Chemistry 2740 Spring 2021 Test 3 Solutions

1. (a) In experiments 1, 2 and 3, the H^+ concentration is the same, but the GSH concentration increases. Note the following:

$$\frac{[\text{GSH}]_2}{[\text{GSH}]_1} = 4.0, \qquad \frac{k_{\text{obs}}^{(2)}}{k_{\text{obs}}^{(1)}} = 3.88.$$

$$\frac{[\text{GSH}]_3}{[\text{GSH}]_2} = 2.5, \qquad \frac{k_{\text{obs}}^{(3)}}{k_{\text{obs}}^{(2)}} = 2.50.$$

Thus, we see that the observed rate constant increases in direct proportion to the GSH concentration, indicating that the reaction is first-order with respect to GSH.

In experiments 2, 4 and 5, the GSH concentration is the same, but the H^+ concentration increases. An immediate observation is that the rate constant *decreases* as the H^+ concentration increases. We are therefore looking at some sort of inverse relationship, so the ratios of rates are inverted in the calculations below.

$$\frac{[\text{H}^+]_4}{[\text{H}^+]_2} = 2, \qquad \frac{k_{\text{obs}}^{(2)}}{k_{\text{obs}}^{(4)}} = 1.94.$$

$$\frac{[\text{H}^+]_5}{[\text{H}^+]_4} = 2, \qquad \frac{k_{\text{obs}}^{(4)}}{k_{\text{obs}}^{(5)}} = 2.1.$$

These data are consistent with an order of -1 with respect to H^+.

Since we already know that the reaction is of the first order with respect to Ru_2O^{4+}, the rate law is

$$v = k[\text{Ru}_2\text{O}^{4+}][\text{GSH}]/[\text{H}^+].$$

(b) The observed rate constant is related to the rate constant in the rate law by

$$k_{\text{obs}} = k[\text{GSH}]/[\text{H}^+].$$

Thus,

$$k = k_{\text{obs}}[\text{H}^+]/[\text{GSH}].$$

We have to calculate the rate constant for each experiment and then average the results. For example, with the first experiment, we get

$$k = \frac{(0.75 \times 10^{-4}\,\text{s}^{-1})(0.01\,\text{mol}\,\text{L}^{-1})}{0.20 \times 10^{-3}\,\text{mol}\,\text{L}^{-1}}$$
$$= 3.8 \times 10^{-3}\,\text{s}^{-1}.$$

We obtain the following values:

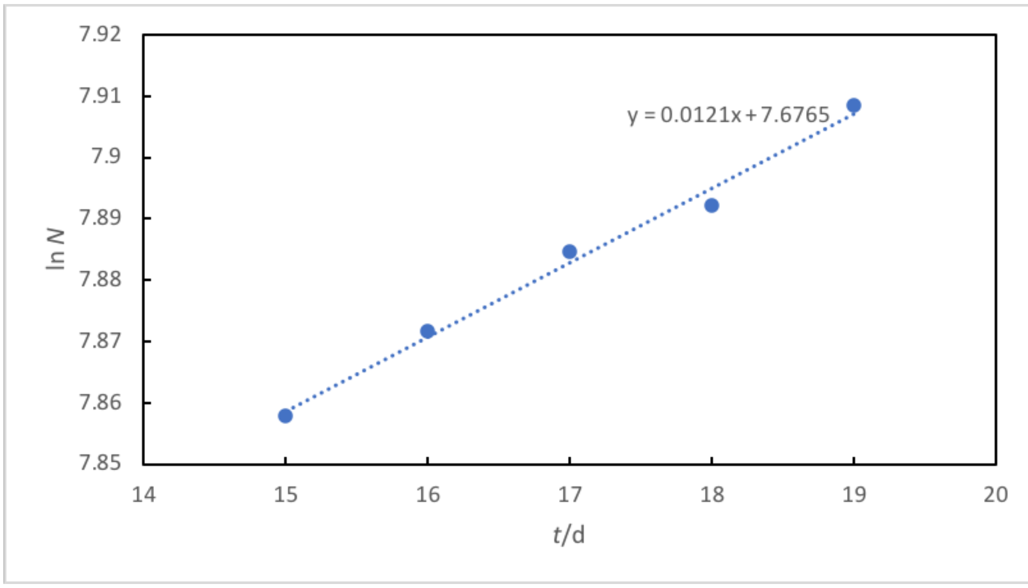


Figure 1: Graph of $\ln N$ vs t for the Lethbridge Covid-19 data

Experiment	1	2	3	4	5
$k/10^{-3}\text{s}^{-1}$	3.8	3.6	3.6	3.8	3.6

The average value is

$$k = 3.68 \times 10^{-3}\,\text{s}^{-1}.$$

2. We first need to get the slope of a graph of $\ln N$ vs t. The graph is shown in figure 1.

   The slope of the graph is

   $$\text{slope} = k = 0.0121\,\text{d}^{-1}.$$

   The effective reproduction number is calculated by

   $$\begin{aligned} R_e &= e^{k\tau} = \exp\left[(0.0121\,\text{d}^{-1})(16\,\text{d})\right] \\ &= 1.2. \end{aligned}$$

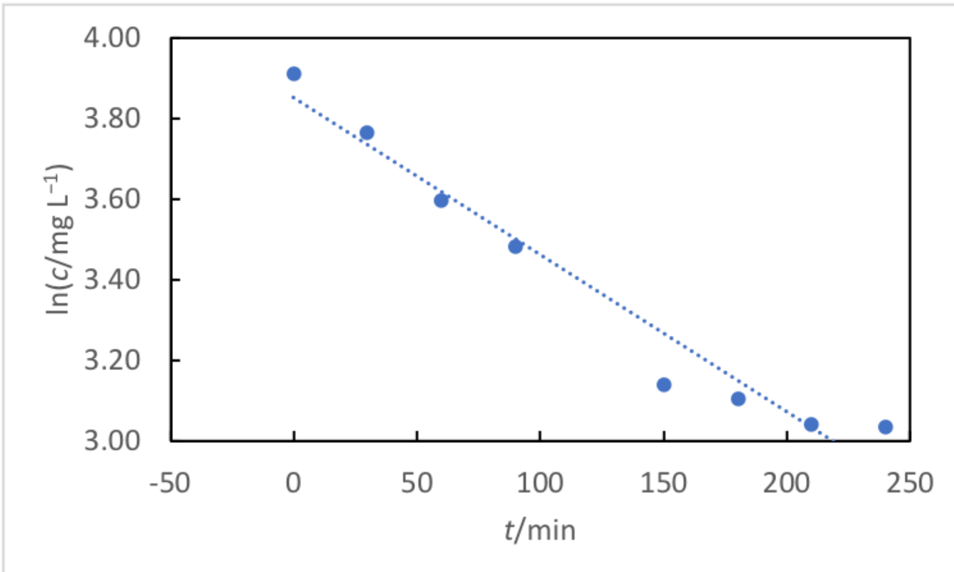
   This tells that each infection results in approximately 1.2 new infections, i.e. that the size of the infected population is growing.

3. (a) A first-order reaction would show a linear $\ln c$ vs t relationship, while a second-order reaction would show a linear relationship of c^{-1} vs t. The two graphs are shown in figure 2. The 1st order plot is clearly nonlinear. The 2nd order plot has a couple of bad points (at $t = 150.0$ and 240.1 min), but otherwise the points are a good fit to the line. I would therefore conclude that the data obey second-order kinetics.

   (b) In the second-order plot, the rate constant is the slope, so we have

   $$k = 1.30 \times 10^{-4}\,\text{L}\,\text{mg}^{-1}\text{min}^{-1}.$$

(a)



(b)

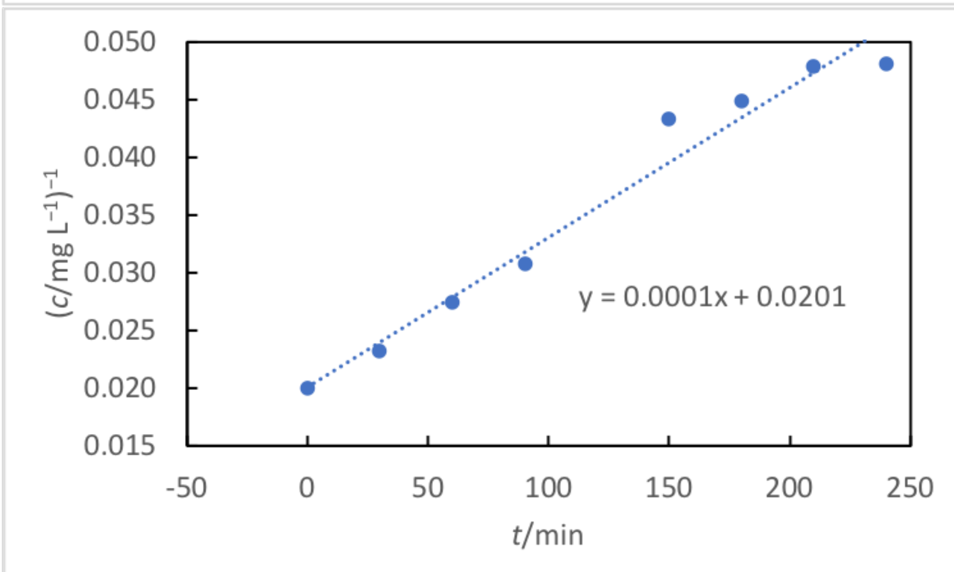


Figure 2: (a) 1st order plot using the zinc data of Rajendran and Thangavelu (2021), and (b) 2nd order plot.

(c) The integrated second-order rate law is

$$\begin{aligned}
\frac{1}{[\mathrm{As}]} &= \frac{1}{[\mathrm{As}]_0} + kt. \\
\therefore t &= \frac{1}{k}\left(\frac{1}{[\mathrm{As}]} - \frac{1}{[\mathrm{As}]_0}\right) \\
&= \frac{1}{1.30 \times 10^{-4}\,\mathrm{L\,mg^{-1}min^{-1}}}\left(\frac{1}{0.010\,\mathrm{mg\,L^{-1}}} - \frac{1}{0.035\,\mathrm{mg\,L^{-1}}}\right) \\
&= 5.5 \times 10^{5}\,\mathrm{min},
\end{aligned}$$

which is over a year. A bit too long to be practical, which is why the authors of the study experimented with many different metals, reaction conditions, etc.