer inside tubes with diffusion through cylindrical layers using analog equations to convective heat transfer inside tubes with conduction through cylindrical layers (equations in BSL section 10.6)

5. Examples

example of mass transfer in tubes

Fresh water enters a pipe. I.D. = 1 inch = 0.0254 m. $\langle V \rangle \approx 0.3$ m/s.
Mineral "A" dissolves from pipe wall in low concentration.
Assume liquid properties $\mathcal{D}_{AW} = 2\cdot10^{-9}$ m²/s, $\rho = 1000$ kg/m³, $\mu = 0.001$ Pa s, all constant. Assume solute is at equilibrium solubility, $x_{A0} \approx 10^{-5}$, at wall. x_{Ab1} = inlet bulk conc., = 0.

What is mole fraction of A 10 m down length of pipe?



1) Is analogy to heat transfer OK?
Yes - solute is dilute, therefore rate of mass transfer must be low.

2) Which correlation to use?

First check $Re = \frac{DV\rho}{\mu} = \frac{(0.0254)(0.3)(1000)}{0.001} = 7620$

Cannot use Eq. 14.3-16 because Re < 20,000
" 14.3-17 " Re > 2100
" Fig 14.2-1 " Re > 2100

Can use Fig 14.3-2. From this figure, for Re = 7620,

$$\frac{T_{b2}-T_{b1}}{(T_0-T_b)_{ln}}\frac{D}{4L}(Pr)^{2/3}\left(\frac{\mu_b}{\mu_0}\right)^{-0.14} = 0.004 \rightarrow \frac{x_{Ab2}-x_{Ab1}}{(x_0-x_b)_{ln}}\frac{D}{4L}(Sc)^{2/3}\left(\frac{\mu_b}{\mu_0}\right)^{-0.14} = 0.004$$

$$Sc = \frac{\mu}{\rho\mathcal{D}_{AB}} = \frac{0.001}{(1000)(2\cdot10^{-9})} = 500, \quad \frac{\mu_b}{\mu_0} = 1, \quad \frac{D}{4L} = \frac{0.0254}{4(10)} = 6.35\cdot10^{-4}, \rightarrow \frac{x_{Ab2}-x_{Ab1}}{(x_0-x_b)_{ln}} = 0.100$$

Now since $x_{A01} = x_{A02}$,

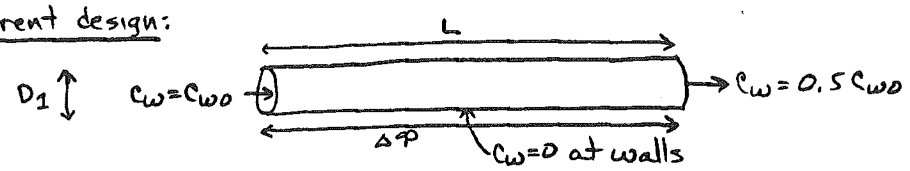
$$\frac{x_{Ab2}-x_{Ab1}}{\left[\frac{(x_{A01}-x_{Ab1})-(x_{A02}-x_{Ab2})}{\ln[(x_{A01}-x_{Ab1})/(x_{A02}-x_{Ab2})]}\right]} = \frac{x_{Ab2}-x_{Ab1}}{\left[\frac{x_{Ab2}-x_{A01}}{\ln[(x_{A01}-x_{Ab1})/(x_{A02}-x_{Ab2})]}\right]} = \ln\left(\frac{x_{A01}-x_{Ab2}}{x_{A02}-x_{Ab2}}\right)$$

$$\therefore\ 0.100 = \ln\left(\frac{x_{A0}-0}{x_{A0}-x_{Ab2}}\right) \rightarrow x_{Ab2} = 0.095\, x_{A0} = (0.095)\cdot10^{-5}$$

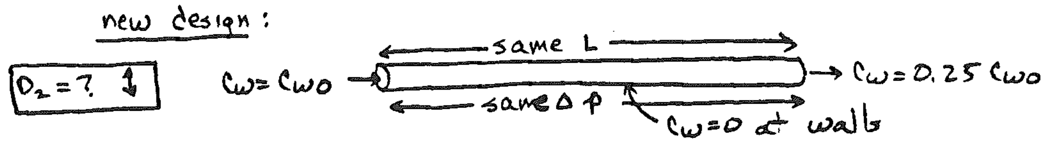
In a length of 10 m, the bulk concentration has only come 10% of the way to equilibrium. One reason is $\mathcal{D}_{AB}$ is often much smaller than α in heat-transfer problems. Also, mass-transfer is much swifter when the diameter is narrower, as in rock pores (modeled as narrow tubes).

An engineer is injecting a solution containing a toxic waste into narrow tubes of diameter D_1 and length L, from which the toxic waste is removed at the walls. That is, the concentration of the waste c_W is c_{W0} at the entrance of the tubes, and is ($0.5\ c_{W0}$) at the exit of the tubes. (At the tube walls, $c_W=0$.) The engineer needs to reduce c_W at the exit to $0.25\ c_W$, and he can change only the diameter of the tubes, not their length. He does know that the fluid is in laminar flow through the tubes and is flowing with a fixed $\Delta\mathcal{P}$. What new value of tube diameter D_2 would be required to achieve the desired value of c_W at the tube outlet?

current design:



new design:



In the original experiment laminar flow applied. Since $\Delta\mathcal{P}$ is fixed, and $v \sim R^2$ in laminar flow, $Re = Dv\rho/\mu \sim D\,D^2 \approx D^3$; thus as D decreases Re decreases and laminar flow still applies.

For laminar flow one next asks whether $(c_{wb2} - c_{wo})/(c_{wb1} - c_{wo}) > 0.2$; in the first experiment, this ratio is 0.5, and the new design gives a ratio of 0.25; this the inequality is satisfied.

There fore there are 3 potential ways to solve the problem: Fig ~~[illegible]~~ 14.3-2, Fig ~~[illegible]~~ 14.2-1, and Eq ~~[illegible]~~ 14.3-17. We can't use Figure ~~[illegible]~~ 14.3-2, because we don't know the actual value of Re (and it may be off the chart). Eq. ~~[illegible]~~ 14.3-17 gives

$$Nu_{AB} = 1.86\,(Re\,Sc\,D/L)^{1/3}(\mu_b/\mu_0)^{0.14}$$

← transport" law"; still need conservation eq.

where we ignore the viscosity term. "Eq. IIIm" gives

$$Nu_{AB} = \frac{c_{Ab2} - c_{Ab1}}{(c_{A0} - c_{Ab})_{ln}} \frac{D^2}{4L\mathcal{D}_{AB}} \langle v \rangle = 1.86\,(Re\,Sc\,D/L)^{1/3}$$

For this case, in which $c_{A0} = 0 =$ uniform, $\frac{c_{Ab2} - c_{Ab1}}{(c_{A0} - c_{Ab})_{ln}} = \ln \frac{c_{A0} - c_{Ab1}}{c_{A0} - c_{Ab2}} = \ln \frac{0 - c_{wo}}{0 - 0.5 c_{wo}}$ $= \ln 2$ for the new design, this term is $\ln 4$.

Combining the two equations gives

$$1.86\,(Re\,Sc\,D/L)^{1/3} = \ln\left(\frac{c_{A0} - c_{Ab1}}{c_{A0} - c_{Ab2}}\right) \frac{D^2}{4L\mathcal{D}_{AB}} \langle v \rangle$$

or $$\ln\left(\frac{c_{A0} - c_{Ab1}}{c_{A0} - c_{Ab2}}\right) = \frac{1.86\,(Re\,Sc\,D/L)^{1/3}}{D^2 \langle v \rangle / (4L\mathcal{D}_{AB})}$$

Since fluid properties and L are fixed,

$$\ln\left(\frac{c_{A0} - c_{Ab1}}{c_{A0} - c_{Ab2}}\right) \sim (Re\,D)^{1/3} / [D^2 \langle v \rangle] \sim [D^3 D]^{1/3} / [D^2 D^2] \sim (D^4)^{-2/3} \sim D^{-8/3}$$

Since the left size is to be changed from $\ln 2$ to $\ln 4$,

$$\frac{\ln 2}{\ln 4} = \frac{(D_1)^{-8/3}}{(D_2)^{-8/3}} = \left(\frac{D_1}{D_2}\right)^{-8/3}; \quad \left(\frac{D_1}{D_2}\right) = \left(\frac{\ln 2}{\ln 4}\right)^{-3/8} = (0.5)^{-3/8} = 1.30$$

$D_2 = (D_1)(0.771)$.