

Exercise 1: Reaction of sucrose

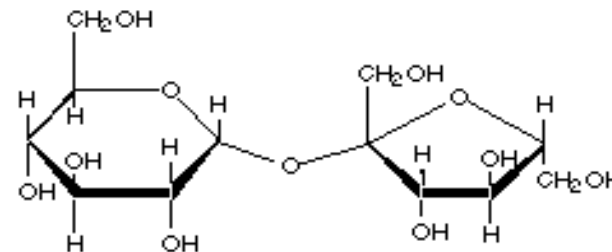


The rate equation for the reaction of sucrose in water is:

$$\text{rate} = -k[\text{C}_{12}\text{H}_{22}\text{O}_{11}].$$

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

Find k .

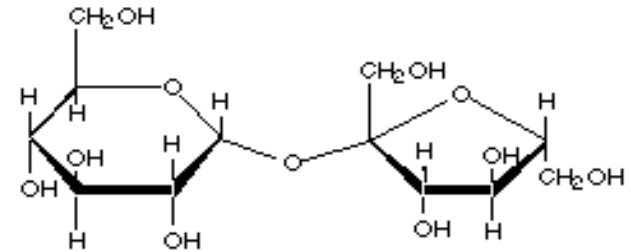


Sucrose

Exercise 1: Solution



$$\ln 4.50 \text{ g/L} / 5.00 \text{ g/L} = -k_1 (2.57 \text{ h})$$
$$k = 0.0410 \text{ h}^{-1}$$



Sucrose

Exercise 2: Ammonium cyanate



Ammonium cyanate, NH_4NCO , rearranges in water to give urea, $(\text{NH}_2)_2\text{CO}$. If the original concentration of NH_4NCO is 0.458 mol/L and $k = 0.0113 \text{ M}^{-1} \text{ min}^{-1}$, how much time elapses before the concentration is reduced to 0.300 mol/L?



Exercise 2: Solution



Initial concentration of NH_4NCO : $[A]_0 = 0.458 \text{ mol/L}$

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

Final concentration of NH_4NCO : $[A] = 0.300 \text{ mol/L}$

$t = ?$

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

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

Exercise 3: Reaction order



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



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



The decomposition of SO_2Cl_2 is first order in SO_2Cl_2 and has a half-life of 4.1 h. 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?



Exercise 4: Solution



How many half lives does the decline correspond to?

Answer: 3

$$3 \times 4.1\text{h} = 12.3\text{h}$$

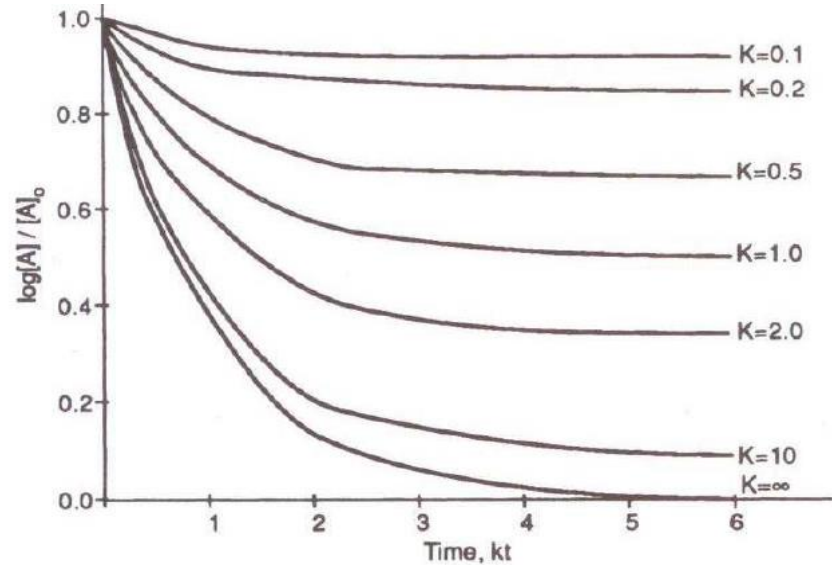
Reversible reactions

Find a curve where $k_{\text{forward}} \ll k_{\text{reverse}}$

Find a curve where $k_{\text{forward}} \gg k_{\text{reverse}}$

small K : $k_{\text{forward}} \ll k_{\text{reverse}}$

large K : $k_{\text{forward}} \gg k_{\text{reverse}}$

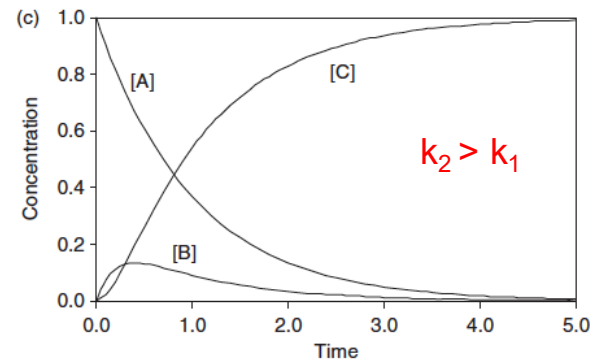
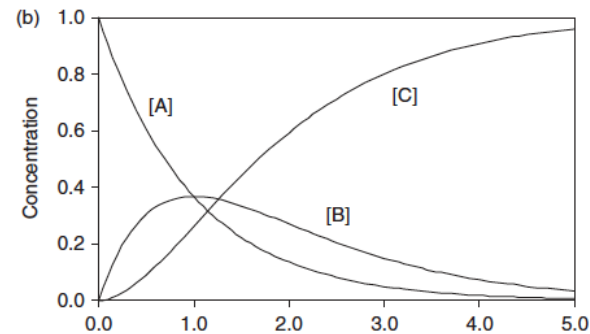
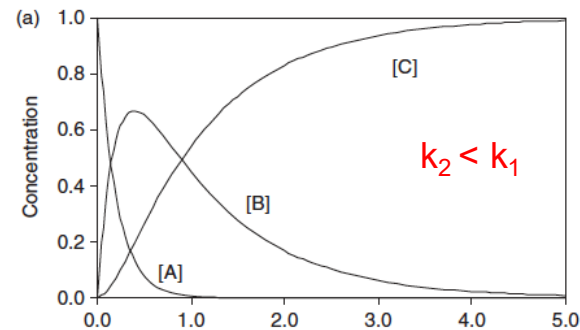


Effect of equilibrium constant $K (= k_f/k_r)$ on shape of reactant disappearance curves for reversible first-order reactions. Dimensionless time in units of kt ; $k = k_f + k_r$; k_f fixed at 10 t^{-1} ; k_r varied to give K values shown by curves. Graph computed from Equation 2-43a reformulated to $[A]/[A]_0 = 1/(1 + K) + \{K/(K + 1)\}\exp(-kt)$.

From: P.L. Brezonik, *Chemical kinetics in process dynamics in aquatic systems*

Consecutive reactions

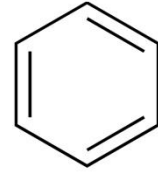
- Where is $k_2 > k_1$?
- Where is $k_2 < k_1$?



Environmental engineering challenge

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 $50 \mu\text{M}$. Five days later, the concentration is $23.6 \mu\text{M}$. Assume that the only transformation mechanism is biodegradation and that it follows first-order kinetics.

Benzene



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 $< 0.1 \mu\text{M}$)?
- 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, $[\text{benzene}]_0$ is unknown.

At $t_1 = 5$ days, $[\text{benzene}]_1 = 50 \mu\text{M}$

At $t_2 = 10$ days, $[\text{benzene}]_2 = 23.6 \mu\text{M}$

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

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

To determine $[\text{benzene}]_0$, use

$$[\text{benzene}]_1 = [\text{benzene}]_0 e^{-kt_1} \text{ to get } [\text{benzene}]_0 = \underline{106 \mu\text{M}}$$

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

$$\text{rate after 5 days} = -k * 50 \mu\text{M} = \underline{-7.5 \mu\text{M d}^{-1}}$$

- c) Solve the following equation using $[\text{benzene}] = 0.1 \mu\text{M}$ and $[\text{benzene}]_0$ calculated in a).

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

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

Solve for t to find $t > 46.4 \text{ d}$.

- 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 $23.6 \mu\text{M}$. So the flushing will start on day 10 (not 0). This means that after day 10, the rate constant becomes

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

You have to calculate how long it takes to get from 23.6 to $< 0.1 \mu\text{M}$, 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 $23.6 \mu\text{M}$.

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