Dynamics and Kinetics. Exercises 2: Solutions

Problem 1

a) For first order reactions, we have

$$[SO_2Cl_2]_t = [SO_2Cl_2]_0 e^{-kt}. \quad (1)$$

Percentage that has decomposed is

$$\%\text{Decomp} = \frac{[SO_2Cl_2]_0 - [SO_2Cl_2]_t}{[SO_2Cl_2]_0} \times 100\%.$$

(2)

Inserting $[SO_2Cl_2]_t$ from Eq. (1) into Eq. (2), simplifying, and evaluating for t = 3600s and kt = 0.0792, we get

$$\%\text{Decomp} = \left(1 - e^{-kt}\right) \times 100\% \quad = 7.6\%$$

b) To find how long it will take to decompose 50% of SO_2Cl_2, we need to find out $t_{1/2}$

$$\begin{aligned}
[SO_2Cl_2]_{t_{1/2}} = \frac{[SO_2Cl_2]_0}{2} &= [SO_2Cl_2]_0 e^{-kt_{1/2}}, \\
\ln\left(\frac{1}{2}\right) &= -kt_{1/2}, \\
\ln 2 &= kt_{1/2}, \\
t_{1/2} &= \frac{\ln 2}{k} = 31506.7\text{s} = 8.75 \text{ hours.}
\end{aligned}$$

Problem 2

a) Rate of consumption of NO_3 and NO is

$$v_{\text{consum}} = -\frac{d[NO_3]}{dt} = -\frac{d[NO]}{dt} = k_{\text{consum}}[NO_3][NO].$$

b) Rate of production of NO_2 is

$$v_{\text{product}} = \frac{d[NO_2]}{dt} = k_{\text{product}}[NO_3][NO].$$

c) We may also define the rate of the reaction v:

$$v = \frac{1}{2}\frac{d[\mathrm{NO_2}]}{dt} = \frac{1}{2}v_{\mathrm{product}};$$
$$v = -\frac{d[\mathrm{NO_3}]}{dt} = -\frac{d[\mathrm{NO}]}{dt} = v_{\mathrm{consum}},$$

Therefore

$$v_{\mathrm{consum}} = \frac{1}{2}v_{\mathrm{product}} = v$$

And

$$k_{\mathrm{consum}} = \frac{1}{2}k_{\mathrm{product}} = k.$$

Problem 3

a) For a reaction of order n

$$v = k\prod_{i}^{r}[i]^{n_i},$$

and the order satisfies

$$n = n_1 + n_2 + \cdots + n_r.$$

Let us denote units of k by $[k]$. We have

$$\frac{\mathrm{mol}}{\mathrm{l}\cdot\mathrm{s}} = [k]\left(\frac{\mathrm{mol}}{\mathrm{l}}\right)^{n},$$
$$[k] = \frac{\mathrm{mol}}{\mathrm{l}\cdot\mathrm{s}}\left(\frac{\mathrm{mol}}{\mathrm{l}}\right)^{-n},$$
$$[k] = \left(\frac{\mathrm{mol}}{\mathrm{l}}\right)^{1-n}\mathrm{s}^{-1}.$$

Therefore, for first order reactions: $[k] = s^{-1}$.

For second order reactions: [k] $=\left(\frac{mol}{1}\right)^{-1} s^{-1}$.

For third order reactions: [k] $= \left(\frac{mol}{1}\right)^{-2} s^{-1}$.

Conversion factors for k. The Avogadro's constant $N_A = 6.022 \cdot 10^{23}\mathrm{mol}^{-1}$. For simplicity, we will denote by N_A not the Avogadro's constant, but the *unitless* number $6.022 \cdot 10^{23}$. Considering that 1mol = N_A molecules,

$$\left(\frac{\mathrm{mol}}{\mathrm{l}}\right)^{1-n} = \left(\frac{\mathrm{mol}}{\mathrm{l}}\cdot\frac{N_A\,\mathrm{molecules}}{1\mathrm{mol}}\right)^{1-n}$$
$$= N_A^{1-n}\left(\frac{\mathrm{molecules}}{\mathrm{l}}\right)^{1-n}$$

Therefore, the conversion factor for first order reactions = 1.

Conversion factor for second order reactions = N_A^{-1}

Conversion factor for third order reactions = N_A^{-2}.

b) For that kind of reaction $n = \frac{1}{2} + \frac{2}{3} = \frac{7}{6}$. Using the above general formula gives

$$[k] = \left(\frac{\text{mol}}{\text{l}}\right)^{1-\frac{7}{6}} \text{s}^{-1} = \left(\frac{\text{mol}}{\text{l}}\right)^{-\frac{1}{6}} \text{s}^{-1}.$$

Problem 4

If we consider the radioactive decay of ^{14}C to ^{14}N as an elementary reaction, this will be of first order:

$$^{14}\text{C} \xrightarrow{k} {}^{14}\text{N},$$

$$v = k[^{14}\text{C}].$$

Therefore, we may apply the solution of the differential equation for a first order reaction:

$$[^{14}\text{C}]_t = [^{14}\text{C}]_0 e^{-kt}. \tag{1}$$

First, we need to obtain the value of k, so we use the information about the half-life.

$$\begin{aligned} \frac{[^{14}\text{C}]_0}{2} &= [^{14}\text{C}]_0 e^{-kt_{1/2}}, \\ \ln(2) &= kt_{1/2}, \\ k &= \frac{\ln(2)}{t_{1/2}} = \frac{\ln(2)}{5730} = 1.210 \times 10^{-4}\text{years}^{-1}. \end{aligned}$$

Now, we use Eq. (1) to find out the age of the wood sample, knowing that $[^{14}\text{C}]_{t\text{sample}} = [^{14}\text{C}]_0 \times 0.72$:

$$\begin{aligned} [^{14}\text{C}]_0 \times 0.72 &= [^{14}\text{C}]_0 e^{-kt_{\text{sample}}}, \\ -\ln(0.72) &= kt_{\text{sample}}, \\ t_{\text{sample}} &= -\frac{\ln(0.72)}{1.210 \times 10^{-4}\text{years}^{-1}} = 2715 \text{ years}. \end{aligned}$$