Chemistry 2740 Spring 2022 Test 3 Solutions

1. (a)

$$\begin{aligned}\frac{db}{dt} &\approx \frac{\Delta b}{\Delta t} = \frac{4.32\times 10^{-3}\,\mathrm{mol\,L^{-1}}}{32\,\mathrm{s}} = 1.4\times 10^{-4}\,\mathrm{mol\,L^{-1}s^{-1}}\\ v &= \frac{1}{2}\frac{db}{dt} = \frac{1}{2}\left(1.35\times 10^{-4}\,\mathrm{mol\,L^{-1}s^{-1}}\right) = 6.8\times 10^{-5}\,\mathrm{mol\,L^{-1}s^{-1}}\end{aligned}$$

(b) The half-life is constant for a first-order reaction, but depends on the initial concentration for any other order.

(c)

$$\frac{d[\mathrm{X}]}{dt} = 2k_1[\mathrm{X_2}] - 2k_{-1}[\mathrm{X}]^2 - k_2[\mathrm{X}][\mathrm{Y}]$$

(d) For a second-order reaction,

$$\frac{1}{x} = \frac{1}{x_0} + kt$$

We have $x_0 = 0.53\,\mathrm{mol\,L^{-1}}$. When 20% of the cyclopentadiene has been converted to product, 80% remains, so we have $x = 0.80(0.53\,\mathrm{mol\,L^{-1}}) = 0.42\,\mathrm{mol\,L^{-1}}$. Therefore

$$\begin{aligned}t &= \frac{1}{k}\left(\frac{1}{x} - \frac{1}{x_0}\right)\\ &= \frac{1}{6.13\times 10^{-2}\,\mathrm{L\,mol^{-1}s^{-1}}}\left(\frac{1}{0.42\,\mathrm{mol\,L^{-1}}} - \frac{1}{0.53\,\mathrm{mol\,L^{-1}}}\right)\\ &= 7.7\,\mathrm{s}\end{aligned}$$

2. (a) In experiments 2 and 3, the concentration of $\mathrm{HgCl_2}$ is changed while the concentration of $\mathrm{C_2O_4^{2-}}$ is constant. The ratio of the $[\mathrm{HgCl_2}]$ concentrations is $0.171/0.096 = 1.78$ and the ratio of the rates is $9.8/5.5 = 1.78$. The reaction is therefore first order in $[\mathrm{HgCl_2}]$. Similarly, we can determine the order with respect to $[\mathrm{C_2O_4^{2-}}]$ from experiments 1 and 2. This is a little harder to figure out by inspection, so I'm going to calculate the order:

$$\alpha = \frac{\log(v_2/v_1)}{\log([\mathrm{C_2O_4^{2-}}]_2)/[\mathrm{C_2O_4^{2-}}]_1)} = \frac{\log(5.5/2.1)}{\log(0.21/0.13)} = 2$$

The rate law is therefore

$$v = k[\mathrm{HgCl_2}][\mathrm{C_2O_4^{2-}}]^2$$

To calculate the rate constant, rearrange the rate law to

$$k = \frac{v}{[\mathrm{HgCl_2}][\mathrm{C_2O_4^{2-}}]^2}.$$

From experiment 1, we have

$$k = \frac{2.1 \times 10^{-7}\,\mathrm{mol\,L^{-1}s^{-1}}}{(0.096\,\mathrm{mol\,L^{-1}})(0.13\,\mathrm{mol\,L^{-1}})^2} = 1.3 \times 10^{-4}\,\mathrm{L^2mol^{-2}s^{-1}}.$$

If we repeat this calculation for the other two experiments and average, we get

$$k = 1.298 \times 10^{-4}\,\mathrm{L^2mol^{-2}s^{-1}}.$$

(b) This is definitely not an elementary reaction because the rate law does not match the molecularity of the reaction.

Some slightly less convincing evidence:

i. Termolecular elementary reactions are rare.
ii. Many bonds are made and broken in going from reactants to products.

3. $A = kN$. We have A (albeit on a per kilogram of concrete basis) and the half-life, from which we can calculate k, so we should be able to calculate N.

$$\begin{aligned} k &= \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{1600\,\mathrm{y}} = 4.3 \times 10^{-4}\,\mathrm{y^{-1}} \\ &\equiv \frac{4.3 \times 10^{-4}\,\mathrm{y^{-1}}}{(365.25\,\mathrm{d\,y^{-1}})(24\,\mathrm{h\,d^{-1}})(3600\,\mathrm{s\,h^{-1}})} \\ &= 1.4 \times 10^{-11}\,\mathrm{s^{-1}} \end{aligned}$$

For each kilogram of concrete, we have

$$\begin{aligned} N &= \frac{A}{k} = \frac{35.8\,\mathrm{atoms\,s^{-1}}}{1.4 \times 10^{-11}\,\mathrm{s^{-1}}} = 2.6 \times 10^{12}\,\mathrm{atoms} \\ &\equiv \frac{2.6 \times 10^{12}\,\mathrm{atoms}}{6.022\,142 \times 10^{23}\,\mathrm{atoms\,mol^{-1}}} = 4.3 \times 10^{-12}\,\mathrm{mol} \end{aligned}$$

Since we started out by considering one kilogram of concrete, the concentration of radium in the concrete is $4.3 \times 10^{-12}\,\mathrm{mol\,kg^{-1}}$.

4. In order to test whether the results of a time-course experiment fit a first- or second-order rate law, we plot $\ln[\mathrm{NM}]$ vs t to test for first-order behavior, and $[\mathrm{NM}]^{-1}$ vs t for second-order. The graphs are shown in figures 1 and 2 We get a good fit in the first-order plot, but a terrible fit in the second-order plot. We conclude that the data obey first-order kinetics. The rate constant is related to the slope of the regression line. By linear regression, we find a slope of $-0.068\,\mu\mathrm{s}^{-1}$. Thus,

$$k = -(\text{slope}) = 0.068\,\mu\mathrm{s}^{-1}$$

I'm not crazy about units of $\mu\mathrm{s}^{-1}$ although these are acceptable in the SI system. My preference would be to convert to s^{-1}:

$$\begin{aligned} k &= (0.068\,\mu\mathrm{s}^{-1})\left(10^6\frac{\mu\mathrm{s}}{\mathrm{s}}\right) \\ &= 6.8 \times 10^4\,\mathrm{s}^{-1} \end{aligned}$$

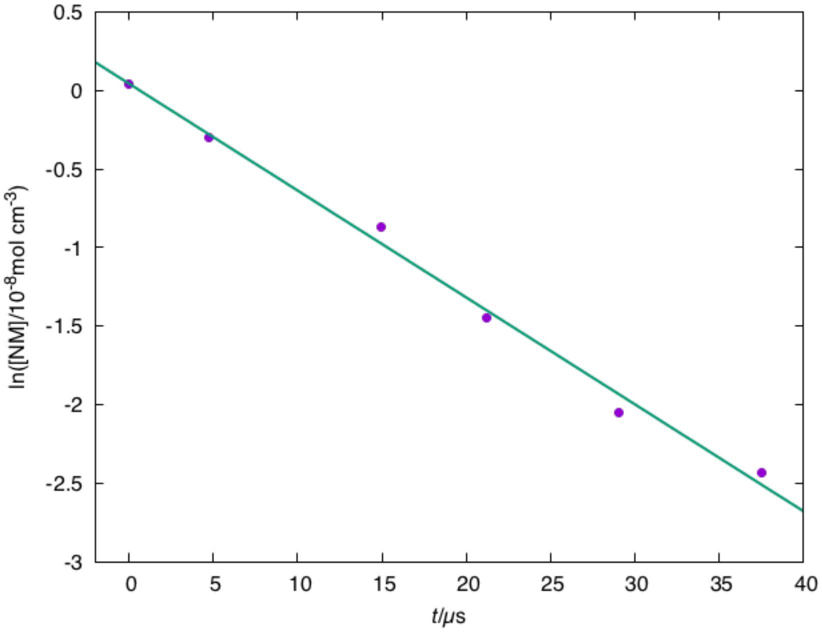

Figure 1: First-order plot for the data of question 4

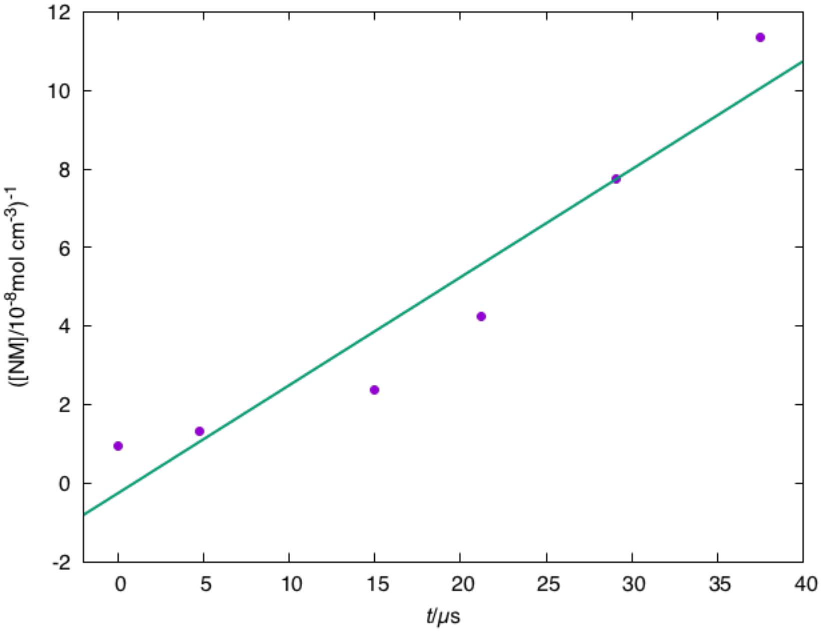

Figure 2: Second-order plot for the data of question 4