

6.4 Mathematical solutions for limiting cases

Mathematically Eqs. (6.12), (6.13), and (6.14) represent a set of differential equations of first order with constant coefficients which can always be solved by an exponential approach. Many kinetic problems are simplified to this degree to make possible an analytic solution of the full kinetic scheme and an application of some standard tricks to further analyze certain limiting cases. Later on we will calculate the full problem and so double check the validity of the following (simple) calculations.

1. First let us assume just a tiny opening A_{23} between the vapor phase in the bottle to the surrounding, leading to a tiny value of k_2 , much smaller than k_1 and k_3 . So the transport of carbon dioxide out of the bottle is the slowest process and therefore called the rate determining step. We have to wait for a long time, i.e. solve the problem for large times in order to be sensitive to this slow carbon dioxide loss. k_1 and k_3 are so large that it just takes an irrelevant time for the carbon dioxide within the bottle to relax into nearly thermodynamic equilibrium, i.e. $dI_1/dt \approx 0$ holds for the time scale under investigation. So according to Eq. (6.12) we get

$$k_1 I_1 = k_3 I_2 \quad . \quad (6.15)$$

This approach and the corresponding result is called the pre-steady state condition and is often applied in the discussion of transport and kinetic phenomena. Additionally the conservation of carbon dioxide molecules reads $I_1(t) + I_2(t) + I_3(t) = I_0$ where $I_0 = I_1(0) + I_2(0)$ is the starting amount of carbon dioxide molecules in the bottle. Including all relations into Eq. (6.13) we get

$$\frac{dI_3}{dt} = -k_2 \frac{k_1}{k_1 + k_3} (I_3 - I_0) \quad , \quad (6.16)$$

which is a simple first order inhomogeneous linear differential equation. Introducing a new variable $I(t) = I_3(t) - I_0$ the differential equation becomes homogeneous. Taking $I_3(0) = 0$ the final solution of this differential equation is

$$I_3(t) = I_0 \left[1 - \exp \left(-\frac{k_2 k_1}{k_1 + k_3} t \right) \right] \quad . \quad (6.17)$$

So the kinetics of the outlet is not only defined by its direct kinetic coefficient but by the type of thermodynamic equilibrium which forms within the bottle, i.e. $k_{effective} = \frac{k_2 k_1}{k_1 + k_3}$ is a combination of all individual kinetic coefficients.

2. Next we will discuss a completely open bottle, k_2 will become extremely large. All vapor will nearly instantly leave the bottle, so in good approximation $I_2 = 0$. Now the conservation of carbon dioxide molecules reads $I_1(t) + I_3(t) = I_0$ where $I_0 = I_1(0)$ is the starting amount of carbon dioxide molecules in the bottle. Including this into Eq. (6.12) we get

$$\frac{dI_1}{dt} = -k_1 I_1 \quad \text{resp.} \quad I_1(t) = I_0 \exp(-k_1 t) \quad \text{and} \quad I_3(t) = I_0 [1 - \exp(-k_1 t)] \quad . \quad (6.18)$$

So from such an experiment we can extract the pure kinetic coefficient k_1 . The process related to the smallest kinetic coefficient is called the rate limiting step. In a sequence of reactions this process takes longest time and therefore dominates the whole time evolution.

3. As a third limiting case we will discuss $k_2 = 0$, i.e. having no gas leaking out of the bottle. Now the conservation of carbon dioxide molecules reads $I_1(t) + I_2(t) = I_0$ where $I_0 = I_1(0) + I_2(0)$ is the constant overall amount of carbon dioxide molecules in the bottle. Including this into Eq. (6.13)

$$\frac{dI_2}{dt} = k_1 I_0 - (k_1 + k_3) I_2 = -(k_1 + k_3) \left(I_2 - \frac{k_1}{k_1 + k_3} I_0 \right) \quad (6.19)$$

Introducing a new variable $I(t) = I_2(t) - \frac{k_1}{k_1 + k_3} I_0$ the above differential equation gets homogeneous and the solution is

$$I_2(t) - \frac{k_1}{k_1 + k_3} I_0 = \left(I_2(0) - \frac{k_1}{k_1 + k_3} I_0 \right) \exp(-(k_1 + k_3) t) \quad (6.20)$$

So now the effective kinetic coefficient is $k_{effective} = k_1 + k_3$. For $t \rightarrow \infty$ steady state is reached with $I_2(t \rightarrow \infty) = \frac{k_1}{k_1 + k_3} I_0$ and $I_1(t \rightarrow \infty) = I_0 - I_2(t \rightarrow \infty) = \frac{k_3}{k_1 + k_3} I_0$. We see that $k_1 I_1(t \rightarrow \infty) = k_3 I_2(t \rightarrow \infty)$. This is of course the thermodynamic equilibrium composition which e.g. follows directly from Eq. (6.12) taking $dI_1/dt = 0$.

4. For the fourth example we now additionally assume a full bottle, i.e. $V_1 \gg V_2$. So the second slowest kinetic coefficient is k_1 . This should now be the rate determining step. Following the discussion above we would expect the transport from the vapor phase into the water to be much faster than the backward process. BUT our experience tells us just the opposite: When shaking the bottle much gas is leaving the water! Where is the error? Actually we ignored several steps in the reaction chain *within* the water! Carbon acid is formed according to



Additionally the solubility of carbon dioxide in water is small, leading to a phase separation (as discussed in section 5.9) in two phases, one water phase with a small concentration of carbon dioxide and one vapor phase with a small concentration of water(vapor). The kinetics of such redox reaction will be discussed in detail in the summer term. Here it is enough to state that, according to the principle of Le' Chatelier, increasing the pressure will support the formation of carbon acid while reducing the pressure will favor the formation of carbon dioxide. While shaking, some regions within the water will exhibit a reduced local pressure; here carbon dioxide is formed which due to the low solubility nearly instantly leads to the formation of gas bubbles. Much kinetics is involved in this nucleation of gas bubbles, their subsequent growth, their possible sticking to the bottle walls and upwards movement due to the buoyant force (induced by gravity). The backward reaction from carbon dioxide within gas bubbles to carbon acid is much slower, so most of the gas bubbles which formed by shaking the bottle will move upwards into the vapor phase. Only by a comparably slow process this carbon dioxide will again enter the water as described above. The whole process can be summarized again as a reaction scheme similar to Eq. (6.10) with I_1 being carbon dioxide stored as carbon acid, I_2 carbon dioxide bubbles in water, and I_3 carbon dioxide in the above vapor phase. k_1 , k_2 , and k_3 are the corresponding kinetic coefficients which, by solving the set of differential equations, makes it possible to calculate the effective kinetic coefficients as used above. This way one can take into account more and more transport and kinetic processes to describe the time dependencies in a system.

Let us summarize our results:

- In most cases transport and kinetics are much more difficult to understand and to describe than the thermodynamic equilibrium!
- Often various types of forces have to be taken into account: In our example friction forces (sticking to the bottle wall, bubble movement through the viscous water) and gravity.
- Depending on the treatment, e.g. open bottle with and without shaking, different processes have to be taken into account. BUT: Often one effective kinetic coefficient can be assumed to describe such processes. So the equation in limiting case 2 will hold. Just strongly different values for k_1 can be expected.
- By combining several experiments with different limiting cases often a full set the kinetic coefficients can be extracted.
- This heuristic approach does not need any microscopic understanding of the underlying transport mechanisms and kinetic processes. In summer term we will close the missing link to the microscopic world.