Exercise 1: Reaction of sucrose

Meret Aeppli

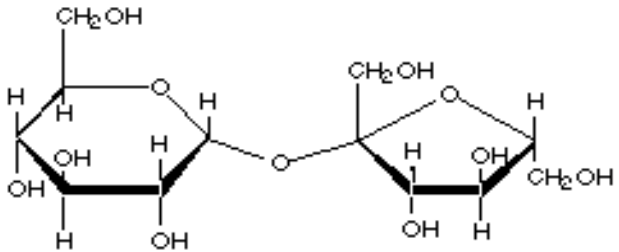
The rate equation for the reaction of sucrose in water is:

$$\text{rate} = -k[C_{12}H_{22}O_{11}].$$

After 2.57 h at 27°C, 5.00 g/L of sucrose has decreased to 4.50 g/L.

Find k.

$$C_{12}H_{22}O_{11} + H_2O \Rightarrow 2\,C_6H_{12}O_6$$



Sucrose

Exercise 1: Solution

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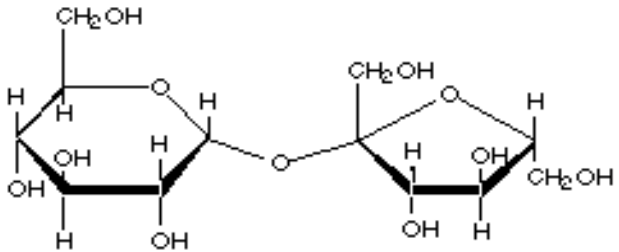
ln 4.50 g/L / 5.00 g/L = - k1 (2.57 h)

k = 0.0410 h^{-1}



Sucrose

Exercise 2: Ammonium cyanate

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Ammonium cyanate, NH_4NCO, rearranges in water to give urea, $(NH_2)_2CO$. If the original concentration of NH_4NCO is 0.458 mol/L and k = 0.0113 M^{-1} min^{-1}, how much time elapses before the concentration is reduced to 0.300 mol/L?

$NH_4NCO \rightarrow (NH_2)_2CO_{(aq)}$ rate = $-k[NH_4NCO]^2$

Exercise 2: Solution

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Initial concentration of NH_4NCO: $[A]_0 = 0.458$ mol/L

$k = 0.0113\ M^{-1}\ min^{-1}$

Final concentration of NH_4NCO: $[A] = 0.300$ mol/L

$t = ?$

Integrated rate law for second order kinetics: $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$

Solve for t: $\frac{1}{k}\left(\frac{1}{[A]} - \frac{1}{[A]_0}\right) = t = \frac{1}{0.0113}\left(\frac{1}{0.300} - \frac{1}{0.458}\right) = \underline{102\ min}$

Exercise 3: Reaction order

Meret Aeppli

What is the reaction order in A and the overall reaction order of the following equations?

1. $-d[A]/dt = k[B]$
2. $-d[A]/dt = k[A]^2$
3. $-d[A]/dt = k[A]^{1.5}[B]$

Exercise 3: Solution

Meret Aeppli

What is the reaction order in A and the overall reaction order of the following equations?

1. $-d[A]/dt = k[B]$: zero order in A, first order overall
2. $-d[A]/dt = k[A]^2$: second order in A, second order overall
3. $-d[A]/dt = k[A]^{1.5}[B]$: 1.5 order in A, 2.5 order overall

Exercise 4: Half-life of SO_2Cl_2

Meret Aeppli

The decomposition of SO_2Cl_2 is first order in SO_2Cl_2 and has a half-life of 4.1 hr. If you begin with 1.6×10^{-3} mol of SO_2Cl_2 in a flask, how many hours elapse before the quantity of SO_2Cl_2 has decreased to 2.00×10^{-4} mol?

$$SO_2Cl_{2(g)} \rightleftharpoons SO_{2(g)} + Cl_{2(g)}$$

Exercise 4: Solution

Meret Aeppli

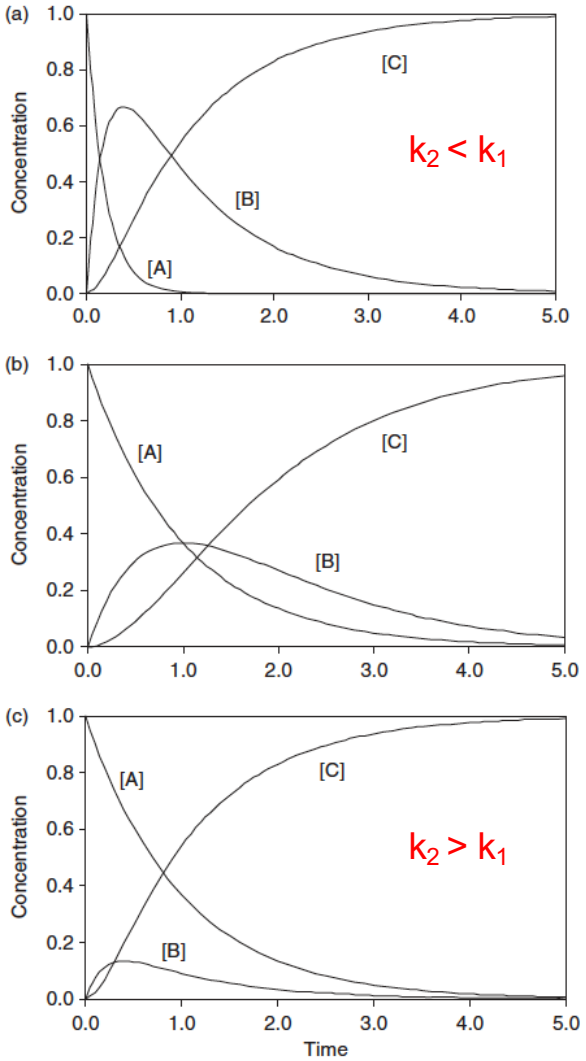
How many half lives does the decline correspond to?

Answer: 3

3*4.1h = 12.3h

Consecutive reactions

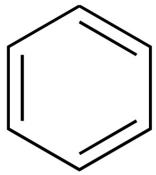
- Where is $k_2 > k_1$?
- Where is $k_2 < k_1$?



Water Chemistry, by Brezonik and Arnold (Oxford University Press).

Environmental engineering challenge

Benzene



An unknown quantity of benzene has entered a well-mixed reservoir that is used as a drinking storage. As an environmental engineer, you are asked to evaluate the water quality, and decide if the water is still ok for human consumption. It takes you 5 days until you can take the first water sample from the reservoir, and you measure a benzene concentration of 50 µM. Five days later, the concentration is 23.6 µM. Assume that the only transformation mechanism is biodegradation and that it follows first-order kinetics.

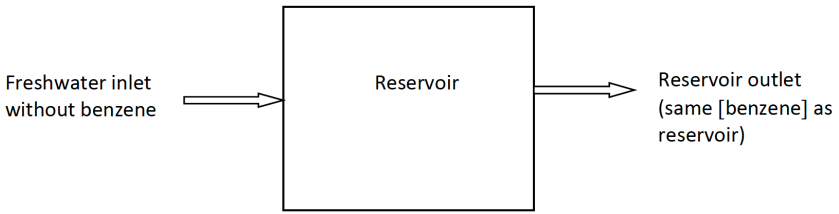
Environmental engineering challenge

a) What was the initial concentration of benzene in the reservoir?

b) What is the biodegradation rate after 5 days?

c) How long will it take until the water is potable again (benzene concentration < 0.1 µM)?

d) Based on exercise c), you decide that the time for the reservoir to reach drinking water quality is too long. Therefore, you suggest that the reservoir is flushed (i.e., a continuous input of fresh water and a continuous outlet of mixed pond water are installed, see picture), to dilute the benzene concentration in addition to biodegradation. The flushing can be considered a first-order reaction with a reaction rate constant of 0.2 day^{-1}. How long will it take now until the water is potable?



Environmental engineering challenge

a) First determine the rate constant k. You know the following:

At t_0 = 0 days, $[benzene]_0$ is unknown.

At t_1= 5 days, $[benzene]_1$ = 50 µM

At t_2 = 10 days, $[benzene]_2$ = 23.6 µM

Use the first-order rate law to determine k (note that you can pick $[benzene]_1$ as your initial concentration, $[benzene]_2$ as your final concentration, and $t_2 - t_1$ as the time of reaction).

$\ln \frac{[benzene]_2}{[benzene]_1} = -k(t_2-t_1)$ therefore k = 0.15 d^{-1}

To determine $[benzene]_0$, use

$[benzene]_1 = [benzene]_0 e^{-kt1}$ to get $[benzene]_0$ = <u>106 µM</u>

b) The rate (d[benzene]/dt = -k[benzene]) is dependent on the concentration of benzene at the time at which the rate is calculated. Use k from above, and $[benzene]_1$ to find the rate after 5 days.

rate after 5 days = -k*50 µM = <u>-7.5 µM d^{-1}</u>

Environmental engineering challenge

c) Solve the following equation using [benzene] = 0.1 µM and $[benzene]_0$ calculated in a).

$\ln \frac{[benzene]}{[benzene]_0} = -kt$

Thus, $t = -\ln \frac{[benzene]}{[benzene]_0} \frac{1}{k}$

Solve for t to find t > 46.4 d.

d) By the time you have made all the previous calculations, you are already on day 10 (not 0!), and at a benzene concentration of 23.6 µM. So the flushing will start on day 10 (not 0). This means that after day 10, the rate constant becomes

$k_{total} = k_{biodgradation} + k_{flushing} = -0.15 - 0.2 = -0.35\ d^{-1}$

You have to calculate how long it takes to get from 23.6 to < 0.1 µM, with a k_{total} of $-0.35\ d^{-1}$. You can use the same equations as above, but this time the "initial" benzene concentration is 23.6 µM.

$\ln \frac{[benzene]}{[benzene]_0} = -kt$ and thus, $t = -\ln \frac{0.1}{23.6} \frac{1}{-0.35} =$ 15.6 d.