Simple problems

1. Diffusion in a Stefan tube
2. Dissolution of a spherical object
3. Diffusion with heterogeneous reaction at surface
4. Diffusion with homogeneous reaction
5. Diffusion into a falling film
6. Gas absorption from a rising bubble
7. Diffusion and reaction in a porous catalyst
8. Transient diffusion through a polymer film
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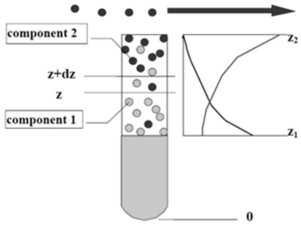
Diffusion in a Stefan tube



Physical system

1. Liquid 1 in the tube
2. Gas 2 flowing across the mouth of the tube
3. Gas 2 is nonsoluble in liquid 1

$$\begin{pmatrix}\text{Rate of}\\ \text{mass in}\end{pmatrix} - \begin{pmatrix}\text{Rate of}\\ \text{mass out}\end{pmatrix} + \begin{pmatrix}\text{Rate of mass}\\ \text{production}\end{pmatrix} = (\text{Accummulation})$$

$$S \cdot N_1\big|_z - S \cdot N_1\big|_{z+\Delta z} + 0 = 0$$

Taking the shell as thin as possible:

$$-\frac{dN_1}{dz} = 0$$

which simply states that the molar flux is constant along the tube.

Step 6: Apply the Fick's law

$$N_1 = -cD_{12}\frac{dx_1}{dz} + x_1\left(N_1 + N_2\right)$$

is *equal to zero* as the species 2 is nonsoluble in liquid 1. This is called the bootstrap condition.

Thus, we solve for N_1 in terms of the concentration gradient.

$$N_1 = -\frac{cD_{12}}{1-x_1}\frac{dx_1}{dz}$$

Substitute this into the mass balance equation:

$$-\frac{dN_1}{dz} = 0$$

we get

$$\frac{d}{dz}\left(\frac{cD_{12}}{1-x_1}\frac{dx_1}{dz}\right) = 0$$

For constant total pressure and constant diffusion coefficient, we have:

$$\frac{d}{dz}\left(\frac{1}{1-x_1}\frac{dx_1}{dz}\right) = 0$$

which is a second-order differential equation in terms of mole fraction.

The two boundary conditions are:

$$z = z_1; \quad x_1 = x_{1,0} = \frac{p_1^0}{P}$$

vapor pressure

total pressure

$$z = z_2; \quad x_1 = x_{1,L}$$

$$\frac{d}{dz}\left(\frac{cD_{12}}{1-x_1}\frac{dx_1}{dz}\right) = 0$$

that is

$$\frac{cD_{12}}{1-x_1}\frac{dx_1}{dz} = K_1(\text{constant})$$

and hence

$$cD_{12}\ln\left(\frac{1}{1-x_1}\right) = K_1 z + K_2$$

Here, we have two constants K_1 and K_2, so apply the two boundary conditions:

$$@\, z = z_1; \quad cD_{12}\ln\left(\frac{1}{1-x_{1,0}}\right) = K_1 z_1 + K_2$$

$$@\, z = z_2; \quad cD_{12}\ln\left(\frac{1}{1-x_{1,L}}\right) = K_1 z_2 + K_2$$

Solving for K_1 and K_2, we get:

$$K_1 = \frac{cD_{12}}{z_2 - z_1}\ln\left(\frac{1-x_{1,0}}{1-x_{1,L}}\right)$$

$$K_2 = cD_{12}\ln\left(\frac{1}{1-x_{1,L}}\right) - \frac{cD_{12}z_1}{z_2 - z_1}\ln\left(\frac{1-x_{1,0}}{1-x_{1,L}}\right)$$

Thus, the concentration profile is:

$$\boxed{\left(\frac{1-x_1}{1-x_{1,0}}\right) = \left(\frac{1-x_{1,L}}{1-x_{1,0}}\right)^{(z-z_1)/(z_2-z_1)}}$$

The quantity of interest is the molar flux from the liquid surface (evaporation rate):

$$N_1 = -\frac{cD_{12}}{1-x_1}\frac{dx_1}{dz}$$

Where should we evaluate the above derivative to obtain the evaporation rate? At the liquid surface?

During the integration for the concentration profile, we see that:

$$\frac{cD_{12}}{1-x_1}\frac{dx_1}{dz} = K_1$$

Thus, the evaporation rate is:

$$N_1 = \frac{cD_{12}}{z_2 - z_1}\ln\left(\frac{1-x_{1,L}}{1-x_{1,0}}\right)$$

This is the desired relation.

If the gas 2 is sweeping past the mouth fast enough, the concentration of the species 1 at the mouth will be effectively zero; hence the evaporatic rate is:

$$N_1 = \frac{cD_{12}}{z_2 - z_1}\ln\left(\frac{1}{1-x_{1,0}}\right)$$

Written in terms of pressure, we get:

$$N_1 = \frac{(P/RT)D_{12}}{z_2 - z_1}\ln\left(\frac{1}{1-p_i^0/P}\right)$$

The total molar rate is:

$$N_1 + \overset{\boxed{0}}{\cancel{N_2}} = \frac{(P/RT)D_{12}}{z_2 - z_1}\ln\left(\frac{1}{1-p_i^0/P}\right)$$

We note that the molar flux of the species 2 is:

$$N_2 = \underbrace{-cD_{12}\frac{dx_2}{dz}}_{\text{diffusive flux down the tube}} + \underbrace{x_2\frac{(P/RT)D_{12}}{z_2 - z_1}\ln\left(\frac{1}{1-p_i^0/P}\right)}_{\text{convective flux up the tube}} = 0$$

<u>Drop in liquid level</u>

Due to evaporation, the liquid level will drop, and to determine this drop in level versus time, we have to do the mass balance equation around the liquid.

$$\frac{d(Sz_1\rho_L)}{dt} = -SM_1\frac{(P/RT)D_{12}}{z_2 - z_1}\ln\left(\frac{1}{1-p_1^0/P}\right)$$

The initial condition is:

t=0; $z_1 = z_{10}$

Integration gives the solution:

$$[z_2 - z_1(t)]^2 - (z_2 - z_{10})^2 = \left[2\frac{M_1(P/RT)D_{12}}{\rho_L}\ln\left(\frac{1}{1-p_1^0/P}\right)\right]t$$

The time it takes to empty the tube is:

$$t^* = \frac{z_2^2 - (z_2 - z_{10})^2}{\left[2\frac{M_1(P/RT)D_{12}}{\rho_L}\ln\left(\frac{1}{1-p_1^0/P}\right)\right]}$$

<u>Example:</u>

Species 1: Carbon tetrachloride

Species 2: Air

R = 82.05 cm^3-atm/mole/K

<u>Operating conditions</u>

P = 760 mmHg

T = 273 K

<u>Species characteristics</u>

p_1^0 = 33 mmHg

M_1 = 154 g/mole

ρ_L = 1.59 g/cc

D_{12} = 0.0636 cm^2/sec

<u>Tube height and initial liquid level</u>

z_2 = 40 cm

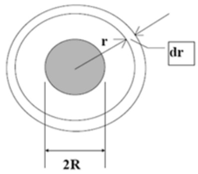
z_{10} = 25 cm

<u>Answer:</u>

t^* = 651 days

Dissolution of a sphere

Sparingly soluble sphere in a surrounding fluid of infinite extent.



The object (species 1) dissolves in surrounding fluid 2 with the solubility of C_{10}.

$$\begin{pmatrix}\text{Rate of}\\ \text{mass in}\end{pmatrix} - \begin{pmatrix}\text{Rate of}\\ \text{mass out}\end{pmatrix} + \begin{pmatrix}\text{Rate of mass}\\ \text{production}\end{pmatrix} = (\text{Accummulation})$$

The mass balance equation around the thin shell at r and having a thickness of dr is:

$$\left(4\pi r^2 N_1\right)\Big|_r - \left(4\pi r^2 N_1\right)\Big|_{r+\Delta r} + 0 = 0$$

Divide the equation by $4\pi\Delta r$, and take the limit of the result when Δr approaches zero, we get

$$\lim_{\Delta r \to 0} \frac{\left(r^2 N_1\right)\Big|_r - \left(r^2 N_1\right)\Big|_{r+\Delta r}}{\Delta r} = -\frac{d}{dr}\left(r^2 N_1\right) = 0$$

$$N_1 = -cD_{12}\frac{dx_1}{dr} + x_1\left(N_1 + N_2\right)$$

can be taken as zero as the species 1 (object) is only sparingly soluble in liquid 2

Thus, the mass balance equation will become:

$$\frac{d}{dr}\left(r^2 c D_{12}\frac{dx_1}{dr}\right) = 0$$

r=R (surface of object); $C_1 = C_{10}$

r $\to \infty$; $C_1 = 0$

$$C_1 = C_{10}\frac{R}{r} \qquad N_1\big|_{r=R} = \frac{D_{12}C_{10}}{R}$$

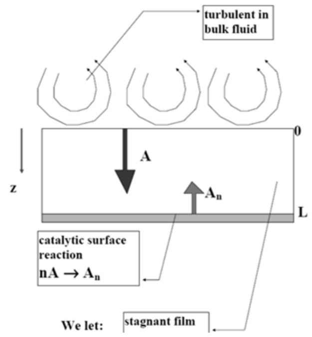
$$N_1\big|_{r=R} = k_m\left(C_{10} - 0\right)$$

Matching this with the solution obtained from first principles, we get:

$$\frac{k_m(2R)}{D_{12}} = 2$$

this is known as the Schmidt number, which is equal to 2 for stagnant environment

Diffusion with heterogeneous reaction



The species A as 1

The species A_n as 2

According to the surface chemical reaction, we must have:

$$N_1 = -n N_2$$

This is the bootstrap condition, needed in addition to the Fick's law equation.

Recall that the bootstrap condition in the last example of the Stefan tube is:

$$N_2 = 0$$

The Fick's law equation is:

$$N_1 = -cD_{12}\frac{dx_1}{dz} + x_1\left(N_1 + N_2\right)$$

But the bootstrap relation is:

$$N_2 = -\frac{1}{n}N_1$$

Thus, solving for N_1 in terms of the concentration gradient gives:

$$N_1 = -\frac{cD_{12}}{\left[1 - \frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}$$

Substitute this Fick's law into the mass balance equation, we have:

$$\frac{d}{dz}\left\{\frac{cD_{12}}{\left[1-\frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}\right\}=0$$

The boundary conditions will be at two ends of the stagnant film:

$$z = 0; \qquad x_1 = x_{10}$$

$$z = L; \qquad N_1\big|_{z=L} = kcx_1\big|_{z=L}$$

where L is the thickness of the film.

The surface chemical reaction rate is:

$$kcx_1\big|_{z=L} \equiv \frac{\text{moles of A reacted}}{\text{area of catalyst} - \text{time}}$$

Observing the boundary condition at the surface of the catalyst, we see that

when $k \to \infty$ (very fast chemical reaction), the surface concentration of the species 1 will be practically zero.

Thus, the boundary condition at the surface in the case of fast reaction is:

$$z = L; \qquad x_1\big|_{z=L} = 0$$

We will now solve for the case of fast reaction first, and then return to the case of finite reaction later.

Recall the mass balance equation

$$\frac{d}{dz}\left\{\frac{cD_{12}}{\left[1-\frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}\right\}=0$$

Integrating once:

$$\frac{cD_{12}}{\left[1-\frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}=K_1$$

Integrating once more:

$$cD_{12}\ln\left[\frac{1}{1-(n-1)x_1/n}\right]=\frac{(n-1)}{n}K_1 z+K_2$$

Two unknown constants of integration with two boundary conditions.

Apply the boundary conditions:

@ $z = 0$;

$$cD_{12}\ln\left[\frac{1}{1-(n-1)x_{10}/n}\right]=K_2$$

@ $z = L$; $\qquad \frac{(n-1)}{n}K_1 L + K_2 = 0$

from which we can solve for K_1 and K_2.

The concentration distribution:

$$\left[1-\frac{(n-1)}{n}x_1\right]=\left[1-\frac{(n-1)}{n}x_{10}\right]^{(1-z/L)}$$

This equation shows how the concentration of the species 1 will distribute itself in the stagnant film.

The distribution of the species 2 is simply:

$$x_2 = 1 - x_1$$

To calculate the reaction rate, we simply calculate the Fickian flux at the catalytic surface.

$$N_1\big|_{z=L}=-\frac{cD_{12}}{\left[1-\frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}\bigg|_{z=L}$$

But remember that during the integration, we have:

$$N_1\big|_{z=L}=-\frac{cD_{12}}{\left[1-\frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}\bigg|_{z=L}=-K_1$$

that is:

$$N_1\big|_{z=L}=\frac{[n/(n-1)]cD_{12}}{L}\ln\left[\frac{1}{1-(n-1)x_{10}/n}\right]$$

This flux at the surface is exactly the same as the chemical reaction rate.

Now we turn to the case when the chemical reaction is finite.

Recall the mass balance equation and the boundary conditions are:

$$\frac{d}{dz}\left\{\frac{cD_{12}}{\left[1-\frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}\right\}=0$$

$$z = 0; \qquad x_1 = x_{10}$$

$$z = L; \qquad N_1\big|_{z=L} = kcx_1\big|_{z=L}$$

Integrating the mass balance once:

$$\frac{cD_{12}}{\left[1-\frac{(n-1)}{n}x_1\right]}\frac{dx_1}{dz}=K_1$$

Integrating once more:

$$cD_{12}\ln\left[\frac{1}{1-(n-1)x_1/n}\right]=\frac{(n-1)}{n}K_1 z+K_2$$

Apply the boundary conditions:

@ z = 0;

$$cD_{12}\ln\left[\frac{1}{1-(n-1)x_{10}/n}\right]=K_2$$

@ z = L; $\quad K_1=-kcx_{1,L}$

The concentration distribution is:

$$\ln\left[\frac{1-(n-1)x_{1,0}/n}{1-(n-1)x_1/n}\right]=-\frac{(n-1)}{n}\cdot\frac{kx_{1,L}}{D_{12}}z$$

where $x_{1,L}$ is still an unknown mole fraction at the catalytic surface. It is determined by setting z = L

$$\ln\left[\frac{1-(n-1)x_{1,L}/n}{1-(n-1)x_{1,0}/n}\right]=\frac{(n-1)}{n}\cdot\left(\frac{kL}{D_{12}}\right)x_{1,L}$$

which is a nonlinear algebraic equation in terms of the mole fraction at the catalytic surface.

Knowing the mole fraction at the catalytic surface

$$\ln\left[\frac{1-(n-1)x_{1,L}/n}{1-(n-1)x_{1,0}/n}\right]=\frac{(n-1)}{n}\cdot\left(\frac{kL}{D_{12}}\right)x_{1,L}$$

the chemical reaction rate can be obtained from:

$$N_1\big|_{z=L}=\frac{[n/(n-1)]cD_{12}}{L}\ln\left[\frac{1-(n-1)x_{1,L}/n}{1-(n-1)x_{1,0}/n}\right]$$

$$=kcx_{1,L}$$

We see that the nonlinear algebraic equation for $x_{1,L}$ involves a dimensionless group

$$\left(\frac{kL}{D_{12}}\right)\equiv\frac{\text{chemical reaction rate}}{\text{diffusion rate}}$$

Case 1: **If this group is very large, that is the chemical reaction rate is much larger than the diffusion rate, we get:**

$$x_{1,L}=0$$

and the chemical reaction rate is:

$$N_1\big|_{z=L}=\frac{[n/(n-1)]cD_{12}}{L}\ln\left[\frac{1}{1-(n-1)x_{1,0}/n}\right]$$

which is exactly the equation we obtained earlier for fast reaction.

Case 2: **When the dimensionless group is less than unity, that is the reaction is very slow compared to the diffusion rate, we have:**

$$x_{1,L}=x_{1,0}$$

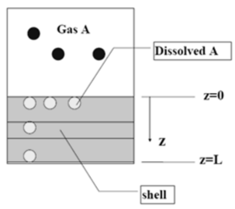
Thus, the chemical reaction rate is:

$$N_1=kcx_{1,0}$$

The chemical reaction in the case of fast diffusion is dominated entirely by chemical kinetics.

Diffusion & homogeneous reaction

The difference between this and the last two examples is the appearance of the reaction term in the mass balance equation, in contrast to the second example where the reaction term appears in the boundary condition.



Physical system

1. **Gas A dissolves sparingly in liquid B**
2. **Dissolved A reacted with B, following a first order kinetics with expression**

$$\left(\frac{\text{moles of A reacted}}{\text{volume}-\text{time}}\right)=kC_1$$

3. **Isothermal system**
4. **Let species A be 1, and species B be 2**

Solubility, in general, increases linearly with pressure and decreases with temperature.

$$\left(\begin{matrix}\text{Rate of}\\ \text{mass in}\end{matrix}\right)-\left(\begin{matrix}\text{Rate of}\\ \text{mass out}\end{matrix}\right)+\left(\begin{matrix}\text{Rate of mass}\\ \text{production}\end{matrix}\right)=(\text{Accummulation})$$

$$(SN_1)\big|_z-(SN_1)\big|_{z+\Delta z}-(S\Delta z)kC_1=0$$

Divide the shell mass balance by $S\Delta z$, and then take the limit when $\Delta z\to 0$:

$$-\frac{dN_1}{dz}-kC_1=0$$

chemical reaction appearing in the mass balance equation

Apply the Fick's law

negligible because A is sparingly soluble in B

$$N_1 = -cD_{12}\frac{dx_1}{dz} + x_1(N_1 + N_2)$$

Thus

$$N_1 = -D_{12}\frac{dC_1}{dz}$$

Substitute this into the mass balance equation, we get:

$$D_{12}\frac{d^2C_1}{dz^2} - kC_1 = 0$$

This is a typical form of simultaneous diffusion and reaction equation.

At the gas-liquid interface, we have the solubility condition:

@ $z = 0$; $C_1 = C_{10}$ (solubility)

For constant T and P, this solubility is a constant.

The other boundary condition is at the bottom of the liquid pool.

At the bottom, mass can not penetrate, thus:

@ $z = L$; $N_1 = 0$

Using the Fick's law at this point (z=L), we have:

$$@\ z = L;\quad N_1\big|_{z=L} = -D_{12}\left.\frac{dC_1}{dz}\right|_{z=L} = 0$$

$$\frac{C_1}{C_{10}} = \frac{\cosh\left[\left(1-\frac{z}{L}\right)\sqrt{\frac{kL^2}{D_{12}}}\right]}{\cosh\left(\sqrt{\frac{kL^2}{D_{12}}}\right)}$$

Note that the three parameters of the system, namely

1. **reaction rate constant, k**
2. **depth of the liquid pool, L**
3. **diffusion coefficient, D_{12}**

are grouped together.

It is dimensionless. It is known as the Damkohler* number (1937).

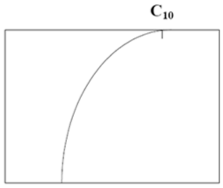
$$Da = \frac{kL^2}{D_{12}}$$

***: German chemist (1908-1944)**

The solution:

$$\frac{C_1}{C_{10}} = \frac{\cosh\left[\left(1-\frac{z}{L}\right)\sqrt{Da}\right]}{\cosh\left(\sqrt{Da}\right)}$$

The good thing about the dimensionless group is that systems having the same value of the dimensionless will behave identically.



To calculate the mass transfer of A (gas absorption rate) into the liquid B, we simply apply the Fick's law and evaluate at the gas-liquid interface.

$$N_1\big|_{z=0} = -D_{12}\left.\frac{dC_1}{dz}\right|_{z=0}$$

$$N_1\big|_{z=0} = \frac{C_{10}D_{12}}{L}\sqrt{Da}\cdot\tanh\left(\sqrt{Da}\right)$$

$$N_1\big|_{z=0} = \frac{C_{10}D_{12}}{L}\sqrt{\frac{kL^2}{D_{12}}}\cdot\tanh\left(\sqrt{\frac{kL^2}{D_{12}}}\right)$$

This is the gas absorption rate per unit interfacial area.

Let's have a look at the Damkohler number:

$$Da = \frac{kL^2}{D_{12}} \equiv \frac{(L^2/D_{12})}{(1/k)} \equiv \frac{\text{diffusion time}}{\text{reaction time}}$$

There are two extreme cases:

<u>Case</u> 1:

When Da << 1, the diffusion time is very short compared to the reaction time.

<u>Case 2:</u>

When Da >> 1, the diffusion time is much larger than the reaction time.

Case 1: Da << 1

This means that dissolved A will have time to penetrate throughout the liquid B before reaction could take place. One expects:

$$C_1(z) = C_{10}$$

and

$$N_1 = LkC_{10}$$

To prove this expectation, we take the limit of the solution

$$\lim_{Da \to 0} N_1\Big|_{z=0} = \frac{C_{10} D_{12}}{L} Da = LkC_{10}$$

In this case, there is no diffusivity term as the system is ***kinetically controlled***

Also the limit of the concentration distribution will give:

$$C_1\,(z) = C_{10}$$

Case 2: Da >> 1

In this case, the reaction is so fast, so the penetration of the dissolved A can not go far into the liquid pool.

The gas absorption rate is:

$$\lim_{Da>>1} N_1\Big|_{z=0} = \frac{C_{10} D_{12}}{L}\sqrt{Da} = C_{10}\sqrt{k \cdot D_{12}}$$

Observation:

1. Rate is proportional to the solubility
2. Rate is proportional to square root of chemical reaction rate
3. Rate is proportional to square root of diffusivity
4. Rate is independent of the depth of the liquid pool (is this expected?).

This case is the diffusion-controlled case.

Before we leave this example, there is a quantity that engineers use to quantify the influence of diffusion.

This is the ratio of the true absorption rate to the ideal absorption rate (in the absence of diffusion):

$$\eta = \frac{N_1\big|_{z=0}}{N_1^{\text{no diffusion}}\big|_{z=0}} = \frac{\tanh\left(\sqrt{Da}\right)}{\sqrt{Da}} = \frac{\tanh\left(\sqrt{\frac{kL^2}{D_{12}}}\right)}{\sqrt{\frac{kL^2}{D_{12}}}}$$

This ratio is known as the effectiveness factor.