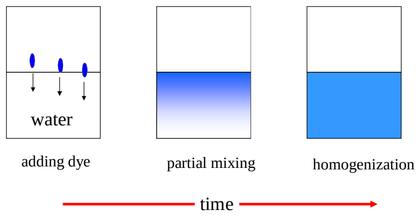
Laws of Diffusion

DIFFUSION IN SOLIDS

Definition

Diffusion: a *molecular* kinetic process that leads to homogenization, or mixing, of the chemical components in a phase.



Kinetic Characteristics

Diffusion is also a thermally activated process that follows the well-known relationship,

$$D = D_0 \cdot e^{-\Delta E / R_g T}$$

where

- D = Diffusion coefficient
- D_0 = Pre-factor
- ΔE = Activation energy
- R_g = Universal gas constant
- T = Temperature

Phenomenological Laws

$$\varphi = -A \frac{k}{\mu} \frac{\mathrm{d}P}{\mathrm{d}x}$$

Darcy's Law

Porous flow

$$Q = -k \frac{\mathrm{d}T}{\mathrm{d}z}$$

Fourier's Law

Heat flow

$$J = -D \frac{\mathrm{d}C}{\mathrm{d}x}$$

Fick's First Law

Mass flow

Fick's First Law

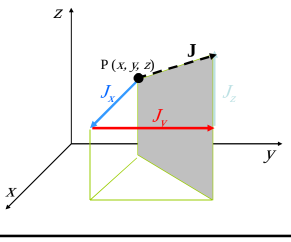
$$\mathbf{J}(x,y,z) = J_x \mathbf{e}_x + J_y \mathbf{e}_y + J_z \mathbf{e}_z$$ Mass flux vector

Component form of Fick's 1st law:
(Isotropic system)

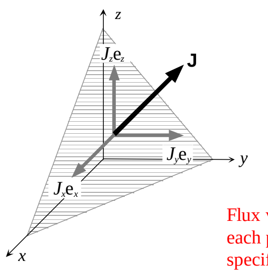
$$J_x = -D\left(\frac{\partial C}{\partial x}\right)_{y,z,t}$$

$$J_y = -D\left(\frac{\partial C}{\partial y}\right)_{z,x,t}$$

$$J_z = -D\left(\frac{\partial C}{\partial z}\right)_{x,y,t}$$

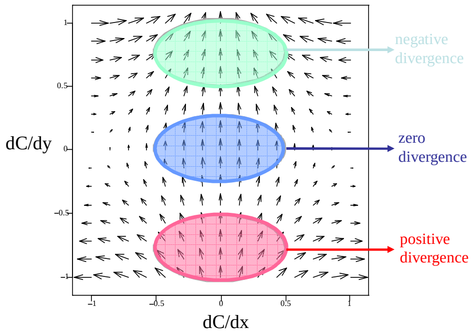


Mass-flux Vector



Flux vectors may be visualized at each point in a medium by specifying their directions and magnitudes.

Gradient Vector Field



Divergence Operators

Cartesian Coordinates:

$$\mathrm{div}\mathbf{F} = \left(\frac{\partial F_x}{\partial x}\right) + \left(\frac{\partial F_y}{\partial y}\right) + \left(\frac{\partial F_z}{\partial z}\right)$$

Cylindrical Coordinates:

$$\mathrm{div}\mathbf{F} = \frac{1}{r}\frac{\partial}{\partial r}(r \cdot F_r) + \frac{1}{r}\left(\frac{\partial F_\theta}{\partial \theta}\right) + \left(\frac{\partial F_z}{\partial z}\right)$$

Spherical Coordinates:

$$\mathrm{div}\mathbf{F} = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 \cdot F_r) + \frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}(\sin\theta \cdot F_\theta) + \frac{1}{r\sin\theta}\left(\frac{\partial F_\phi}{\partial \phi}\right)$$

Fick's First Law

$$\nabla C\,(x,y,z,t) \equiv \left(\frac{\partial C}{\partial x}\right)_{y,z,t} \mathbf{e}_x + \left(\frac{\partial C}{\partial y}\right)_{z,x,t} \mathbf{e}_y + \left(\frac{\partial C}{\partial z}\right)_{x,y,t} \mathbf{e}_z$$

Vector form of Fick's first law:

$$\mathbf{J} = -D\nabla C$$

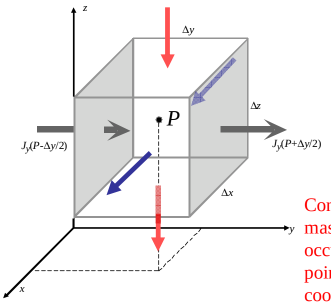
Units

$$J_i = -D\frac{\partial C}{\partial x}$$

$$J_i\ [\text{units?}] = D\left[\frac{\text{cm}^2}{\text{s}}\right] \cdot \left(\frac{\partial C}{\partial x}\right) \left[\frac{\text{g}}{\text{cm}^4}\right], \quad (i = x, y, z)$$

$$J_i[\text{units}] = \frac{\text{g}}{\text{s} \cdot \text{cm}^2}$$

Mass-flow Control Volume



Control volume indicating mass flows in the y-direction occurring about an arbitrary point P in the Cartesian coordinate system, x,y,z.

Mass Conservation

Inflow – Outflow = Accumulation Rate (*A.R.*)

$$\left[J_y\left(P - \frac{\Delta y}{2}\right) - J_y\left(P + \frac{\Delta y}{2}\right)\right]\Delta x \Delta z = (A.R.)_y$$

$$\left[J_y - \left(\frac{\partial J_y}{\partial y}\right)\cdot\frac{\Delta y}{2} - \left(J_y + \left(\frac{\partial J_y}{\partial y}\right)\cdot\frac{\Delta y}{2}\right)\right]\Delta x \Delta z = (A.R.)_y$$

$$-\left(\frac{\partial J_y}{\partial y}\right)\Delta y \Delta x \Delta z = (A.R.)_y$$

Mass Conservation

Total Inflow − Total Outflow = $(A.R.)_{total}$

$$-\left(\frac{\partial J_x}{\partial x}+\frac{\partial J_y}{\partial y}+\frac{\partial J_z}{\partial z}\right)\Delta x\Delta y\Delta z = \left(\frac{\partial C}{\partial t}\right)\Delta x\Delta y\Delta z$$

$$\nabla\cdot\mathbf{J} = \left[e_x(\partial/\partial x)+e_y(\partial/\partial y)+e_z(\partial/\partial z)\right]\cdot\mathbf{J}(x,y,z)$$

$$-\nabla\cdot\mathbf{J} = \frac{\partial C}{\partial t}$$

or

$$\frac{\partial C}{\partial t}+\nabla\cdot\mathbf{J} = 0$$

continuity equation

Fick's Second Law

(Linear Diffusion Equation)

$$-\nabla\cdot(-D\ \nabla C) = \frac{\partial C}{\partial t}$$

$$D\ (\nabla\cdot\nabla C) = \frac{\partial C}{\partial t}$$

or

$$\nabla^2 C = \frac{1}{D}\left(\frac{\partial C}{\partial t}\right)$$

Fick's 2nd law

Fick's Second Law

(Cartesian Coordinates)

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

Laplacian

$$D\left(\frac{\partial^2 C}{\partial x^2}+\frac{\partial^2 C}{\partial y^2}+\frac{\partial^2 C}{\partial z^2}\right) = \frac{\partial C}{\partial t}$$

Fick's Second Law

(Cylindrical Coordinates)

$$\nabla^2 \equiv \frac{1}{r}\left\{\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)+\frac{\partial}{\partial \theta}\left(\frac{1}{r}\frac{\partial}{\partial \theta}\right)+\frac{\partial}{\partial z}\left(r\frac{\partial}{\partial z}\right)\right\}$$

Laplacian

$$\frac{D}{r}\left\{\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)+\frac{\partial}{\partial \theta}\left(\frac{1}{r}\frac{\partial C}{\partial \theta}\right)+\frac{\partial}{\partial z}\left(r\frac{\partial C}{\partial z}\right)\right\} = \frac{\partial C}{\partial t}$$

Fick's Second Law

(Spherical Coordinates)

$$\nabla^2 \equiv \frac{1}{r^2}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right)+\frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial^2\phi}\right)\right\}$$

Laplacian

$$\frac{D}{r^2}\left\{\frac{\partial}{\partial r}\left(r^2\left(\frac{\partial C}{\partial r}\right)\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\left(\frac{\partial C}{\partial \theta}\right)\right)+\frac{1}{\sin^2\theta}\left(\frac{\partial^2 C}{\partial^2\phi}\right)\right\} = \frac{\partial C}{\partial t}$$

Important Diffusion Symmetries

Linear Flow (1-D flow)

$$D\left(\frac{\partial^2 C}{\partial x^2}\right) = \frac{\partial C}{\partial t}$$

(D = constant)

$$\frac{\partial}{\partial x}\left[D\left(\frac{\partial C}{\partial x}\right)\right] = \frac{\partial C}{\partial t}$$

(D = variable)

Important Diffusion Symmetries

Axisymmetric (radial) Flow

$$D\left[\left(\frac{\partial^2 C}{\partial r^2}\right)+\frac{1}{r}\left(\frac{\partial C}{\partial r}\right)\right] = \frac{\partial C}{\partial t} \quad (D = \text{constant})$$

$$\frac{1}{r}\frac{\partial}{\partial r}\left[rD\left(\frac{\partial C}{\partial r}\right)\right] = \frac{\partial C}{\partial t} \quad (D = \text{variable})$$

Important Diffusion Symmetries

Spherical symmetry

$$D\left[\left(\frac{\partial^2 C}{\partial r^2}\right)+\frac{2}{r}\left(\frac{\partial C}{\partial r}\right)\right] = \frac{\partial C}{\partial t} \quad (D = \text{constant})$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 D\left(\frac{\partial C}{\partial r}\right)\right] = \frac{\partial C}{\partial t} \quad (D = \text{variable})$$

Exercises

1. Given the concentration field C=sin(πx) [g/cm^3], plot the gradient field, and then determine the flux field using Fick's 1st law, assuming that the diffusion coefficient, D=1 [cm^2/s]. The use of a mathematical software package or spreadsheet provides an invaluable aid in solving diffusion problems such as suggested by these exercises, and many others introduced in later chapters of this book.

In one dimension, the gradient is defined as

$$\nabla C \equiv \left(\frac{\partial C}{\partial x}\right)\cdot \mathbf{e}_x = \pi\cos(\pi x)\cdot \mathbf{e}_x$$

Key Points

- Diffusion is a molecular scale mixing process, as contrasted with convective, or mechanical mixing. Mixing in solids occurs by diffusive motions of atoms or molecules.
- Fick's 1st and 2nd laws are based on fundamental physics (mass conservation) and empirical observations (experiments).
- Diffusion involves scalar fields, C(**r**, *t*), which have associated vector gradient fields, ∇ C(**r**, *t*).
- Fick's 2nd law is in general non-linear, but is

Steady Steady State Diffusion:

If we treat solid as homogenous material where the solute diffusing actually dissolves in the solid to form a homogenous solution, the flux can be expressed as:

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

for a slab with diffusion across constant cross sectional area

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

For diffusion where the cross-sectional area is not the same, such as into a cylinder:

$$\frac{\overline{N}_A}{A} = -D_{AB}\frac{dc_A}{dz} \rightarrow \frac{\overline{N}_A}{2\pi rL} = -D_{AB}\frac{dc_A}{dr}$$

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

Fick's Law

Assumptions for Simple Application of Fick's Law:

Diffusivity is constant (not fxn of conc.)
No Bulk Flow
Concentration gradient remains unchanged with time (Rate of Diffusion is constant.)

$$N_A = \frac{D_A(C_{A1}-C_{A2})}{z} \quad \text{For flat slab}$$

$$w = N_A S_{av} = \frac{D_A S_{av}(C_{A1}-C_{A2})}{z} \quad \textbf{for other shapes}$$

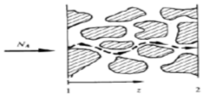
where S_{av} is the average cross section for diffusion

$$S_{av} = \frac{2\pi l(r_2-r_1)}{\ln(r_2/r_1)} \quad \text{and } z = r_2 - r_1 \text{ for cylindrical geometry}$$

and r_1 and r_2 are the inner and outer radii

$$S_{av} = 4\pi r_1 r_2 \quad \text{and } z = r_2 - r_1 \quad \text{for spherical geometry}$$

Diffusion in Porous Solids



At constant total pressure, you need to take into account

1) tortuosity factor k_t determining extra diffusional path (both the longer diffusional path and the fact that the pores are at an angle to the surface)
2) porosity, determining fraction of open area

for the "effective" diffusion coefficient.

The effective diffusion coefficient $D_{AB,eff}$ is usually determined experimentally.

$D_{AB,eff}$ = (porosity)*$D_{AB}/(k_t)^2$

(Sometimes the tortuosity factor is not quoted and tortuosity = k_t^2 is given instead)

Types of Movement in Pores

1. Knudsen diffusion
2. Molecular (Fick's) diffusion
3. Transition diffusion
4. Surface Diffusion
5. Hydrodynamic flow (Poiseuille's law)

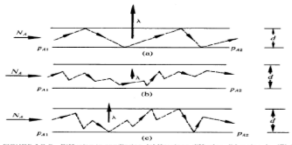


FIGURE 4.2-2 Diffusion in capillaries: (a) Knudsen diffusion, (b) molecular (Fick's) diffusion, (c) transition diffusion

$$\lambda = \frac{3.2\mu}{P}\left(\frac{RT}{2\pi g_c M}\right)^{0.5}$$

is the mean free path where M is the molecular weight, P is the total pressure in g force/cm^2=1033.2 x no. of atm, μ is the viscosity (poises), g_c = 980 g mass-cm/g force-sec^2, R = 84,780 g force-cm/K gmole

Knudsen Diffusion occurs when the mean free path is significant relative to the pore size--the molecules collides with the walls and the diameter of the pore is important.

The Diffusion coefficient for Knudsen diffusion is

$$D_{K,A} = 0.97x10^3\,\bar{r}\left(\frac{T}{M_A}\right)^{0.5}$$

where r is the radius in cm of the pore, temperature in K, and $D_{K,A}$ is the Knudsen diffusivity in terms of cm^2/s

Using d as the diameter of the pore, the criteria for apply Knudsen's diffusion is $d/\lambda < 0.2$.

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

$$N_A = \frac{D_{KA}P(x_{A1} - x_{A2})}{RTL}$$

where x_A is the concentration of A, L is the diffusion length

Transition Diffusion occurs when $0.2 < d/\lambda < 20$.

Here both molecule-to -molecule (Fickian) diffusion as well as molecule-wall diffusion takes place.

Flux is then given by the equation incorporating both molecular and Knudsen's diffusion.

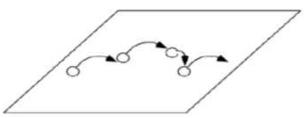
Treybal gives you the full, integrated diffusion+convection equation for the transitional area where molecular and Knudsen diffusion are present.

$$\mathbf{N_A} = \frac{\mathbf{N_A}}{\mathbf{N_A + N_B}}\frac{\mathbf{D_{AB,eff}P}}{\mathbf{RTz}}\ln\left[\frac{\frac{\mathbf{N_A}}{\mathbf{N_A+N_B}}\left(1+\frac{\mathbf{D_{AB,eff}}}{\mathbf{D_{K,eff}}}\right)-\mathbf{y_{A2}}}{\frac{\mathbf{N_A}}{\mathbf{N_A+N_B}}\left(1+\frac{\mathbf{D_{AB,eff}}}{\mathbf{D_{K,eff}}}\right)-\mathbf{y_{A1}}}\right]$$

using the relationship $\frac{\mathbf{D_{AB,eff}}}{\mathbf{D_{K,A,eff}}} = \frac{\mathbf{D_{AB}}}{\mathbf{D_{K,A}}}$

where y_A's are the gas phase concentrations of A. We often don't know the true tortuosity or diffusion length so $D_{AB\ effective}$ is measured for one gas mixture and compared to theoretical diffusivity get the correction factor that can be applied for all gas mixtures and to get $D_{K,\ effective}$'s .

Surface Diffusion occurs when the solutes adsorb onto the surface of the pores and jumps from one adsorption site to another. (Like 2-D Fickian diffusion)



Hydrodynamic Flow occurs when there is a difference in total pressure across the porous solid.

For gases in small pores, the flow is laminar and compressible:

$$N_A = \frac{d^2 g_c P_{AV}(P_1 - P_2)}{32\mu lRT} \quad \textbf{where } \mathbf{P_{AV}} = \frac{P_1 - P_2}{2}$$

If we pull the slab out of the liquid at time θ, the amount of solute removed is $c_{A0} - c_{A\infty}$, where the average concentration of the solute in the slab = $c_{A\theta}$

To evaluate the fraction of solute in the slab, the normalized slab concentration can be found by integrating the diffusion equation + continuity equation in 3 dimension.

$$\frac{\partial c_A}{\partial\theta} = D_{AB}\left(\frac{\partial \mathbf{c_A}}{\partial \mathbf{x}^2} + \frac{\partial \mathbf{c_A}}{\partial \mathbf{y}^2} + \frac{\partial \mathbf{c_A}}{\partial \mathbf{z}^2}\right)$$

$$\mathbf{E} = \frac{\mathbf{c_{A,\theta}} - \mathbf{c_{A,\infty}}}{\mathbf{c_{A,0}} - \mathbf{c_{A,\infty}}} = f\left(\frac{D\theta}{a^2}\right) = \mathbf{E_a} \quad \textbf{where 2a is the thickness}$$

The function of the right hand side is an infinite series, E_a which can be found using a chart of E_a versus $D\theta/a^2$.

(Notice how this is similar to error function results we used for infinite slab.)

The Analogous Solution Exist for other Configurations with the solution scaled to the main geometric dimensions of the solid where the diffusion is taking place and solutions can be read off a chart.

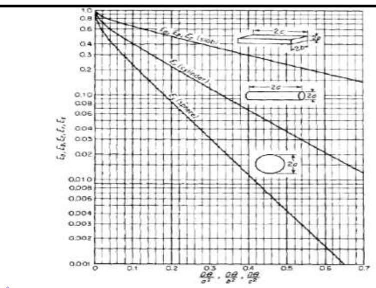


Figure 4.2 Unsteady-state diffusion.

For a bar with sealed ends (diffusion through faces but not through the ends of a long thin bar)--

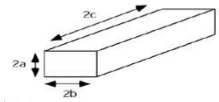
$$\mathbf{E} = \mathbf{E_a E_b} = \mathbf{f}\left(\frac{\mathbf{D\theta}}{\mathbf{a^2}}\right)\mathbf{f}\left(\frac{\mathbf{D\theta}}{\mathbf{b^2}}\right)$$

where 2a is the thickness and 2b is the width of the bar

For a brick-shaped bar where diffusion is important through all 6 faces,

$$\mathbf{E} = \mathbf{E_a E_b E_c} = \mathbf{f}\left(\frac{\mathbf{D\theta}}{\mathbf{a^2}}\right)\mathbf{f}\left(\frac{\mathbf{D\theta}}{\mathbf{b^2}}\right)\mathbf{f}\left(\frac{\mathbf{D\theta}}{\mathbf{c^2}}\right)$$

where 2a is the thickness, 2b is the width, and 2c is the length of the bar



For a sphere,

$$\mathbf{E} = f\left(\frac{\mathbf{D\theta}}{a^2}\right) = \mathbf{E_s}$$ **where a is the radius**

For a cylinder with sealed edges,

$$\mathbf{E} = f'\left(\frac{\mathbf{D\theta}}{a^2}\right) = \mathbf{E_r}$$ **where a is the radius of the cylinder**

on the other hand, if the diffusion occurs also at the ends of the cylinder as well as the sides,

$$\mathbf{E} = f\left(\frac{\mathbf{D\theta}}{c^2}\right)f'\left(\frac{\mathbf{D\theta}}{a^2}\right) = \mathbf{E_c E_r}$$

where a is the radius of the cylinder and 2c is the length

Other rules to keep in mind:

If only diffusion is only taking place in one face, then the effective thickness is doubled the true value when calculating the value of E

Certain assumptions have been made with these solutions.

(a) there is no resistance to diffusion in the fluid surrounding the liquid (well mixed)

(b) the liquid reservoir is so large that the concentration remains at $c_{A\infty}$ despite the diffusion of A out of the solid.

These solutions are parallel to those for Fourier's equation for heat conduction! Thus if the geometry has been solved for heat conduction, we can use it directly

for diffusion-- just consider diffusion rather than thermal diffisivity and concentration rather than temperature.

Note: Here we are calculating *<u>AVERAGE</u>* Concentration rather than Concentration as a function of distance and time.

The solutions to the differential equations can be plotted as a function also of distance form the midpoint of the object (dimensionless group $n = x/x_1$ where slab thickness $= x_1$)

In addition, if diffusion <u>and</u> convection are important on the surface of the object, <u>then</u> the ratio $m = D_{AB}/k\,x_1$ is also used to plot the solution. k is the mass transfer coefficient (We will elaborate on the mass transfer coefficient later).

A graph such as the one below includes these parameters. (Note: $X = D_{AB}\theta/x_1^2$)

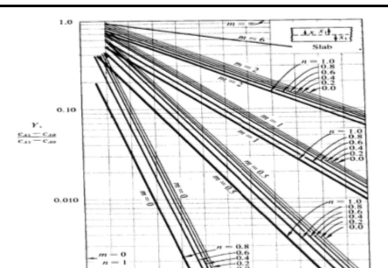


FIGURE 5.2-3 Unsteady-state mass transport in a large flat slab. (From H. P. Gurney and J. Lurie, *Ind. Eng. Chem.* **15**, 1170 (1923). With permission.)

$c_{A\theta}$ = concentration of A at time θ
c_{A1} = concentration of A in the bulk or at equilibrium
c_{A0} = initial concentration of A in the solid
x_1 = is distance from center line to surface of the solid
x = is the distance from the centerline of the solid
$n = x/x_1$

A clay slab has a uniform distribution of 14 mass percent water. The slab is 5.5 cm thick and the edges are sealed to prevent mass transfer. Air at 19°C and low humidity is blown over the large faces of the clay. The drying rate is dominated by the water diffusion in the slab. Calculate the effective diffusivity (diffusion coefficient) when the average moisture content drops to 9 percent in 360 minutes.

Assume that if I left the clay slab sitting for a very long time that the equilibrium moisture content will reach 1.9 mass percent.

$$E = \frac{\bar{c}_{A,\theta} - c_{A,\infty}}{c_{A,0} - c_{A,\infty}} = \frac{\bar{x}_{A,\theta} - x_{A,\infty}}{x_{A,0} - x_{A,\infty}}$$

Instead of concentration c used, it will be x, mass of moisture per unit mass of dry solid. This is more convenient because the total mass will change as the clay dry but the total dry mass will not. Therefore it is better to normalize the concentration this way.

$x_{A,0}$= 14/86 = 0.1628 kg moisture/kg dry solid

$\bar{x}_{A,\theta}$ =9/91 = 0.0989 kg moisture/kg dry solid

$x_{A,\infty}$ = 1.9/98.1= 0.0194 kg moisture/kg dry solid

E = 0.55

Look up the intercept on the curve for slab where E = 0.55,

Dt/a^2 = 0.16

$D = 5.6 \times 10^{-5}$ cm²/s

After 3600 minutes, what is the concentration in the midpoint of the slab? What is the concentration 1.65 cm from the surface of the slab?

Use Y graphs.

At the midpoint, x = 0, x_1 is the half thickness of the slab = 2.75 cm, and $n = x/x_1 = 0$. $Dt/a^2 = Dt/x_1^2 = 1.6 = X$ for this slab at this time.

Thus you find that

$$\frac{c_{A,\theta} - c_{A,\infty}}{c_{A,0} - c_{A,\infty}} = \frac{x_{A,\theta} - x_{A,\infty}}{x_{A,0} - x_{A,\infty}} \approx 0.02$$

ie the concentration at the midpoint is 2% of the original concentration.

At 1.65 cm from the surface, the x = 2.75 – 1.65 = 1.1, $x/x_1 = 0.4 = n$.

$$\frac{c_{A,\theta} - c_{A,\infty}}{c_{A,0} - c_{A,\infty}} = \frac{x_{A,\theta} - x_{A,\infty}}{x_{A,0} - x_{A,\infty}} \approx 0.015$$

We use m = 0 in these cases because we are assuming the mass transfer from the slab surface to the blowing air is so fast that only diffusion within the slab controls the moisture removal.

Additional Note

If only one face is exposed to diffusion/mass transfer, then double the thickness used in calculating the dimensionless group Dt/a^2 or $D\theta/a^2$

Example:

If I have a slab of 3 cm thick and only one side of the slab is exposed, the dimensionless group X = D/ta2 in the graphs will be $D/t(3cm)^2$ instead of $D/t(1.5cm)^2$ when both sides of the slab is exposed.

Also

$\frac{c_{A,\theta} - c_{A,\infty}}{c_{A,0} - c_{A,\infty}}$ is sometimes written as

$$\frac{c_{A,\infty} - c_{A,\theta}}{c_{A,\infty} - c_{A,0}} \text{ or } \frac{c_{A(surface)} - c_{A,\theta}}{c_{A(surface)} - c_{A,0}}$$

Worked Problem

An alloy has been formed into porous spheres with a radii of r = 6 mm. The voids are completely filled with a solution of KCl in water of concentration of 0.2 g KCl/cm^3. After exposure to pure flowing water, 85% of the salt is removed from the spheres in 4.65 hours. The temperature was 26^{0}C and the average diffusivity of KCl in water is 1.83 x 10^{-9} m^2/s.

If the spheres had been soaked with a K_2CrO_4 solution of concentration 0.26 g/cm^3, determine the time required for 85% of the salt to leave when the spheres are placed in a moving stream of water which contains 0.03 g K_2CrO_4/cm^3. The

average diffusivity of K_2CrO_4 in water is 1.13 x 10^{-9} m^2/s at 26°C.

K_2CrO_4

You have to find the effective diffusion coefficient from the information given in the first part.

Step 1. Determine the effective diffusivity of KCl from the sphere

Step 2. Compare the effective diffusivity of KCl to that of the KCl in bulk solution and get the correction factor due to porosity and tortuosity

Step 3. Apply the correction factor to K_2CrO_4 solution.

Since the data is given as average concentration, use the definition of E and the associated charts.

Since the sphere is exposed to running water, $C_{A,\infty} = 0$
C_{A0} is the original concentration in the sphere

What is E?

$$E = \frac{C_{A\theta} - C_{A\infty}}{C_{A0} - C_{A\infty}} = \frac{C_{A\infty} - C_{A\theta}}{C_{A\infty} - C_{A0}} = .15$$

Looking at the E chart for spheres, we find that

$D_{eff}\ \theta / a^2 = .14$

For spheres a = 6mm = .006m and time is 4.65 h = 16,740 s

Thus D_{eff} = 3.01 x 10^{-10} m^2/s which is .1645 of the bulk diffusion coefficient.

So everything being equal, the K_2CrO_4 solution diffusion can be calculated also.

$$E_{sphere} = \frac{(.26)(.15) - .03}{.26 - .03} = .0391$$

and $D_{eff}\ \theta / a^2 = .28$

Now apply the .1645 correction factor to the diffusion coefficient of K_2CrO_4 in water.

$D_{K2CrO4} = 1.8591 \times 10^{-10}\ m^2/s$

$\theta = .28 \times a^2 / D_{K2CrO4}$
for 85% of the K_2CrO_4

Comment:

E charts are used when AVERAGE CONCENTRATION is known or desired for a particular time

whereas the Y charts are used when CONCENTRATION AT PARTICULAR TIME AND POSITION is known or desired.

The E and Y charts are just graphical representations of the solutions to the differential equations describing the diffusion problem.

TWO Types of Problems:

You know the amount removed (or remaining) in the slab/cylinder/sphere and you want to determine either the effective diffusivity, time or size.

OR

You know the effective diffusivity, time, and size and you want to know the average concentration in the slab/cylinder/sphere.

As you can see, there are numerous variations of the two types of problems depending on what concentrations you know and what physical parameters (time, diffusivity, size) you know.

Mass Transfer Coefficients:

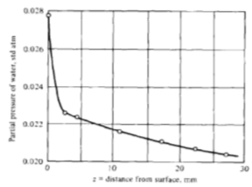


Figure 3.1 Evaporation c into air [61].

When rapid transport caused by turbulent flow occurs, the presence of the eddies moving randomly contributes to the overall mass transfer process from the surface (solid or fluid) to the bulk liquid.

Adjacent to the surface, is a thin laminar-type sublayer where mass transfer occurs by molecular diffusion.

Between these two regimes is a transition region where both molecular diffusion and eddy transport both contributes.

We can try to account for the additional transport by putting in a mass transport diffusivity ε_m. Such that:

$$j = -(D_{AB} + \varepsilon_{AB})\frac{dC_A}{dz}$$

$$N_A = -C(D_{AB} + \varepsilon_{AB})\frac{dx_A}{dz} + \frac{C_A}{C}(N_A + N_B)$$

$$N_A = \frac{N_A}{N_A + N_B}\frac{(D_{AB} + \varepsilon_{AB})C}{z_2 - z_1}\ln\left[\frac{\frac{C_{A2}}{C} - \frac{N_A}{(N_A + N_B)}}{\frac{C_{A1}}{C} - \frac{N_A}{(N_A + N_B)}}\right]$$

$$N_A = \frac{N_A}{N_A + N_B}k_c' C \ln\left[\frac{\frac{C_{A2}}{C} - \frac{N_A}{(N_A + N_B)}}{\frac{C_{A1}}{C} - \frac{N_A}{(N_A + N_B)}}\right]$$

or

$$N_A = \frac{N_A}{N_A + N_B} F \ln \left[\frac{\frac{N_A}{(N_A + N_B)} - \frac{C_{A2}}{C}}{\frac{N_A}{(N_A + N_B)} - \frac{C_{A1}}{C}} \right] \quad \text{in Treybal}$$

where F is $\frac{D_{AB}C}{z}$

F is the local Mass Transfer Coefficient based on local fluid motion

The overall mass transfer value is based on average fluid conditions so F_{AV} is sometimes used with constant C_{A1} and C_{A2}.

The mass transfer coefficient F is often written as k's with different subscripts (indicating commonly occurring situations) as part of the simple form:

Flux = k (concentration difference)

Two Commonly Occurring Cases:

Equimolar Counter Diffusion $N_A = -N_B$

$$N_A = k_g'(p_{A1} - p_{A2}) = k_y'(y_{A1} - y_{A2}) = k_c'(C_{A1} - C_{A2})$$

$$k_x'(x_{A1} - x_{A2}) = k_L'(C_{A1} - C_{A2}) \quad \text{(for liquids)}$$

Diffusion of A through Stagnant B (N_B=0)

$$N_A = k_g (p_{A1} - p_{A2}) = k_y (y_{A1} - y_{A2}) = k_c (C_{A1} - C_{A2})$$

$$k_x (x_{A1} - x_{A2}) = k_L(C_{A1} - C_{A2}) \quad \text{(for liquids)}$$

Flux Equation for Special Cases

$\varphi_N = 1.0$ Equimolar Counterdiffusion	$\varphi_N = x_{BM}$ Diffusion of *A* through Stagnant *B*	Units of Coefficient
GASES		
$N_A = k_G'(p_{A1} - p_{A2})$	$N_A = k_G(p_{A1} - p_{A2})$	$\frac{\text{moles transferred}}{\text{time(area)(pressure)}}$
$N_A = k_y'(y_{A1} - y_{A2})$	$N_A = k_y(y_{A1} - y_{A2})$	$\frac{\text{moles transferred}}{\text{time(area)(mole fraction)}}$
$N_A = k_c'(c_{A1} - c_{A2})$	$N_A = k_c(c_{A1} - c_{A2})$	$\frac{\text{moles transferred}}{\text{time(area)(moles/vol)}}$
	$N_AM_A = k_Y(Y_{A1} - Y_{A2})$	$\frac{\text{mass transferred}}{\text{time(area)(mass } A\text{/mass } B)}$
LIQUIDS		
$N_A = k_x'(x_{A1} - x_{A2})$	$N_A = k_x(x_{A1} - x_{A2})$	$\frac{\text{moles transferred}}{\text{time(area)(mole fraction)}}$
$N_A = k_L'(c_{A1} - c_{A2})$	$N_A = k_L(c_{A1} - c_{A2})$	$\frac{\text{moles transferred}}{\text{time(area)(moles/vol)}}$

Practice Problems:

1. If k_G= 0.88 lb mole/hr-ft^2-atm was determined for diffusion of A through stagnant B, what is the flux of the solutes from a surface (where p_{A1} = 0.2 atm and P = 1 atm) into a mixture of A and B where p_{A2} = 0.05 atm and p_{B2} = 0.95 atm (countercurrent equimolar diffusion)?

Solution: k_G must be converted to k_G' !

Solution

The value of k_G for *A* through stagnant *B* must be converted to k_G'. Then, $p_{B2} = 0.95$, $p_{B1} = 1.00 - 0.20 = 0.80$. To calculate p_{BM},

$$p_{BM} = \frac{p_{B2} - p_{B1}}{\ln(p_{B2}/p_{B1})} = \frac{0.95 - 0.80}{\ln(0.95/0.80)} = 0.870 \text{ atm}$$

Then from Table 6.3-1, $k_G' = k_G p_{BM}/P = 0.88(0.87)/1.0 = 0.765$. Then, $N_A = k_G'(p_{A1} - p_{A2}) = 0.765(0.20 - 0.05) = 0.115$ lb mole *A*/hr-ft^2.

Example 6.3-1 Vaporization of *A* from a Solid Surface

Pure gas *B* at 1.0 atm pressure is flowing over a solid surface (a blotting paper) from which pure *A* is vaporizing. The liquid *A* completely wets the surface of the blotting paper. Hence, the partial pressure at the surface is the vapor pressure of pure *A* at 25°C, which is 0.10 atm. The mass transfer coefficient k_y has been estimated as 0.05 lb mole/hr-ft^2 (mole fraction). Calculate the rate of vaporization of *A*.

Solution

This is a case of *A* diffusing through stagnant *B*. Then $y_{A1} = 0.10/1.00 = 0.10$ at the surface. $y_{A2} = 0$ in the pure gas *B*. Using Eq. (6.3-11),

$$N_A = k_y(y_{A1} - y_{A2}) = 0.05(0.10 - 0) = 5.0 \times 10^{-3} \text{ lb mole } A \text{ diffusing/hr-ft}^2$$

Where do These Conversions Come From?

$$N_A = k_c' \frac{C}{\varphi_N}(x_{A1} - x_{A2}) = \frac{k_c'}{\varphi_N}(C_{A1} - C_{A2}) \quad \text{where}$$

$$\varphi_N = \frac{(x_{A1} - x_{A2})}{\frac{N_A}{N_A + N_B} \ln\left\{\frac{\frac{N_A}{N_A+N_B} - x_{A2}}{\frac{N_A}{N_A+N_B} - x_{A1}}\right\}}$$

$$= \frac{\left(\frac{N_A}{N_A+N_B} - x_{A2}\right) - \left(\frac{N_A}{N_A+N_B} - x_{A1}\right)}{\frac{N_A}{N_A + N_B} \ln\left\{\frac{\frac{N_A}{N_A+N_B} - x_{A2}}{\frac{N_A}{N_A+N_B} - x_{A1}}\right\}} = \frac{(N_R - x_A)_{LM}}{N_R}$$

where $N_R = N_A/(N_A+N_B)$

Semnan University , Chemical Engineering Department *A. Haghighi A.*

Two Cases:

Equimolar Counter Diffusion

$N_A = k_c'(C_{A1} - C_{A2})$

Diffusion of A through Stagnant B

$N_R = 1$

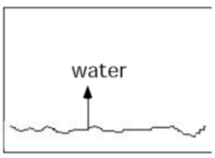
$\phi_N = (1 - x_A)_{LM} = x_{BM} = (x_{B2} - x_{B1})/\ln(x_{B2}/x_{B1})$

$$N_A = k_c' \frac{C(x_{A1} - x_{A2})}{x_{BM}}$$

Semnan University , Chemical Engineering Department *A. Haghighi A.*

Examples of Using Mass Transfer Coefficients:

Humidification in an enclosed vessel:



Mass Balance gives us

Total Amount Transferred = N_A x Area

= Area x k x (C_A,sat - C_A)

Semnan University , Chemical Engineering Department *A. Haghighi A.*

In addition, we can write the mass balance

(accumulation in gas phase) = (evaporation rate)

$$\frac{d}{dt}(V \times C_A) = A \times N_A = A \times k \times (C_{A,sat} - C_A)$$

Integrating with respect to concentration of A with the initial conditions, $t = 0,\ c_A = 0$

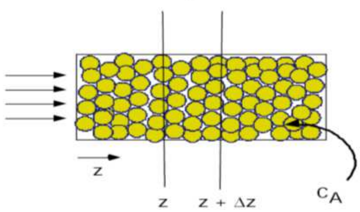
$$\frac{C_A}{C_{A,sat}} = 1 - e^{-(kA/V)t}$$

Semnan University , Chemical Engineering Department *A. Haghighi A.*

Mass Transfer in a Packed Bed

Spheres of particles slowly dissolve in a bed (shown below) as water is flowing past them at velocity v. The liquid just at the surface of the particles = $C_{A,sat}$

The surface area of spheres is a cm²/cm³ bed



Mass Balance

amount of dissolution = (concentration in x flow in) - (concentration out x flow out)

Se[...] *[...]highi A.*

$$\text{Area x } \Delta z \text{ x a x } N_A = \text{Area } (C_A v|_{z+\Delta z} - C_A v|_z)$$

$$\frac{ka}{v}(C_{A,sat} - C_A) = \frac{dC_A}{dz}$$

Integrating both sizes with respect to C_A using the initial conditions $z = 0,\ C_A = 0$

$$\frac{C_A}{C_{A,sat}} = 1 - e^{-(ka/v)z}$$

Semnan University , Chemical Engineering Department *A. Haghighi A.*

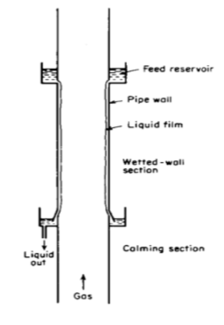


Figure 3.11 Wetted-wall tower.

Benzene Vapor is removed from air to water at 2 atm and 20°C. the mass transfer coefficient k_c' has been predicted to be 0.19 cm/s or

$$0.19\frac{gmole}{s\ cm^2(gmole/cm^3)}$$

The mole fraction of benzene is found to be 1.3 x 10^{-5} M at point 1 at the liquid at the interface and partial pressure of benzene is 0.15 atm at point 2 in the gas. Calculate the rate of absorption of benzene in the water.

Henry's constant = 240 atm

$p_{benzene1}$=240 x 1.3 x 10^{-5} atm =.0031 atm
$y_{benzene\ 1}$= .0031/2= .0016
$y_{benzene2}$ = 0.15 atm /2 atm = .075

The Air is relatively low solubility in water so

$$N_A = k_y(y_{benzene1} - y_{benzene2}) = \frac{k_c'\,P(y_{benzene1} - y_{benzene2})}{RTy_{BM}}$$

$$y_{BM} = \frac{y_{air2} - y_{air1}}{\ln(y_{air2}/y_{air1})} = .9612$$

$$N_A = -1.2x10^{-6} gmole/cm^2 s$$

APPENDIX A.2 PHYSICAL PROPERTIES

Table A.2-1 Vapor Pressure of Liquid Water from 0 to 100°C

Temp., °C	Vapor Pressure mm Hg	Temp., °C	Vapor Pressure mm Hg
0	4.58	45	71.88
5	6.54	50	92.51
10	9.21	60	149.4
15	12.79	70	233.7
20	17.54	80	355.1
25	23.76	90	525.8
30	31.82	95	633.9
35	42.18	100	760.0
40	55.32		

1. Urea is dissolving out of a gel. Assume no preferential partitioning of the solute in the gel and that we put the gel in pure running water.

a) If I have a slab of 3 cm thick and only one side of the slab is exposed, calculate the time for the average concentration to drop to 20% of the original concentration at 5°C. The reported diffusivity of urea in a gel is 4.7 x 10^{-6} cm2/s (at the temperature 5°C).

b) What is the tortuosity in the gel? (Assuming that no other factors affect diffusion of the urea through the gel.). Calculate the theoretical diffusion coefficient of urea in water from the Wilke-Chang equation:

$$D_{AB} = 7.4x10^{-8}(\varphi M_B)^{0.5}\frac{T}{\mu_B V_A^{0.6}}$$

where A indicates solute and B is the solvent properties. The viscosity is in centipoise, temperature T in Kelvin, and V_A is the molecular volume at the normal boiling point (same as used in your gas diffusion calculations). The viscosity of water is 1.5188 cp and the temperature is 5°C. Urea is NH_2CONH_2 (the carbon is in a carbonyl and the nitrogen is part of a primary amine). Compare the calculated bulk diffusion value with the measured value in the gel.

c) If the gel block is 1.6 cm thick, 1.8 cm long, and 1.4 cm high, what is the average concentration in the gel after immersion in clean running water for 10 hours? Assume that the initial concentration of urea in the gel is 1 x 10^{-4} gmole urea/ cm^3.

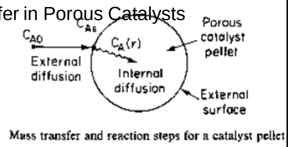
d) For a slab of 6 cm thick, what is the concentration of urea at the midpoint of the gel if Dt/a^2 = 0.56? Assume that the concentration in the gel at the beginning is 1 x 10^{-4} gmole urea/cm^3. Assume diffusion is the dominate mechanism (m = 0).

2. For the same initial and equilibrium concentrations as in the worked problem with the clay slab, consider instead a column of clay with all faces exposed. Determine the average amount of moisture in a clay column of 30 cm long and a diameter of 25 cm after 10 days?

3. Consider now that mass transfer of water from the clay slab to the air needs to be estimated in our clay drying problem. A mass transfer coefficient k_G of 8.36 x 10^{-5} gmol/(m^2 s atm) has been reported for air stream evaporating water from a flat plate at 19°C. What is the rate of water loss from a wet surface when dry air blows across both sides of a 1 m x 1 m slab? Assume that air is not diffusing into the clay.

4. Calculate the value of k_G' for the case in question 3.

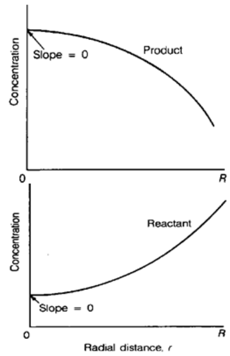
Internal Mass Transfer in Porous Catalysts



Mass transfer and reaction steps for a catalyst pellet

- We have examined the
- potential influence of
- external mass transfer
- on the rate of
- heterogeneous reactions.
- However, where active sites are accessible within the particle, internal mass transfer (molecular diffusion) has a tremendous influence on the rate of reaction within the catalyst. Numerous examples exist:
  - Encapsulated or entrapped enzymes
  - Microporous catalysts for catalytic cracking (zeolites)
- The diffusion rate of reactants and products within the particle often determines the rate at which a microporous catalyst functions.

Concentration Gradients of Diffusing Reactants and Products In a Uniform Catalyst Particle



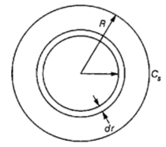


Figure 4-19
Spherical catalyst particle with diffusing reactant. C_s is the concentration of reactant at the particle periphery.