Three simple problems on mass transfer

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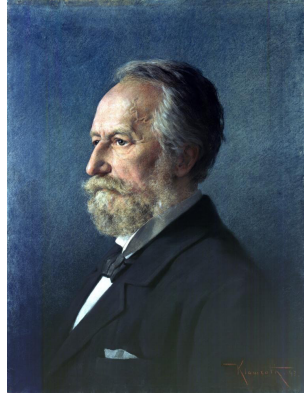February 6, 2014

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Figure 1: Adolf Eugen Fick (1829-1901) was a german physiologist, with an education in physics, mathematics, and medicine. Beyond his contributions to the topic of diffusion, he also gave his name to Fick's principle, which notably enables one to measure the oxygen consumption by organs.
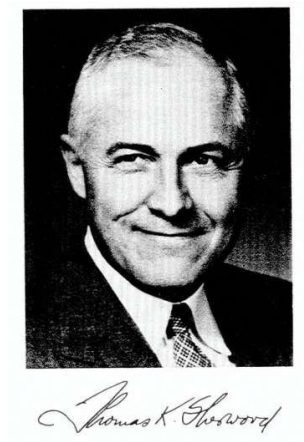

Figure 2: Thomas Kilgore Sherwood (1903-1976) was an american chemical engineer who did most of his career at the MIT. The dimensionless number that used to be named the "Nusselt number for mass transfer" is now named after him: the Sherwood number.

Fick's laws: a back to basics

For now, we consider mass transport in a medium at rest and with no chemical reaction.

The basic laws of diffusion bear the name of Fick. Fick's first law relates the diffusion flux J_D (e.g. in mol/s/cm^2) to a concentration gradient.

$$J_D = -D\nabla C \tag{1}$$

Be aware that this is a vectorial equation. Inspecting this equation shows that the dimensions of D is cm^2/s. We shall come back to this in more details later.

Eq. 1 enables you to calculate how many molecules diffuse across a given surface, once the concentration distribution is known. It does not enable you to calculate what the concentration distribution is. To do that, you need to combine Fick's first law with the general equation of mass conservation, namely

$$\partial_t C + \nabla \cdot J_D = 0 \tag{2}$$

where $\nabla\cdot$ is the divergence operator. In the case where D is a constant, this leads to

$$\partial_t C = D\Delta C \tag{3}$$

which is usually referred to as Fick's second law. This is the equation that has to be solved if you want to calculate a concentration profile.

Of course, Eq. 3 is not sufficient to find C. You need to apply boundary conditions. A common type of condition is when the concentration is known to be equal to a given value C_0 at a surface of the domain

$$C = C_0 \quad \text{at a surface} \tag{4}$$

You may also know the flux of molecules J_0 through a surface. In this case, the condition is

$$D\mathbf{n} \cdot \nabla C = J_0 \quad \text{at a surface} \tag{5}$$

where $\mathbf{n}$ is the normal vector to the surface. You may of course have (slightly) more complicated conditions, such as

$$D\mathbf{n} \cdot \nabla C = kC \quad \text{at a surface} \tag{6}$$

Think about what the latter equation means. When you can expect to encounter this type of boundary condition?

The situation where the concentration does not depend on the time, but only on the position, is referred to as being *stationary*. It is important that you understand that you can have transport phenomena going on although the concentrations are stationary. **It is the gradients that matter for the transport, not the time derivatives**. In a stationary situation, the concentration obeys simply

$$\Delta C = 0 \tag{7}$$

In Cartesian coordinates, the Laplacian operator is

$$\Delta C = \partial_{xx}^2 C + \partial_{yy}^2 C + \partial_{zz}^2 C \tag{8}$$

For spherically symmetric concentration profiles, the expression is

$$\Delta C = \frac{1}{r^2} \partial_r (r^2 \partial_r C) \tag{9}$$

where r is the radial coordinate. For cylindrical symmetry, the expression is

$$\Delta C = \frac{1}{r} \partial_r (r \partial_r C) \tag{10}$$

Note that when analysing diffusion problems, we are often tempted to draw linear concentration profiles. Linear concentration profiles are expected only between flat parallel surface. Profiles can often be approximated by linear functions when the two surface are very close together. To put it precisely, when the distance between the two surfaces is much smaller than the radius of curvature of the surface. We shall come back to this is the exercises.

The three problems presented here have bee chosen as typical of (i) stationary, (ii) transient, and (iii) quasi-stationary diffusion. If you don't see why, ask me!

1 Sparkling water going flat

You are asked to estimate how long it takes for sparkling water to "go flat" when it is kept in a PET bottle. The initial pressure in the bottle is 2 bars, and one asks when the pressure will reach the limit 1.5 bars.

The volume of the bottle is 1.5 L. It is made of PET with thickness 250 microns, and the area of the bottle is 800 cm². The solubility of CO_2 in PET obeys Henry's law $P = kc$ with $k^{PET} = 29.4\ L \times bar/mol$. The solubility of CO_2 in water also obeys Henry's law with $1/k_H^W = 1.7 m^3 (STP)/(m^3 \times bar)$. The diffusion coefficient of CO_2 in PET is $2\ 10^{-13}\ m^2/s$.

Consider that the system reaches rapidly a stationary state. You can also neglect the amount of CO_2 inside the bottle that is in the gas phase.
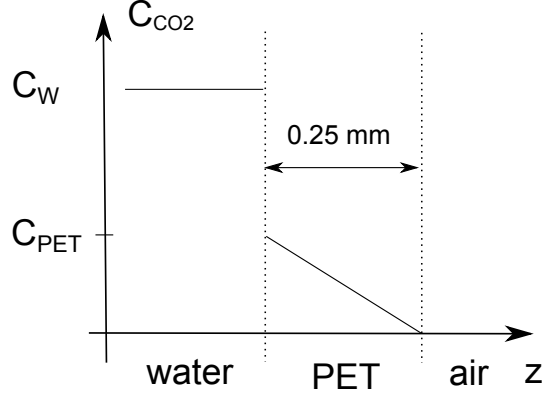
Figure 3: Sketch of the CO_2 concentration profile along a direction perpendicular to the bottle wall.

Solution

We shall first express the two Henry constants in the same units. They are

$$
\begin{aligned}
1/k^W &= 1.7/22.4 = 0.0759 \quad mol/L/bar \\
1/k^{PET} &= 0.034 \quad mol/L/bar
\end{aligned}
$$

where we have used the known volume of a mole of gas in STP conditions.

The CO_2 concentration in the water is related to the pressure through

$$
C_W = \frac{P}{k^W} \tag{11}
$$

and the concentration in the PET at the water/PET interface is

$$
C_{PET} = \frac{P}{k^{PET}} \tag{12}
$$

The value $1/k^{PET}$ being different from $1/k^W$, there is a concentration discontinuity at the water/PET interface.

The PET wall being very thin compared to the radius of the bottle, the PET wall can be assumed to be flat for all practical purposes. When the stationary state is reached, the concentration profile in the PET wall is therefore linear, ranging from the value given in Eq. (12) to 0 at the outer surface of the PET wall. The general situation is sketched in Fig. 1.

The flux per unit surface area is calculated through Fick's first law as

$$J_D = D\frac{C_{PET}}{l} = D\frac{P}{lk^{PET}} \qquad (13)$$

where l is the thickness of the wall (250 microns). To calculate the number of moles of CO_2 that leave the bottle per unit time, one has to multiply that expression by the total area A (800 cm^2).

To calculate the evolution of the pressure in teh bottle, one has to relate it to the total number of CO_2 molecules in it. The relation is

$$N_{CO2} = c_W V_W = P\frac{V_W}{k^W} \qquad (14)$$

where V_W is the volume of water. We have neglected here the amount of CO_2 in the gas phase, as suggested.

Mass conservation requires that (minus) the time-derivative of N_{CO2} be equal to $A \times J_D$, which leads to the following ODE

$$\frac{dP}{dt} = -\frac{P}{\tau} \qquad (15)$$

where τ is a characteristic time given by

$$\tau = \frac{V_W l}{AD}\frac{k^{PET}}{k^W} \qquad (16)$$

Using the numerical values given here, one has $\tau \simeq 542$ days.

The solution of Eq. (15) is an exponential of the form

$$P(t) = P(0)e^{-t/\tau} \qquad (17)$$

2 Vapour concentration over an evaporating surface

Imagine you have an infinite flat surface of water from which molecules evaporate. You are asked to calculate the time-dependent water vapour concentration profile over the surface, assuming that there are initially no water molecules in the air.

1. Write the equation that has to be solved to calculate $C(z, t)$, where z is the height above the surface and t is the time, as well as the boundary conditions. Do not attempt to solve the equation yet.

2. Use dimensional analysis to find the general form of the solution.

3. Using the general form of the solution obtained from dimensional analysis, solve the equation you wrote at point 1. Express the solution in terms of the error function $\text{erf}(x)$ defined as

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} \, dt$$

which takes the value $\text{erf}(\infty) = 1$.

Solution

1. The equation is Fick's second law

$$\partial_t C = D \partial_{zz}^2 C \tag{18}$$

in the domain $z \in (0, \infty)$, with boundary conditions $C(x = 0, t) = C_0$ and $C(x \to \infty, t) = 0$. The constant C_0 is the equilibrium water vapour pressure at the considered temperature.

2. In dimensional form, the solution we are looking for is something like

$$C = f(z, t, D, C_0) \tag{19}$$

where $f()$ is an undetermined function. There are 5 variables and 3 dimensions (moles, length, time) so that the system is governed by two dimensionless variables. The dimension "mole" only appears in C and C_0, so that the first number is

$$\Pi_0 = \frac{C}{C_0} \tag{20}$$

The only dimensionless combination of the remaining variables is

$$\Pi_1 = \frac{z}{\sqrt{Dt}} \tag{21}$$

This means that the solution of the problem has to be of the type

$$\frac{C}{C_0} = F\left(\frac{z}{\sqrt{Dt}}\right) \tag{22}$$

which is the answer to the question.

A few comments. From the boundary conditions, we know that $F(0) = 1$ and $F(\infty) = 0$. The function $F(\xi)$ characterises the shape of the water-vapour concentration front. Of course at this stage, we do not know the shape of the front. For instance, we do not known whether it is sharp of blurry, etc. However, Eq. 22 tells already a lot. For example, let $\xi_{1/2}$ be the value of ξ where $F = 1/2$. We don't know the value of $\xi_{1/2}$ but this is not important. The diffusion front arrives

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at the height z when $z/\sqrt{Dt} = \xi_{1/2}$. In other words, the front moves according to

$$z = \xi_{1/2}\sqrt{Dt} \tag{23}$$

This tells you that if you have to wait four times longer to see the front go two times further. We haven't solved any equation yet, and look what we already know! Isn't that beautiful?

3. Using the general form obtained from dimensional analysis

$$\partial_t C = -\frac{Dz}{2}\frac{1}{\sqrt{Dt}}\frac{dF}{d\xi} \quad \partial_{zz}^2 C = \frac{1}{Dt}\frac{d^2 F}{d\xi^2} \tag{24}$$

Introducing this is Fick's second law, one finds the following ODE

$$\frac{d^2 F}{d\xi^2} = -\frac{\xi}{2}\frac{dF}{d\xi} \tag{25}$$

See how dimensional analysis has enabled us to come from a partial differential equation and transform it into a much simpler ordinary differential equation.

The solution is found to be

$$\frac{dF}{d\xi} = Ae^{-\xi^2/4} \tag{26}$$

where A is an unknown constant. This leads to

$$F(\xi) = A\int_0^\xi e^{-t^2/4}dt + B = A'\text{erf}\left(\frac{\xi}{2}\right) + B \tag{27}$$

where A' is a constant. The values of the constants A' and B are obtained from the boundary conditions. The final result is

$$\frac{C}{C_0} = 1 - \text{erf}\left(\frac{z}{2\sqrt{Dt}}\right) \tag{28}$$

Compare this to 22. We haven't learnt much by solving the equation; most of the information came from the dimensional analysis.

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3   Lifetime of an aerosol

An aerosol consisting a micrometer-sized droplets of liquid in suspension in air. The purpose of the present problem is to determine the kinetics of evaporation of such a droplet, in oder to determine its lifetime. The atmosphere is always subject to natural convection, but the droplets are so small that they are carried away with the air. For practical purposes, you can therefore assume that the air is still.

1. Assuming that the size of the droplet does not change with time, write down the equations that would have to be solved in order to calculate the water vapour concentration profile around the droplet $c(r)$. Use spherical coordinates. What are the boundary conditions?

2. Assuming that $c(r)$ were known to you, how would you calculate the evaporation rate $\dot{N}$ (in mole/s) of the droplet?

3. Use dimensional analysis to find the general form of $\dot{N}$ as a function of all relevant dimensional variables.

4. Solve the equation obtained at point 1, calculate $\dot{N}$, and put the result in the same dimensionless form as in point 3.

5. Using the previous results in a pseudo-stationary approximation, find the ODE that governs the evolution of the droplet radius against time. Solve that equation analytically, and determine the time τ it takes a droplet to evaporate.

6. Assuming a temperature of 30 °C (corresponding to a saturating pressure of 5 kPa), a relative humidity far away from the droplet of 30 %, and a diffusion coefficient $D \simeq 1cm^2/s$, calculate the evaporation time for a droplet with initial size $R_0 = 1 \ \mu m$ and $R_0 = 1 \ mm$.

Solution

1. That's Fick's second law. The stationary version of it, i.e. $\Delta c = 0$. In spherical coordinates, it takes the form

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dc}{dr}\right) = 0 \qquad (29)$$

   With boundary conditions $c = c_0$ at $r = R$ (i.e. saturating vapour pressure at the surface of the liquid) and $c = c_1$ far from the particle $r \to \infty$ where c_1 is the ambient humidity.

2. The evaporation rate is by definition the number of water molecules that diffuse away from the droplet. The rate is therefore calculated by Fick's first law. All we have to do is chose a surface that surrounds the droplet and integrate the flux on it

$$\dot{N} = \int_{surface} D\mathbf{n} \cdot \nabla c \, dA \qquad (30)$$

   where $\mathbf{n}$ is a normal vector to the surface. The choice of the surface does not matter; any surface will give you the same value for $\dot{N}$. This is a consequence of stationarity, be sure you understand why.

   The simplest surface we may consider in our case is that of the droplet itself. The result is therefore

$$\dot{N} = 4\pi R^4 D \left(\frac{dc}{dr}\right)_{r=R} \qquad (31)$$

3. In dimensional form, the relation we are looking for is

$$\dot{N} = f(R, D, c_0, c_1) \qquad (32)$$

   There are 5 variables and 3 dimensions. That's two dimensionless numbers. You have, however, some freedom in the way to write them. A convenient choice is

$$\Pi_0 = \frac{\dot{N}}{DRc_0} \quad \Pi_1 = \frac{c_1}{c_0} \qquad (33)$$

   The general function is therefore

$$\frac{\dot{N}}{DRc_0} = F\left(\frac{c_1}{c_0}\right) \qquad (34)$$

If you are really on the ball, you may have noticed at this stage that c_0 and c_1 are not really two independent numbers, because you expect their difference $c_0 - c_1$ to be the important variable. You are therefore left with only one dimensionless number, namely

$$\Pi_0 = \frac{\dot{N}}{DR(c_0 - c_1)} \tag{35}$$

which can therefore only be a constant. The total evaporation rate is therefore simply

$$\dot{N} = \text{constant} \times DR(c_0 - c_1) \tag{36}$$

4. The solution to Eq. 29 satisfying the boundary conditions is

$$c = (c_0 - c_1)\frac{R}{r} + c_1 \tag{37}$$

Introducing this in Eq. 31 leads to

$$\dot{N} = 4\pi DR(c_0 - c_1) \tag{38}$$

which shows that the unknown constant in Eq. 36 is equal to 4π.

A more familiar way of writing this result is in terms of the Sherwood number. In the case of a spherical object, the Sherwood number is defined as

$$\text{Sh} = \frac{J_D}{D(c_0 - c_1)/(2R)} \tag{39}$$

where J_D is the flux per unit area, i.e. $\dot{N}/(4\pi R^2)$. With that definition, Eq. 38 can simply be written as

$$\text{Sh} = 2 \tag{40}$$

This is probably a familiar result to you.

5. When water evaporates from the droplet, its volume decreases as a result of mass conservation. The equation governing the evolution of its radius is

$$\frac{4\pi R^2}{v_m}\frac{dR}{dt} = -4\pi DR(c_0 - c_1) \tag{41}$$

The left-hand side is the variation of the number of water molecules in the droplet, with v_m the molecular volume, and the right-hand side is simply $\dot{N}$. The equation can be rewritten as

$$\frac{dR^2}{dt} = -2Dv_m(c_0 - c_1) \tag{42}$$

with the solution

$$R(t) = R(0)\sqrt{1 - \frac{t}{\tau}} \tag{43}$$

with

$$\tau = \frac{R(0)^2}{2v_m D(c_0 - c_1))} \tag{44}$$

The quantity τ is the time at which the particle reaches the size $R = 0$. In other words, τ is its lifetime.

6. Let us first put all relevant data in consistent units. The partial pressure 5 kPa is converted to mol/m^3 using the perfect gas law $c = P/(R_G T)$ where $R_G = 8.314$ J/mol/K is the gas constant. This leads to

$$c_0 - c_1 = \frac{5\ 10^3}{8.314 \times (273 + 30)}(1 - 0.3) \simeq 1.39\ 10^{-3} mol/m^3 \tag{45}$$

The molar volume of water is obtained as

$$v_m = \frac{10^{-3}m^3/kg}{1000/18 mol/kg} \simeq 18\ 10^{-6} m^3/mol \tag{46}$$

The diffusion coefficient is $D = 10^{-4}m^2/s$. This leads to $\tau \simeq 0.2s$ for $R(0) = 10^{-6}m$. A droplet that would be 10^3 times larger would evaporate 10^6 times slower. Its evaporation time would be about 55 h in the same conditions.

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A few other problems

1. Find back the form of Fick's second law in spherical coordinates by writing mass balance equations in spherical shells.

2. Any function $f(\mathbf{x})$ satisfying $\Delta f = 0$ at a point $\mathbf{x}_0$ has the following interesting property, which provides an intuitive interpretation to Fick's second law. If you draw an infinitesimally small sphere centred on $\mathbf{x}_0$ and calculate the average value of f on the sphere, you will find it equal to $f(\mathbf{x}_0)$. Can you prove this mathematically?

3. Consider the case of Exercise 2. Use dimensional analysis to find how the evaporation rate J (in mole/s/m^2) depends on time.

4. Gas in a box, with certain molecules in concentration C_0 which can diffuse with coefficient $D0$. At time $t = 0$ one wall is suddenly heated to such a temperature that any molecule touching the wall is chemically decomposed. The question is "how many molecules will have decomposed at time t?". Proceed like in Exercise 2.

5. There are some nasty molecules in a gas, in concentration C_0 with diffusing coefficient D. The molecules are soluble in water, which offers us the possibility of capturing them in an aerosol. Assuming that the molecules are so soluble that they dissolve as soon as they touch the surface of the water droplet, what is the steady-state rate of molecules dissolving in a droplet, as a function of its diameter d? For this exercise, you do not have to solve Fick's equation. Simply start from Sh $= 2$.