

Dynamics and Kinetics. Exercises 1: Solutions

Problem 1

$$\xi = \frac{5 \text{ mol} - 0 \text{ mol}}{2} = 2.5 \text{ mol}$$

Problem 2

For an ideal gas reaction at constant temperature, we have $p = \frac{n}{V}RT = cRT$. So, assuming an elementary irreversible reaction, this would be a first order reaction, for which the rate law is:

$$\ln \frac{p}{p_0} = -kt$$

time (s)	0	1000	2000	3000	4000
$p \text{ CH}_3\text{N}_2\text{CH}_3 (10^{-2} \text{ Torr})$	8.20	5.72	3.99	2.78	1.94
$\ln \left(\frac{p}{p_0} \right)$	0	-0.36	-0.72	-1.08	-1.44

We may notice that the $\ln \frac{p}{p_0}$ term changes after each 1000s always by the same amount: -0.36. So, if we plot $\ln \frac{p}{p_0}$ vs t , the plot will be a straight line with slope $-k$. Therefore

$$-k = \frac{-0.36}{t_2 - t_1}$$

for any couple of consecutive time data t_1, t_2 , and

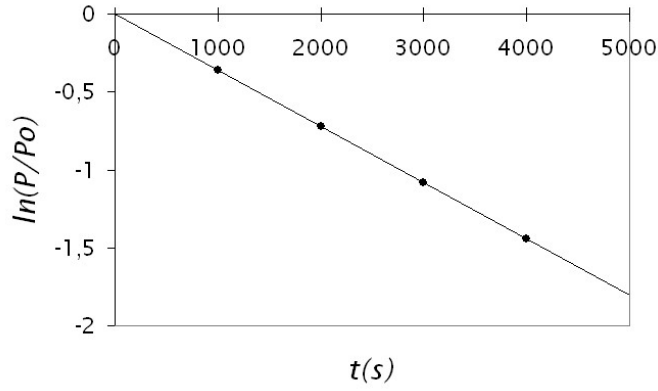
$$k = \frac{0.36}{1000\text{s}} = 3.6 \times 10^{-4} \text{ s}^{-1}$$

In general, for less clean data (i.e., with experimental noise) a least squares fit may be used to find k .

Problem 3

First, we must define the extent of reaction x :

$$\begin{aligned} x &= [A]_0 - [A]_t, \\ x &= \frac{[B]_0 - [B]_t}{2}. \end{aligned}$$



Inserting this in the rate law and using the notation $a_0 := [A]_0, b_0 := [B]_0$, gives an ODE for x :

$$\frac{dx}{dt} = k(a_0 - x)(b_0 - 2x)$$

Separation of variables yields

$$\int_{x_0}^{x_t} \frac{dx}{(a_0 - x)(b_0 - 2x)} = k \int_0^t dt.$$

The integral can be solved by the method of **partial fractions**,

$$\begin{aligned} \frac{1}{(a_0 - x)(b_0 - 2x)} &= \frac{\alpha}{a_0 - x} + \frac{\beta}{b_0 - 2x} \\ &= \frac{\alpha(b_0 - 2x) + \beta(a_0 - x)}{(a_0 - x)(b_0 - 2x)}. \end{aligned}$$

We deduce that $(2\alpha + \beta)x = 0$ and $\alpha b_0 + \beta a_0 = 1$. From the first equation $\beta = -2\alpha$, and therefore $\alpha(b_0 - 2a_0) = 1$, from which

$$\begin{aligned} \alpha &= \frac{1}{b_0 - 2a_0} \\ \beta &= \frac{-2}{b_0 - 2a_0}. \end{aligned}$$

Going back to the integrals, we have

$$\begin{aligned} kt &= \int_{x_0}^{x_t} \frac{dx}{(a_0 - x)(b_0 - 2x)} \\ &= \alpha \int_{x_0}^{x_t} \frac{dx}{(a_0 - x)} + \beta \int_{x_0}^{x_t} \frac{dx}{(b_0 - 2x)} \\ &= \left[-\alpha \ln(a_0 - x) - \frac{\beta}{2} \ln(b_0 - 2x) \right]_{x_0}^{x_t}. \end{aligned}$$

Evaluation of the boundary terms and substitution for β gives

$$kt = -\alpha \ln \left(\frac{a_0 - x}{a_0} \right) + \alpha \ln \left(\frac{b_0 - 2x}{b_0} \right).$$

Finally, by substitution for a , we get

$$kt = \frac{1}{(2a_0 - b_0)} \ln \left(\frac{b_0(a_0 - x)}{a_0(b_0 - 2x)} \right).$$

This expression could be used directly to deduce k from experimental data. However, in order to find the explicit time dependence of concentrations $[A]$ and $[B]$, we must solve for x as a function of time. The result is a function:

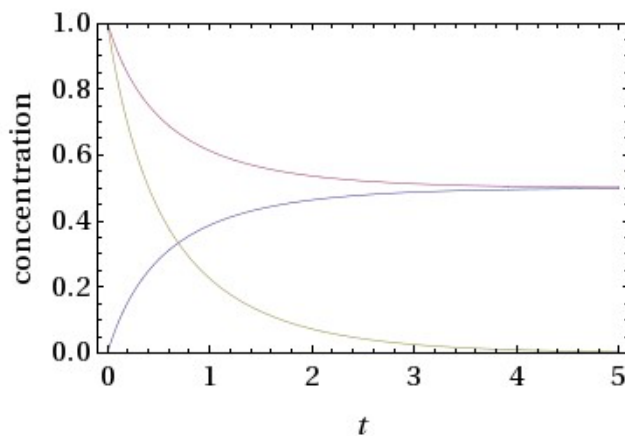
$$x = \frac{a_0 b_0 (e^{2a_0 kt} - e^{b_0 kt})}{2a_0 e^{2a_0 kt} - b_0 e^{b_0 kt}}.$$

Inserting this result for x into the expressions for the extent of reaction, we obtain the time dependence of $[A]_t$ and $[B]_t$:

$$[A]_t = [A]_0 - x$$

$$[B]_t = [B]_0 - 2x$$

Considering, e.g., the values $[A]_0 = [B]_0 = k = 1.0$, we obtain the following behavior for concentrations $[A]_t$, $[B]_t$ and for $x(t)$.



Problem 4

a) We are to consider a reaction:



with a rate law

$$v = -\frac{d[A]}{dt} = k[A]^{\frac{3}{2}}.$$

This ODE can be solved by separation of variables:

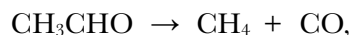
$$-\frac{d[A]}{[A]^{\frac{3}{2}}} = k dt,$$

$$\begin{aligned}
-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^{\frac{3}{2}}} &= k \int_0^t dt, \\
2 \left([A]_t^{-\frac{1}{2}} - [A]_0^{-\frac{1}{2}} \right) &= kt, \\
[A]_t^{-\frac{1}{2}} &= [A]_0^{-\frac{1}{2}} + \frac{kt}{2}.
\end{aligned}$$

At half-life, we have $[A]_{t_{1/2}} = \frac{[A]_0}{2}$, and so

$$\begin{aligned}
\left(\frac{[A]_0}{2} \right)^{-\frac{1}{2}} &= [A]_0^{-\frac{1}{2}} + \frac{kt_{1/2}}{2} \\
\frac{2 \left(\left[\frac{[A]_0}{2} \right]^{-\frac{1}{2}} - [A]_0^{-\frac{1}{2}} \right)}{k} &= t_{1/2}, \\
t_{1/2} &= \frac{2(2^{\frac{1}{2}} - 1)}{k[A]_0^{\frac{1}{2}}}.
\end{aligned}$$

Clearly, this must be a composite reaction. Example of a reaction of order 3/2 is given by the thermal decomposition of acetaldehyde:



$$v = k[\text{CH}_3\text{CHO}]^{\frac{3}{2}}.$$

b) From the lecture, in general, for an n th-order reaction $aA \rightarrow \text{products}$, the rate law is:

$$\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} = akt(n-1)$$

For $n = 3/2$,

$$\begin{aligned}
\frac{1}{[A]_t^{\frac{3}{2}-1}} - \frac{1}{[A]_0^{\frac{3}{2}-1}} &= kt\left(\frac{3}{2} - 1\right) \\
[A]_t^{-\frac{1}{2}} &= [A]_0^{-\frac{1}{2}} + \frac{kt}{2}
\end{aligned}$$

Similarly, the general formula for the half-life is:

$$t_{1/2} = \frac{2^{n-1} - 1}{a(n-1)k[A]_0^{n-1}}.$$

For $n = 3/2$,

$$t_{1/2} = \frac{2^{\frac{3}{2}-1} - 1}{(\frac{3}{2} - 1)k[A]_0^{\frac{3}{2}-1}} = \frac{2^{\frac{1}{2}} - 1}{\frac{1}{2}k[A]_0^{\frac{1}{2}}} = \frac{2(2^{\frac{1}{2}} - 1)}{k[A]_0^{\frac{1}{2}}}.$$

Both results agree with the solution of a).