DIFFUSION IN LIQUIDS AND IN SOLIDS

Diffusion coefficient, D_{AB}

Introduction:

- Fick's law proportionality, D_{AB} , is known as mass diffusivity (simply as diffusivity) or as the diffusion coefficient.
- Diffusivity depends on pressure, temperature, and composition of the system.
- Units: Diffusivity is normally reported in cm^2/s; the SI unit being m^2/s.
- Similar to Kinematic viscosity and thermal diffusivity

Diffusion coefficients for liquids

There are different approaches:

1. Experimental determination of diffusivity
2. Experimental liquid diffusivity data (Table 6.3-1)
3. Predictian of diffusivity in liquids
   A) Stokes- Einstein equation
   B) Wilke-Chang equation

See next slide

TABLE 6.3-1. *Diffusion Coefficients for Dilute Liquid Solutions*

Solute	Solvent	Temperature °C	Temperature K	Diffusivity [$(m^2/s)10^9$ or $(cm^2/s)10^5$]
NH_3	Water	12	285	1.64
		15	288	1.77
O_2	Water	18	291	1.98
		25	298	2.41
CO_2	Water	25	298	2.00
H_2	Water	25	298	4.8
Methyl alcohol	Water	15	288	1.26
Ethyl alcohol	Water	10	283	0.84
		25	298	1.24
n-Propyl alcohol	Water	15	288	0.87
Formic acid	Water	25	298	1.52
Acetic acid	Water	9.7	282.7	0.769
		25	298	1.26
Propionic acid	Water	25	298	1.01
HCl (9 g mol/liter)	Water	10	283	3.3
(2.5 g mol/liter)		10	283	2.5
Benzoic acid	Water	25	298	1.21
Acetone	Water	25	298	1.28
Acetic acid	Benzene	25	298	2.09
Urea	Ethanol	12	285	0.54
Water	Ethanol	25	298	1.13
KCl	Water	25	298	1.870
KCl	Ethylene glycol	25	298	0.119

For very large spherical molecules (A) of 1000 molecular weight or greater diffusing in a liquid solvent (B) of small molecules:

Stokes-Einstein Equation:

$$D_{AB} = \frac{9.96 \times 10^{-16}\, T}{\mu\, V_A^{1/3}}$$

applicable for biological solutes such as proteins

D_{AB} - diffusivity in m^2/s
T - temperature in K
μ - viscosity of solution in kg/m.s
V_A - solute molar volume at its normal boiling point in m^3/kg mol

D_{AB} is proportional to $1/\mu$ and T

TABLE 6.3-2. *Atomic and Molar Volumes at the Normal Boiling Point*

Material	*Atomic Volume* $(m^3/kg\ mol)\ 10^3$	*Material*	*Atomic Volume* $(m^3/kg\ mol)\ 10^3$
C	14.8	Ring, 3-membered as in ethylene oxide	−6
H	3.7		
O (except as below)	7.4		
Doubly bound as carbonyl	7.4	4-membered	−8.5
		5-membered	−11.5
Coupled to two other elements		6-membered	−15
		Naphthalene ring	−30
In aldehydes, ketones	7.4	Anthracene ring	−47.5
In methyl esters	9.1		
In methyl ethers	9.9		
In ethyl esters	9.9		*Molecular Volume* $(m^3/kg\ mol)\ 10^3$
In ethyl ethers	9.9		
In higher esters	11.0		
In higher ethers	11.0	Air	29.9
In acids (—OH)	12.0	O_2	25.6
Joined to S, P, N	8.3	N_2	31.2
N		Br_2	53.2
Doubly bonded	15.6	Cl_2	48.4
In primary amines	10.5	CO	30.7
In secondary amines	12.0	CO_2	34.0
Br	27.0	H_2	14.3
Cl in RCHClR'	24.6	H_2O	18.8
Cl in RCl (terminal)	21.6	H_2S	32.9
F	8.7	NH_3	25.8
I	37.0	NO	23.6
S	25.6	N_2O	36.4
P	27.0	SO_2	44.8

Source: G. Le Bas, *The Molecular Volumes of Liquid Chemical Compounds*, New York: David McKay Co., Inc., 1915.

For smaller molecules (A) diffusing in a dilute liquid solution of solvent (B):

Wilke-Chang:

$$D_{AB} = \frac{1.173 \times 10^{-16} (\Phi M_B)^{1/2} T}{\mu_B V_A^{0.6}}$$

applicable for biological solutes

D_{AB} - diffusivity in m^2/s

M_B - molecular weight of solvent B

T - temperature in K

μ_B - viscosity of solvent B in kg/m.s

V_A - solute molar volume at its normal boiling point in m^3/kg mol

Φ - association parameter of the solvent, which is:

2.6 for water, 1.9 for methanol, 1.5 for ethanol, …

D_{AB} is proportional to $1/\mu_B$ and T

Example

Predict the diffusion coefficient of acetone CH_3COCH_3 in water at 25°C and 50°C using the Wilke-Chang equation. Compare with the experimental value of 1.28×10^{-9} m²/s at 298 K.

Solution:

From Appendix A.2, the viscosity of water at 25°C is $\mu_B = 0.8937 \times 10^{-3}$ Pa s and at 50°C is 0.5494×10^{-3} Pa s. From Table 6.3-2 for CH_3COCH_3 with 3 carbons + 6 hydrogens + 1 oxygen:

$$V_A = 3(0.0148) + 6(0.0037) + 1(0.0074) = 0.0740 \text{ m}^3/\text{kg mol}$$

For the water, association parameter $\Phi = 2.6$ and $M_B = 18.02$ kg mass/kg mol.

For 25°C:

$$D_{AB} = (1.173 \times 10^{-16})(\varphi M_B)^{1/2} \frac{T}{\mu_B V_A^{0.6}}$$

$$= \frac{(1.173 \times 10^{-16})(2.6 \times 18.02)^{1/2}(298)}{(0.8937 \times 10^{-3})(0.0740)^{0.6}}$$

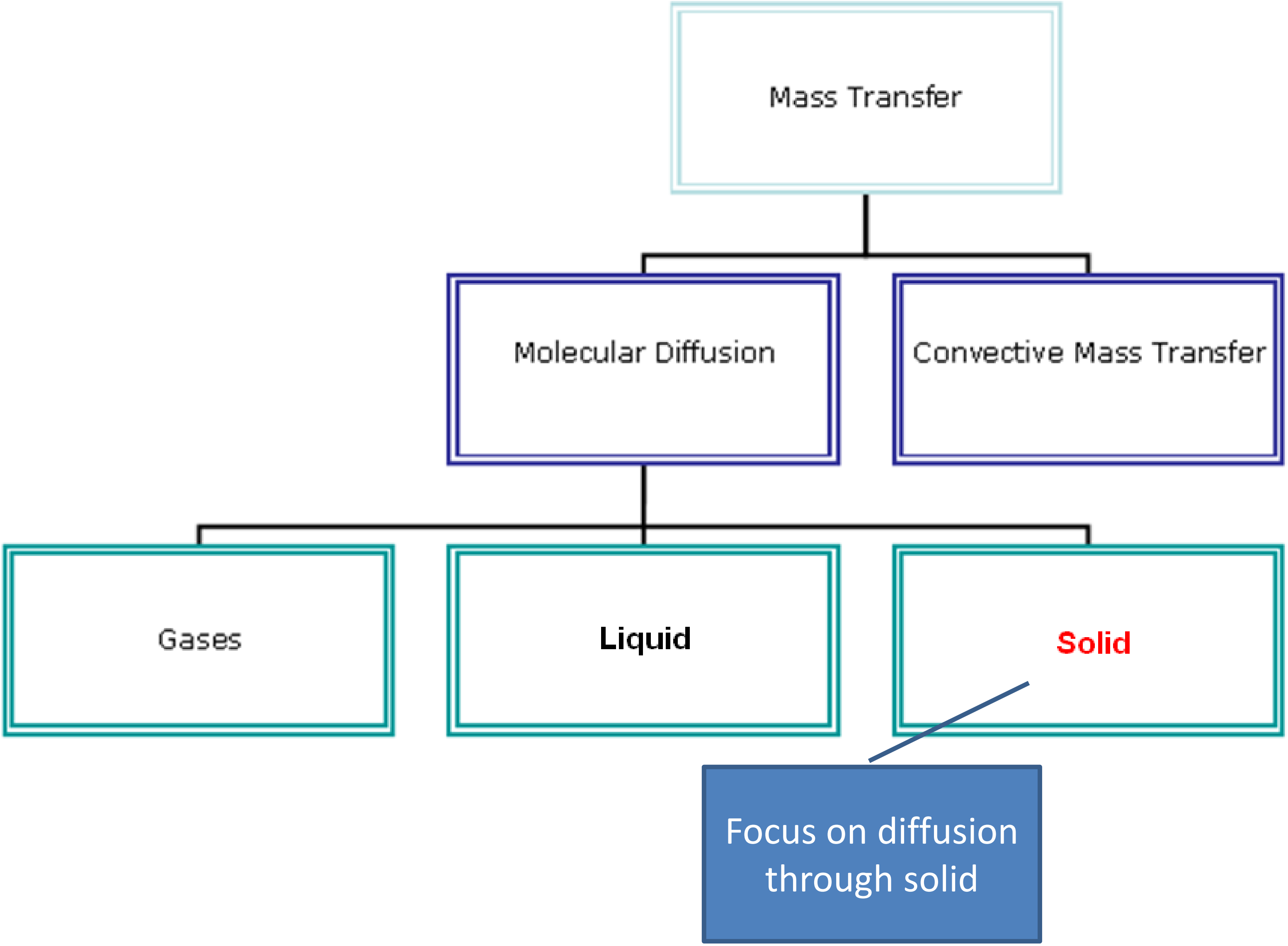
$$= 1.277 \times 10^{-9} \text{ m}^2/\text{s}$$

For 50°C:

$$D_{AB} = \frac{(1.173 \times 10^{-16})(2.6 \times 18.02)^{1/2}(323)}{(0.5494 \times 10^{-3})(0.0740)^{0.6}}$$

$$= 2.251 \times 10^{-9} \text{ m}^2/\text{s}$$

Summary


Mass Transfer
Molecular Diffusion
Convective Mass Transfer
Gases
Liquid
Solid
Focus on diffusion through solid

Diffusion in Solids

Diffusion in solids occurs at a very slow rate.

D_{AB} decrease

In gas: $D_{AB} = 0.1\ cm^2/s$

Time taken **2.09 h**

In liquid: $D_{AB} = 10^{-5}\ cm^2/s$

Time taken **2.39 year**

In solid: $D_{AB} = 10^{-9}\ cm^2/s$

Time taken **239 centuries**

Time increase

Diffusion in Solids

Diffusion in solids occurs at a very slow rate.

However, mass transfer in solids is very important.

Examples:

- Leaching of metal ores
- Drying of timber, and foods
- Diffusion and catalytic reaction in solid catalysts
- Separation of fluids by membranes
- Treatment of metal at high temperature by gases.

Ways of diffusion

1. **Diffusion following Fick's law:** does not depend on the structure of the solid.
2. **Diffusion in porous solids (Knudsen diffusion):** where the structure and void channels are important.

Diffusion in solids following Fick's Law

- Start with the general equation:

$$N_A = -D_{AB}\frac{dc_A}{dz} + \frac{c_A}{c}(N_A + N_B)$$

Bulk term is set to zero in solids

- Therefore, the following equation will be used to describe the process:

$$N_A = -D_{AB}\frac{dc_A}{dz} \qquad \text{.........................} (1)$$

In General, **Diffusion in solids**

- Similar to heat transfer by conduction.
- Ignore the bulk flow (x_A small, $n_B = 0$)
- Hence Fick's law (as Fourier's Law)

$$n_A = -D_{AB} A \left(\frac{dc_A}{dz} \right) \qquad Q = -kA \left(\frac{dT}{dz} \right)$$

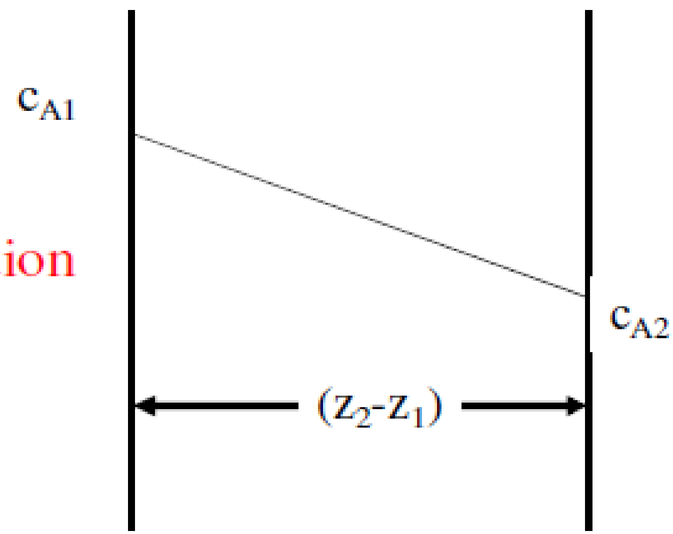
steady-state diffusion through a solid slab

For steady-state diffusion through a solid slab, we get by integrating the previous equation:(Eq. 1)

$$N_A = \frac{D_{AB}\,(c_{A1} - c_{A2})}{z_2 - z_1}$$

where N_A and D_{AB} are taken as constants.

Similar to heat conduction



Notes

- For diffusion in solids $D_{AB} \neq D_{BA}$
- Diffusion coefficient D_{AB} in solid is independent of pressure of the gas or liquid on the outside of the solid
- Solubility is always used to calculate concentration at interface. For example; solubility of gases in solids. Here the solubility of gas is dependent on pressure outside the solid. In general it is directly proportional to the partial pressure of the gas. Correlation is similar to Henry's Law.

$$c_A = \frac{S \text{ m}^3(\text{STP})/\text{m}^3 \text{ solid} \cdot \text{atm}}{22.414 \text{ m}^3(\text{STP})/\text{kg mol } A} \, p_A \text{ atm} = \frac{S p_A}{22.414} \, \frac{\text{kg mol } A}{\text{m}^3 \text{ solid}}$$

- Where S is the solubility constant {m^3 gas (STP)/m^3 solid· Atm}
- Some experimental data for solubility, S are given in tables (**see the next slid and the text**).

TABLE 6.5-1. *Diffusivities and Permeabilities in Solids*

Solute (A)	Solid (B)	T (K)	D_{AB}, Diffusion Coefficient $[m^2/s]$	Solubility, S $\left[\frac{m^3 \text{ solute}(STP)}{m^3 \text{ solid} \cdot atm}\right]$	Permeability, P_M $\left[\frac{m^3 \text{ solute}(STP)}{s \cdot m^2 \cdot atm/m}\right]$
H_2	Vulcanized rubber	298	$0.85(10^{-9})$	0.040	$0.342(10^{-10})$
O_2		298	$0.21(10^{-9})$	0.070	$0.152(10^{-10})$
N_2		298	$0.15(10^{-9})$	0.035	$0.054(10^{-10})$
CO_2		298	$0.11(10^{-9})$	0.90	$1.01(10^{-10})$
H_2	Vulcanized neoprene	290	$0.103(10^{-9})$	0.051	
		300	$0.180(10^{-9})$	0.053	
H_2	Polyethylene	298			$6.53(10^{-12})$
O_2		303			$4.17(10^{-12})$
N_2		303			$1.52(10^{-12})$
O_2	Nylon	303			$0.029(10^{-12})$
N_2		303			$0.0152(10^{-12})$
Air	English leather	298			$0.15–0.68 \times 10^{-4}$
H_2O	Wax	306			$0.16(10^{-10})$
H_2O	Cellophane	311			$0.91–1.82(10^{-10})$
He	Pyrex glass	293			$4.86(10^{-15})$
		373			$20.1(10^{-15})$
He	SiO_2	293	$2.4–5.5(10^{-14})$	0.01	
H_2	Fe	293	$2.59(10^{-13})$		
Al	Cu	293	$1.3(10^{-34})$		

Permeability equations for diffusion in solids

Permeability can be related to Fick's equation as follows.

$$N_A = \frac{D_{AB}(c_{A1} - c_{A2})}{z_2 - z_1} \qquad \textbf{(i)}$$

From Eq. **of solubility**

$$c_{A1} = \frac{Sp_{A1}}{22.414} \qquad c_{A2} = \frac{Sp_{A2}}{22.414} \qquad \textbf{(ii)}$$

Substituting Eq. (**ii**) into (**i**),

$$N_A = \frac{D_{AB}S(p_{A1} - p_{A2})}{22.414(z_2 - z_1)} = \frac{P_M(p_{A1} - p_{A2})}{22.414(z_2 - z_1)} \text{ kg mol/s} \cdot \text{m}^2$$

where the permeability P_M is

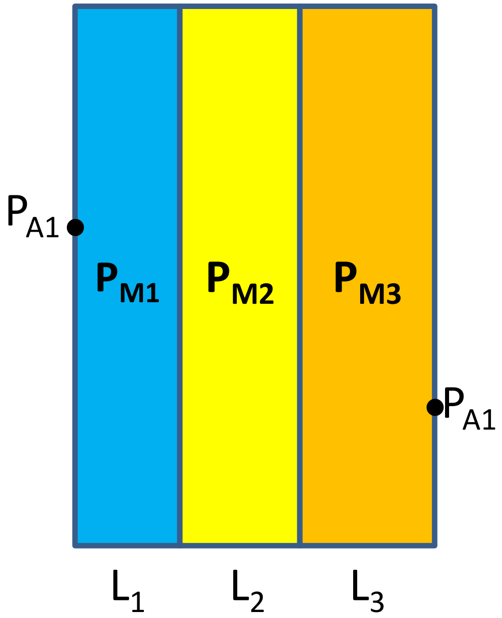
$$P_M = D_{AB}S \frac{\text{m}^3\text{(STP)}}{\text{s} \cdot \text{m}^2\text{C.S.} \cdot \text{atm/m}}$$

Diffusion through multi-solid layers

- Assume 3 solid layers as shown in the figure. The mass diffusion flux is

$$N_A = \frac{p_{A1} - p_{A2}}{22.414} \frac{1}{L_1/P_{M1} + L_2/P_{M2} + \cdots}$$

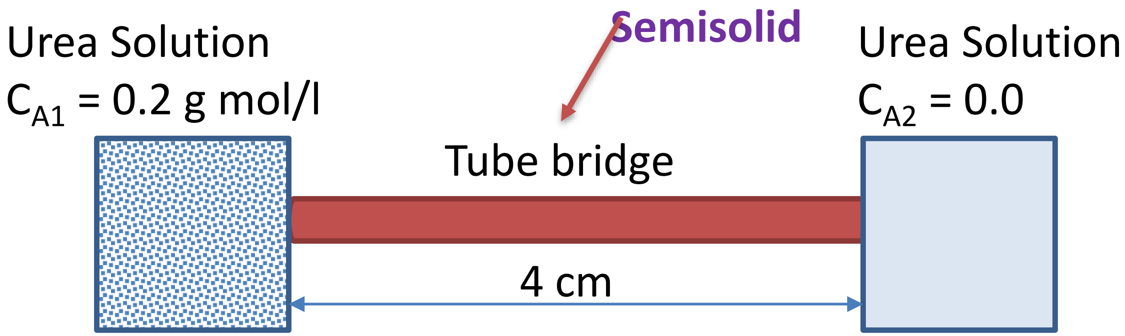
- Where $P_{A1} - P_{A2}$ is the overall partial pressure difference.



Example: Diffusion of Urea in Agar

A tube or bridge of a gel solution of 1.05 wt % agar in water at 278 K is 0.04 m long and connects two agitated solutions of urea in water. The urea concentration in the first solution is 0.2 g mol urea per liter solution and is 0 in the other. Calculate the flux of urea in kg mol/s.m^2 at steady state.

Schematic



Semisolid
Urea Solution
C_{A1} = 0.2 g mol/l
Urea Solution
C_{A2} = 0.0
Tube bridge
4 cm

TABLE 6.4-2. *Typical Diffusivities of Solutes in Dilute Biological Gels in Aqueous Solution*

Solute	Gel	Wt % Gel in Solution	Temperature K	Temperature °C	Diffusivity (m^2/s)
Sucrose	Gelatin	0	278	5	0.285×10^{-9}
		3.8	278	5	0.209×10^{-9}
		10.35	278	5	0.107×10^{-9}
		5.1	293	20	0.252×10^{-9}
Urea	Gelatin	0	278	5	0.880×10^{-9}
		2.9	278	5	0.644×10^{-9}
		5.1	278	5	0.609×10^{-9}
		10.0	278	5	0.542×10^{-9}
		5.1	293	20	0.859×10^{-9}
Methanol	Gelatin	3.8	278	5	0.626×10^{-9}
Urea	Agar	1.05	278	5	0.727×10^{-9}
		3.16	278	5	0.591×10^{-9}
		5.15	278	5	0.472×10^{-9}
Glycerin	Agar	2.06	278	5	0.297×10^{-9}
		6.02	278	5	0.199×10^{-9}
Dextrose	Agar	0.79	278	5	0.327×10^{-9}
Sucrose	Agar	0.79	278	5	0.247×10^{-9}
Ethanol	Agar	5.15	278	5	0.393×10^{-9}
NaCl (0.05 *M*)	Agarose	0	298	25	1.511×10^{-9}
		2	298	25	1.398×10^{-9}

Solution

Data:

$D_{AB} = 0.727 \times 10^{-9}\ m^2/s$

See previous table at given condition

$c_{A1} = 0.2$ g mol/L $= 0.2$ kg mol/m^3

$c_{A2} = 0$

$z_2 - z_1 = 0.04$ m

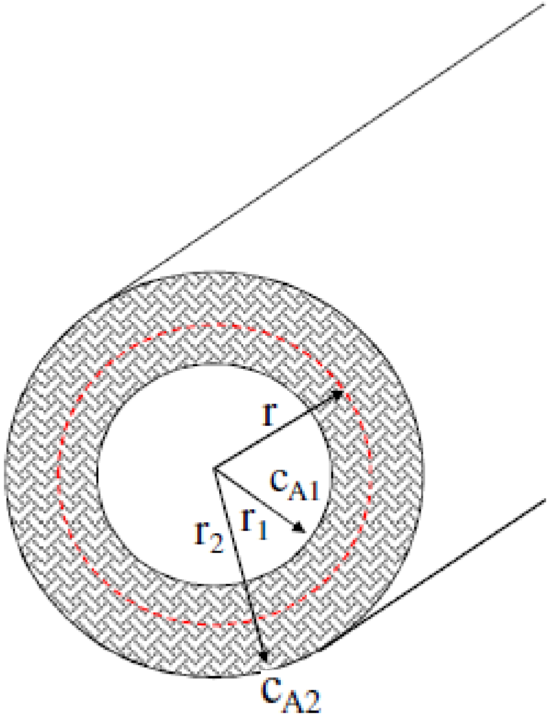
$$\therefore \quad N_A = \frac{D_{AB}(c_{A1} - c_{A2})}{z_2 - z_1} = \frac{0.727 \times 10^{-9}(0.20 - 0)}{0.04 - 0}$$

$$= 3.63 \times 10^{-9}\ \text{kg mol/s} \cdot \text{m}^2$$

Diffusion through a cylinder wall

- For steady-state diffusion through a cylinder wall of inner radius r_1 and outer radius r_2 and length L in the radial direction outward, we get:

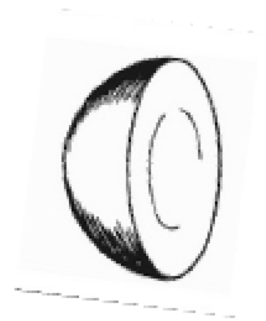
Try to derive the diffusion equation

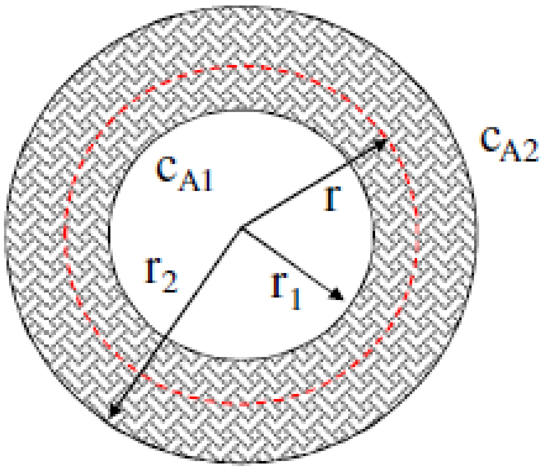


Diffusion through a spherical shell

For steady-state diffusion through a spherical shell of inner radius r_1 and outer radius r_2 in the radial direction outward, we get:

Try to derive the diffusion equation





Summary

Diffusion in Solids which Follow Fick's Law and Does Not Depend on The Structure of Solids

Diffusion in Solid

$D_{AB} \neq D_{BA}$

General Equation

$$N_A = -D_{AB}\frac{dc_A}{dz}$$

Neglect convective term and assume constant concentration

Slab Solid

$$N_A = D_{AB}\frac{(c_{A1} - c_{A2})}{(z_2 - z_1)}$$

Cylinder Wall

$$\bar{N}_A = D_{AB}(c_{A1} - c_{A2})\frac{2\pi L}{ln(r_2 / r_1)}$$

r_1: inner radius r_2: outer radius

Sphere

$$\bar{N}_A = \frac{4\pi r_1 r_2 D_{AB}(c_{A1} - c_{A2})}{(r_2 - r_1)}$$

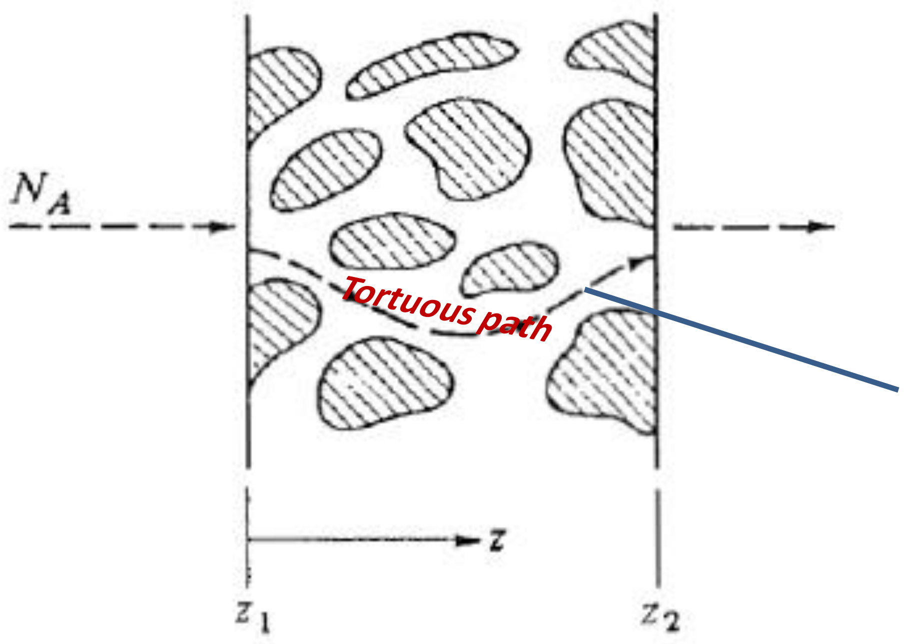
r_1: inner radius r_2: outer radius

Exercises

- Write diffusion expression for multi-solid cylindrical layers. {Hollow cylinder)
- Write diffusion expression for multi-solid spherical layers. {hollow sphere}

Diffusion in Porous Solids

that depends on Structure



A cross section of a typical porous solid

The actual path of the diffusion > $(z_2 - z_1)$ by a factor τ called tortuosity

Diffusion in Porous Solids

that depends on Structure

- Concerned about the porous solid that have pores or interconnected void in solid which will affect the diffusion

Knudsen diffusion

Diffusion in Porous Solids

Diffusion of Liquid

$$N_A = \frac{\varepsilon D_{AB}(c_{A1} - c_{A2})}{\tau(z_2 - z_1)}$$

Diffusion of Gases

$$N_A = \frac{\varepsilon D_{AB}(c_{A1} - c_{A2})}{\tau(z_2 - z_1)} = \frac{\varepsilon D_{AB}(p_{A1} - p_{A2})}{\tau RT(z_2 - z_1)}$$

Pores are filled with liquid 'water'. Solid is inert.

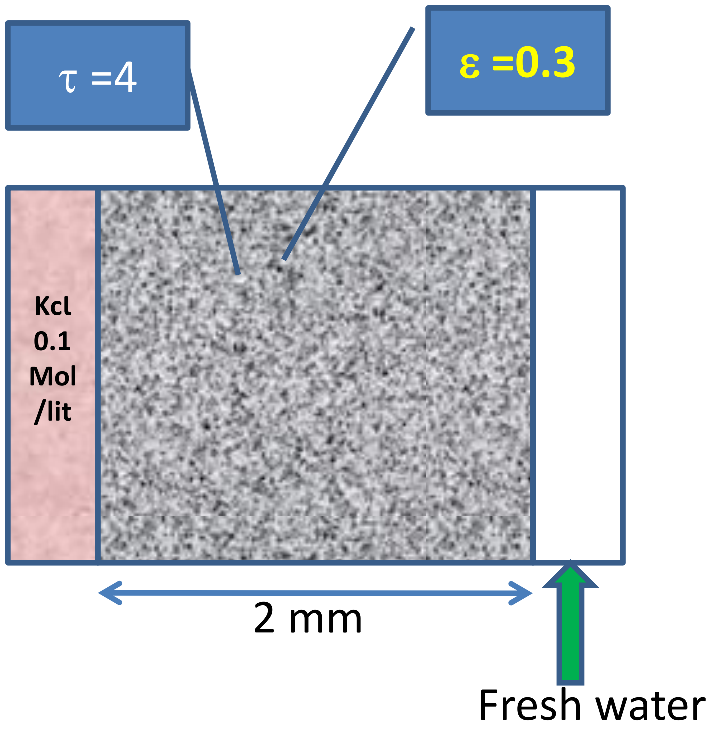
ε –void fraction; τ –tortuosity;

$D_{A,eff} = (\varepsilon D_{AB} / \tau) =$ effective diffusivity

Example: Diffusion of KCl in Porous Silica

A solid of silica 2.0 mm thick is porous, with a void friction ε of 0.30 and a tortuosity τ of 4.0. The pores are filled with water at 298 K. At one face the concentration of KCl held at 0.10 g mol/liter, and fresh water flow rapidly past the other face. Calculate the diffusion of KCl at steady state.

Schematic



solution

Data

$D_{AB} = 1.87 \times 10^{-9}\ m^2/s$ The diffusivity of KCI in water from tables

$c_{A1} = 0.1\ \text{kg mol/m}^3$

$c_{A2} = 0$

$z_2 - z_1 = 0.002\ m$

$$\therefore N_A = \frac{\varepsilon D_{AB}(c_{A1} - c_{A2})}{\tau(z_2 - z_1)} = \frac{0.30(1.870 \times 10^{-9})(0.10 - 0)}{4.0(0.002 - 0)}$$

$$= 7.01 \times 10^{-9}\ \text{kg mol KCl/s} \cdot \text{m}^2$$

Diffusivity in Gases

- Pressure dependence of diffusivity is given by

  $D_{AB} \propto \frac{1}{p}$ (for moderate ranges of pressures, up to 10 atm).

- And temperature dependency is according to

  $D_{AB} \propto T^{3/2}$

- Diffusivity of a component in a mixture of components can be calculated using the diffusivities for the various binary pairs involved in the mixture. The relation given by Wilke is

$$D_{1-mixture} = \frac{1}{\frac{y'_2}{D_{1-2}} + \frac{y'_3}{D_{1-3}} + \ldots\ldots\ldots + \frac{y'_n}{D_{1-n}}}$$

- Where D $_{1\text{-mixture}}$ is the diffusivity for component 1 in the gas mixture; D $_{1\text{-n}}$ is the diffusivity for the binary pair, component 1 diffusing through component n; and y_n' *is the mole fraction of component n in the gas mixture evaluated on a* component –1 – free basis, that is

$$y_2' = \frac{y_2}{y_2 + y_3 + \ldots\ldots y_n}$$