



Last Week's Lecture

Unsteady State Diffusion

This Week:

**Improving your understanding of
Unsteady State Diffusion Problems**

Begin Mass Transfer Coefficients

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/a^2

Example:

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

Also

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

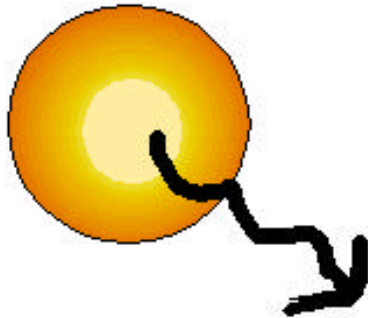
$\frac{C_{A, \infty} - C_{A,0}}{C_{A, \infty} - C_{A,0}}$ or $\frac{C_{A(\text{surface})} - C_{A, \infty}}{C_{A(\text{surface})} - C_{A,0}}$

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/cm³. After exposure to pure flowing water, 85% of the salt is removed from the spheres in 4.65 hours. The temperature was 26°C and the average diffusivity of KCl in water is 1.83×10^{-9} m²/s.

If the spheres had been soaked with a K₂CrO₄ solution of concentration 0.26 g/cm³, 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 K₂CrO₄/cm³. The

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



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,

$$C_{A,s} = 0$$

C_{A0} is the original concentration in the sphere

What is E ?

$$E = \frac{C_A - C_A}{C_{A0} - C_A} = \frac{C_A - C_A}{C_A - C_{A0}} = .15$$

Looking at the E chart for spheres, we find that

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

For spheres $a = 6\text{mm} = .006\text{m}$ and time is $4.65\text{ h} = 16,740\text{ s}$

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

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

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

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

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

$$D_{\text{K}_2\text{CrO}_4} = 1.8591 \times 10^{-10}\text{ m}^2/\text{s}$$

$$= .28 \times a^2 / D_{\text{K}_2\text{CrO}_4}$$

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:

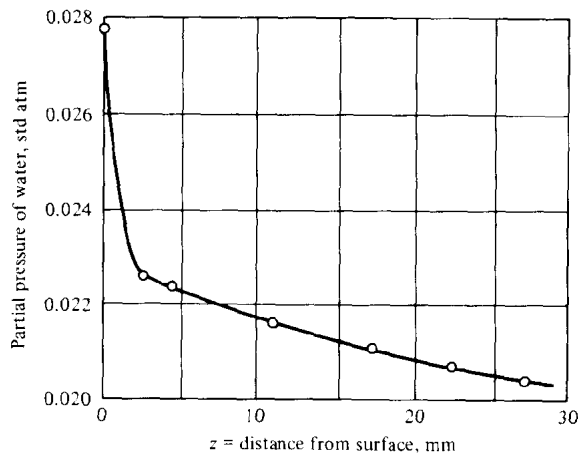


Figure 3.1 Evaporation c into air [61].

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 D_m . Such that:

$$\mathbf{j} = -(\mathbf{D}_{AB} + D_m) \frac{dC_A}{dz}$$

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

$$N_A = \frac{N_A}{N_A + N_B} \frac{(D_{AB} + N_{AB})C}{z_2 - z_1} \ln \frac{\frac{C_{A2}}{C} - \frac{N_A}{(N_A + N_B)}}{\frac{C_{A1}}{C} - \frac{N_A}{(N_A + N_B)}}$$

$$N_A = \frac{N_A}{N_A + N_B} k'_c C \ln \frac{\frac{C_{A2}}{C} - \frac{N_A}{(N_A + N_B)}}{\frac{C_{A1}}{C} - \frac{N_A}{(N_A + N_B)}}$$

or

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

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 $N_A = -N_B$

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

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

Diffusion of A through Stagnant B ($N_B=0$)

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

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

Table 6.3-1 Mass Transfer Coefficients and Flux Equations

General Equation

$$N_A = \frac{k'_c}{\varphi_N} (c_{A1} - c_{A2}) = \frac{k'_c}{\varphi_N} c (x_{A1} - x_{A2}) = \frac{k'_y}{\varphi_N} (y_{A1} - y_{A2})$$

where

$$\varphi_N = \frac{(N_R - x_{A2}) - (N_R - x_{A1})}{N_R \ln [(N_R - x_{A2}) / (N_R - x_{A1})]}, \quad N_R = \frac{N_A}{N_A + N_B}$$

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		
$N_A = k'_G (p_{A1} - p_{A2})$	$N_A = k_G (p_{A1} - p_{A2})$	$\frac{\text{moles transferred}}{\text{time}(\text{area})(\text{pressure})}$
$N_A = k'_y (y_{A1} - y_{A2})$	$N_A = k_y (y_{A1} - y_{A2})$	$\frac{\text{moles transferred}}{\text{time}(\text{area})(\text{mole fraction})}$
$N_A = k'_c (c_{A1} - c_{A2})$	$N_A = k_c (c_{A1} - c_{A2})$	$\frac{\text{moles transferred}}{\text{time}(\text{area})(\text{moles/vol})}$
	$N_A M_A = k_Y (Y_{A1} - Y_{A2})$	$\frac{\text{mass transferred}}{\text{time}(\text{area})(\text{mass A/mass B})}$
LIQUIDS		
$N_A = k'_x (x_{A1} - x_{A2})$	$N_A = k_x (x_{A1} - x_{A2})$	$\frac{\text{moles transferred}}{\text{time}(\text{area})(\text{mole fraction})}$
$N_A = k'_L (c_{A1} - c_{A2})$	$N_A = k_L (c_{A1} - c_{A2})$	$\frac{\text{moles transferred}}{\text{time}(\text{area})(\text{moles/vol})}$

Conversions between Coefficients

GASES

$$k'_c c = k'_c \frac{P}{RT} = k_c \frac{P_{BM}}{RT} = k'_G P = k_G P_{BM} = k_y \frac{P_{BM}}{P} = k'_y$$

LIQUIDS

$$k'_L c = k_L x_{BM} c = k'_L \frac{\rho}{M} = k'_x = k_x x_{BM}$$

Practice Problems:

1. If $k_G = 0.88$ lb mole/hr-ft²-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-ft².

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-ft² (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),

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

Where do These Conversions Come From?

$$N_A = k'_c \frac{C}{N} (x_{A1} - x_{A2}) = \frac{k'_c}{N} (C_{A1} - C_{A2}) \quad \text{where}$$

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

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

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

Two Cases:

Equimolar Counter Diffusion

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

Diffusion of A through Stagnant B

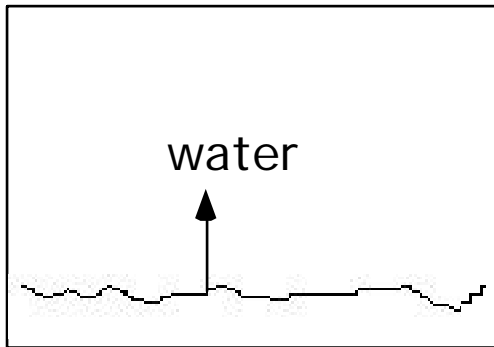
$$N_R = 1$$

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

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

Examples of Using Mass Transfer Coefficients:

Humidification in an enclosed vessel:



Mass Balance gives us

$$\text{Total Amount Transferred} = N_A \times \text{Area}$$

$$= \text{Area} \times k \times (C_{A,\text{sat}} - C_A)$$

In addition, we can write the mass balance

$$(\text{accumulation in gas phase}) = (\text{evaporation rate})$$

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

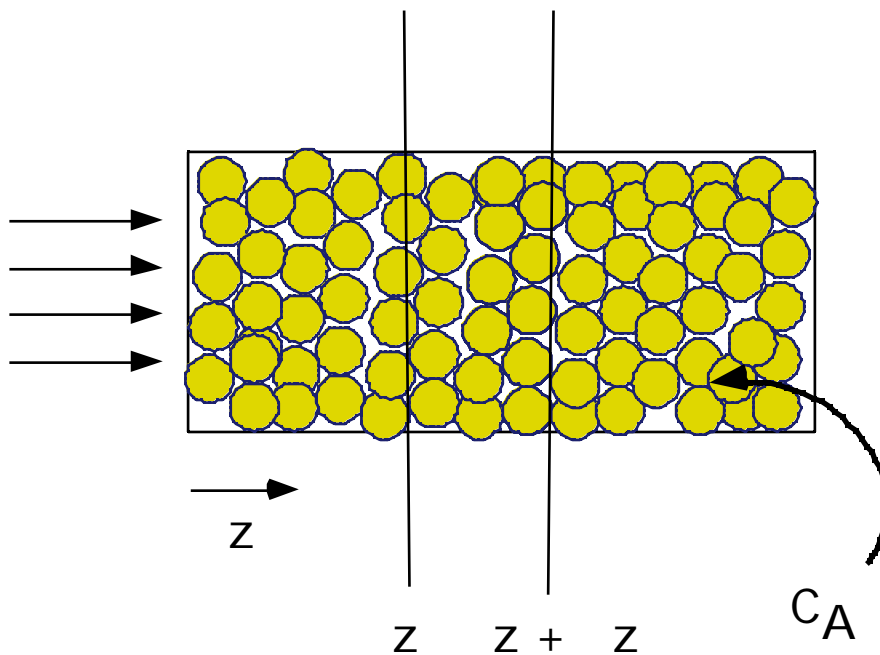
Integrating with respect to concentration of A
with the initial conditions, $t = 0$, $c_A = 0$

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

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 cm^2/cm^3 bed



Mass Balance

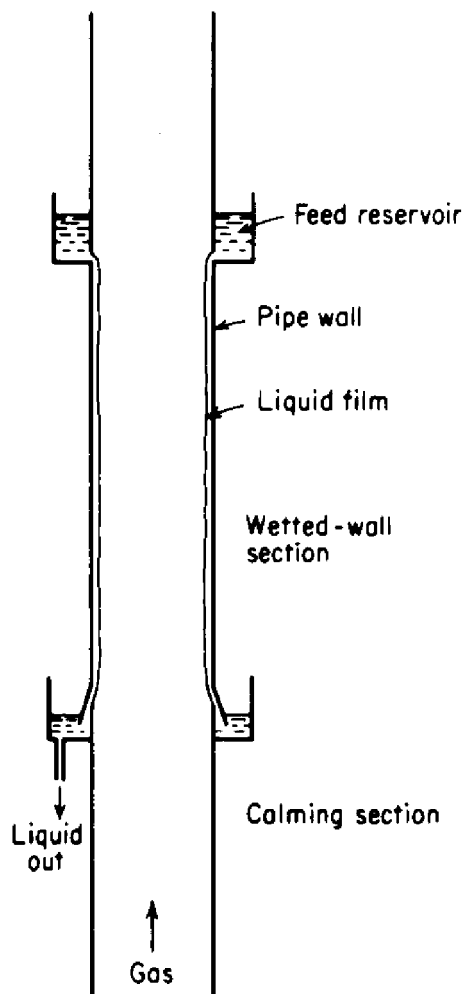
amount of dissolution = (concentration in x flow in) - (concentration out x flow out)

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

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

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

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



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

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

The mole fraction of benzene is found to be 1.3×10^{-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

Figure 3.11 Wetted-wall tower.

$$P_{\text{benzene}1} = 240 \times 1.3 \times 10^{-5} \text{ atm} = .0031 \text{ atm}$$

$$y_{\text{benzene}1} = .0031/2 = .0016$$

$$y_{\text{benzene}2} = 0.15 \text{ atm} / 2 \text{ atm} = .075$$

The Air is relatively low solubility in water so

$$N_A = k_y (y_{\text{benzene}1} - y_{\text{benzene}2}) = \frac{k_c' P (y_{\text{benzene}1} - y_{\text{benzene}2})}{RT y_{BM}}$$

$$y_{BM} = \frac{y_{\text{air}2} - y_{\text{air}1}}{\ln(y_{\text{air}2} / y_{\text{air}1})} = .9612$$

$$N_A = -1.2 \times 10^{-6} \text{ gmole} / \text{cm}^2 \text{ s}$$

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		

CEIC 0010, August 31, 1998

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 $4.7 \times 10^{-6} \text{ cm}^2/\text{s}$ (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:

$$D_{AB} = 7.4 \times 10^{-8} (M_B)^{0.5} \frac{T}{\mu_B V_A^{0.6}}$$

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 $1 \times 10^{-4} \text{ gmole urea/cm}^3$.
- 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 $1 \times 10^{-4} \text{ gmole urea/cm}^3$. 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 $8.36 \times 10^{-5} \text{ gmol}/(\text{m}^2 \text{ s atm})$ 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.