Suggested Problems: Chapter 17

17.1: The average rate is the rate of change in concentration between two discrete moments in time and is calculated by taking the difference in concentration and dividing by the difference in time. An instantaneous rate is the rate of change in concentration at a single discrete moment in time and is equal to the slope of the tangent line to the curve that shows the concentration as a function of time at that time. The initial rate is the instantaneous rate at moment the reaction begins; that is, when $t = 0$.

17.3: The three rates are

$$R = +\frac{1}{2} \times \frac{d[\mathrm{ClF_3}]}{dt}$$

$$R = -\frac{d[\mathrm{Cl_2}]}{dt}$$

$$R = -\frac{1}{3} \times \frac{d[\mathrm{F_2}]}{dt}$$

Note that the equations for the second and third rate laws include a minus sign because the concentration of a reactant decreases with time, but the rate is expressed as a postive value. Note that the equation for the first and the second rate laws include a term to account for the stoichiometry in order to ensure that all three rates have the same value

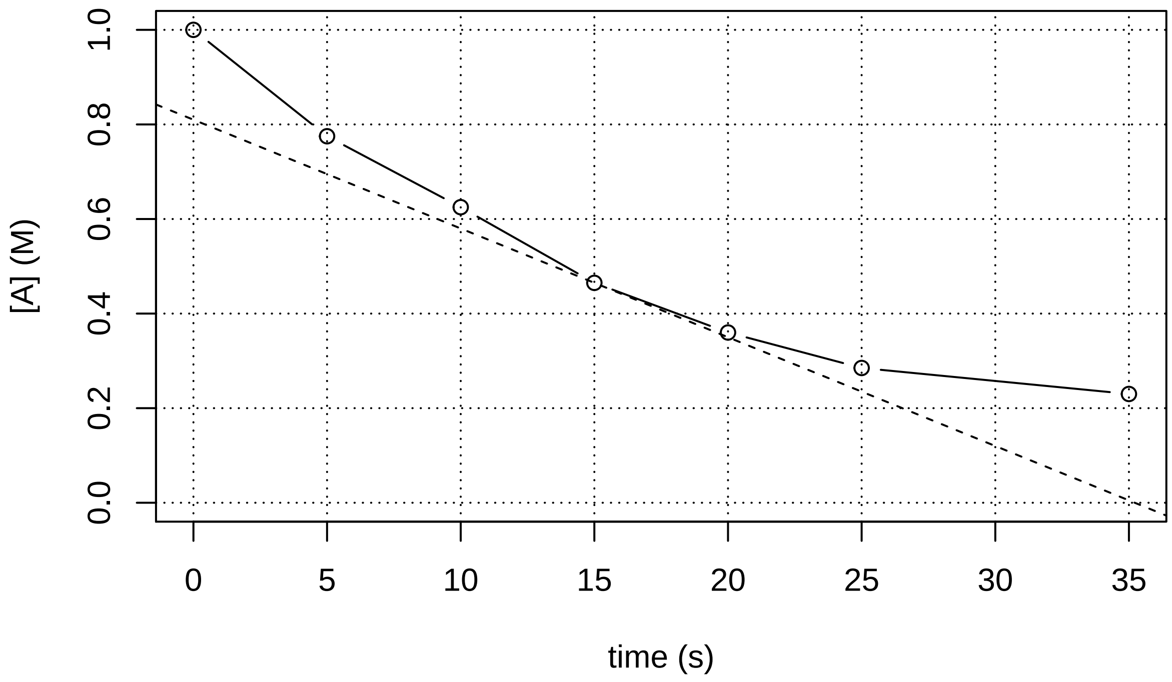
17.5: For (a), between 0.00 s and 10.0 s, the average rate of disappearance for A is

$$R = -\frac{0.625 - 1.00}{10.0 - 0.00} = 0.0375 \text{ M/s}$$

and between 10.0 s and 20.0 s, the average rate of disappearance for A is

$$R = -\frac{0.360 - 0.625}{20.0 - 10.0} = 0.0265 \text{ M/s}$$

Note that because we are interested here in the rate at which A is consumed, we do not account for the stoichiometry. For (b), we need to plot the data, draw the tangent to the data at 15.0 s, and then determine the tangent line's slope; thus



The dashed line is the tangent; to find its slope, which is the rate, we note that the tangent line has a value of 0.80 at a time of 0 s and a value of 0 at a time of 35 s; thus

$$\text{slope} = \frac{0 - 0.80}{35 - 0} = -0.023 \text{ M/s}$$

The instantaneous rate is the negative of the slope, or 0.023 M/s. For (c), the relationship between the reaction's rate when monitoring A and B is

$$R = -\frac{1}{2}\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

which means the rate of formation for B is half the rate of disappearance of A; thus, the average rate of formation of B between 0.00 s and 10.0 s is 0.0188 M/s and the instantaneous rate of formation for B at 15.0 s is 0.0125 M/s.

17.13: For (a), we note that rate increases by a factor of 4 when the reactant's concentration increases by a factor of 2. In general, the relationship between rate and concentration is $R = [\text{reactant}]^y$ where y is the reactant's order; thus, if $4\times = (2\times)^y$, then $y = 2$. For (b), we can use the same logic to write $(3\times) = (3\times)^y$, which gives $y = 1$.

17.15: For (a), if we decrease the pressure of NO_2 by a factor of 2, then we are decreasing its concentration by its factor of 2 and, therefore, decreasing the rate of the reaction by $(0.5)^2$, or by a factor of 4. For (b), increasing the concentration of CO has no effect on the reaction's rate as CO does not appear in the rate law.

17.17: The reaction's rate law is $R = k[\text{NO}][\text{O}_3]$. Substituting in values for k and for the concentrations of NO and O_3 gives the instantaneous rate as

$$R = (2.20 \times 10^{7} \text{ M}^{-1}\text{s}^{-1})(3.3 \times 10^{-6} \text{ M})(5.9 \times 10^{-7} \text{ M}) = 4.3 \times 10^{-5} \text{ M/s}$$

17.19: The rate law is $R = k[{}^{14}_{6}\text{C}]$. Substituting in values for k and for the concentration of ${}^{14}_{6}\text{C}$ gives the instantaneous rate as

$$R = (1.21 \times 10^{-4} \text{ yr}^{-1})(6.5 \times 10^{-9} \text{ M}) = 7.9 \times 10^{-13} \text{ M/yr}$$

17.21: The data shows us that the rate of the reaction is independent of the concentration of ethanol, which means that the reaction's rate law is

$$R = k$$

and the rate constant is 2.0×10^{-2} M/h. The overall order of the reaction is zero.

17.23: The data shows us that the rate of the reaction increases by a factor of 4 when the concentration of NOCl doubles, and increases by a factor of 9 when its concentration triples, which means that the reaction is second order in NOCl, or

$$R = k[\text{NOCl}]^2$$

We can use any experiment to calculate the rate constant; using the first experiment, we have

$$k = \frac{R}{[\text{NOCl}]^2} = \frac{8.0 \times 10^{-10} \text{ M/h}}{(0.10 \text{ M})^2} = 8.0 \times 10^{-8} \text{ M}^{-1} \text{ h}^{-1}$$

The overall reaction order is second.

17.25: The first two experiments show us that when holding the concentration of Cl_2 constant, doubling the concentration of NO increases the rate by a factor of 4; thus, the reaction is second order in NO. Comparing the last two experiments shows us that when holding the concentration of NO contant, doubling the concentration of Cl_2 increases the rate by a factor of 2; thus, the reaction is first order in Cl_2. The overall rate law is

$$R = k[\text{NO}]^2[\text{Cl}_2]$$

Using data from the first experiment, the rate constant is

$$k = \frac{R}{[\text{NO}]^2[\text{Cl}_2]} = \frac{1.14 \text{ M/h}}{(0.50 \text{ M})^2(0.50 \text{ M})} = 9.1 \text{ M}^{-2} \text{ h}^{-1}$$

17.31: The first two experiment show us that when holding the concentration of OCl^- constant, doubling the concentration of I^- increases the rate by a factor of 2; thus, the reaction is first order in I^-. We don't have a pair of experiments in which just the concentration of OCl^- changes, but we still can determine the order for OCl^- by accounting for the effect of I^- by dividing the rate by $[\text{I}^-]^1$, where we note here for reference, that the reaction is first order in I^-. Using the first and the last experiments, the adjusted rates are

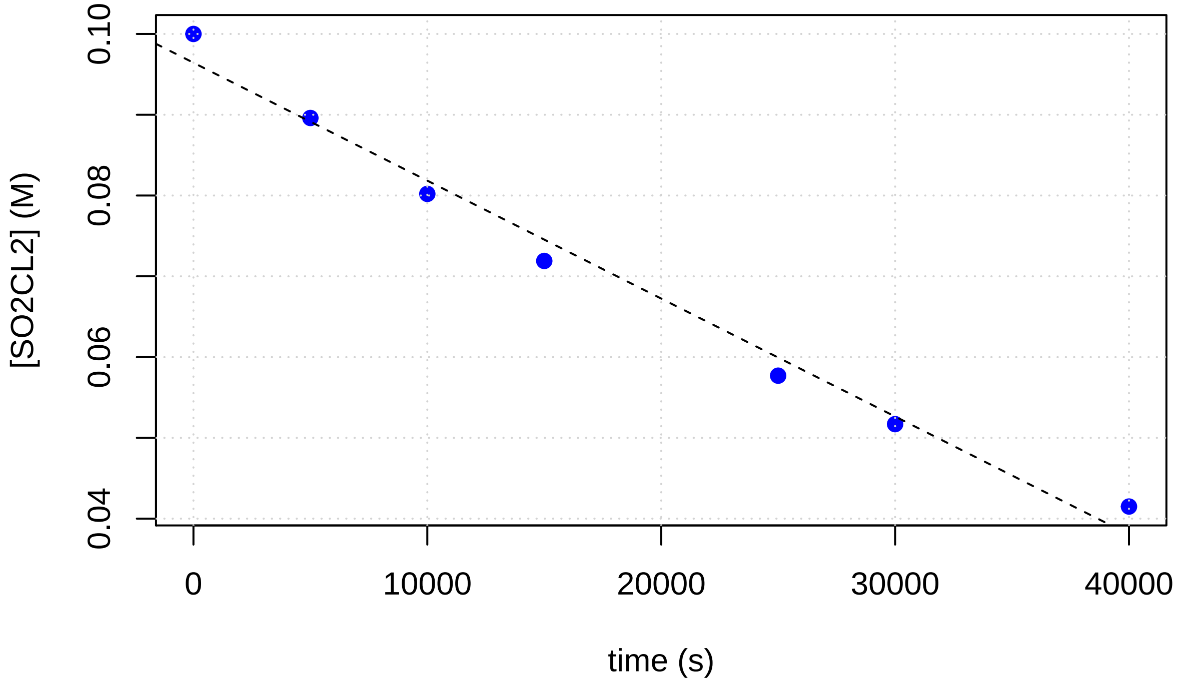
$$R_1 = \frac{3.05 \times 10^{-4} \text{ M/s}}{0.1 \text{ M}} = 3.05 \times 10^{-3} \text{ M/s}$$

$$R_2 = \frac{1.83 \times 10^{-4} \text{ M/s}}{0.3 \text{ M}} = 6.1 \times 10^{-4} \text{ M/s}$$

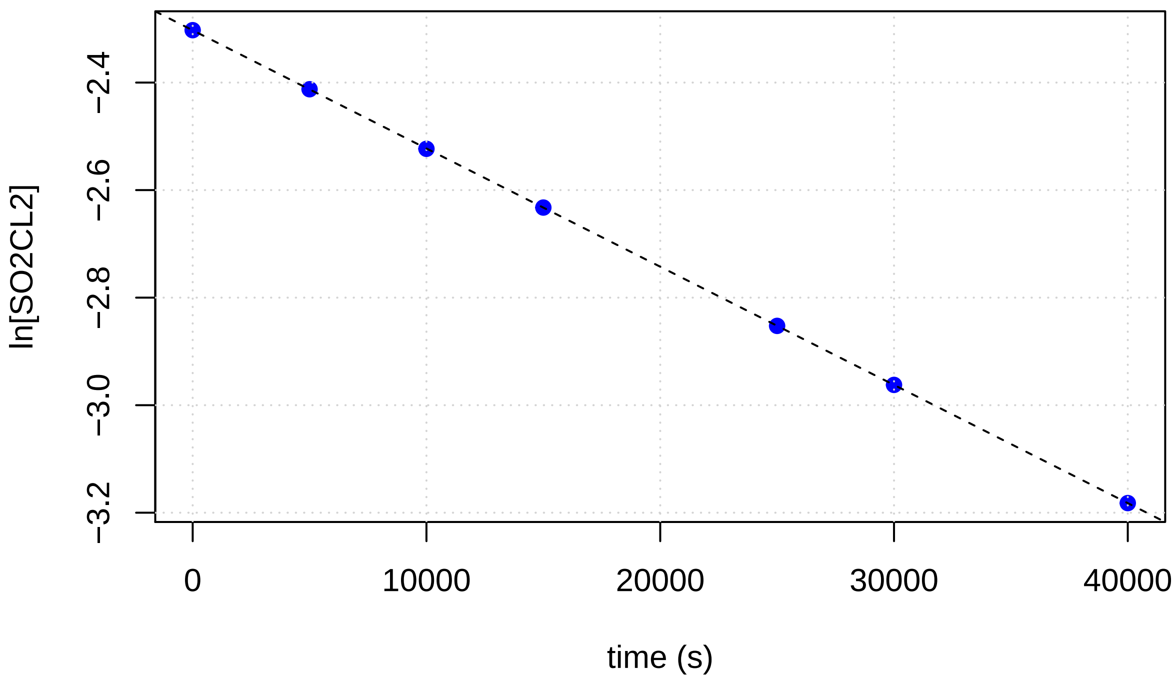
Now we can compare these adjusted rates, noting that when we cut the concentration of OCl^- by a factor of five, the adjusted rate decreases by a factor of 5; thus, the reaction is first order in OCl^-. To find the rate constant, we use the first experiment, obtaining

$$k = \frac{R}{[\text{OCl}^-][\text{I}^-]} = \frac{3.05 \times 10^{-4} \text{ M/s}}{(0.050 \text{ M})(0.10 \text{ M})} = 6.1 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$$

17.33: To determine the reaction's rate law, we first try plotting the $[\text{SO}_2\text{Cl}_2]$ vs. time

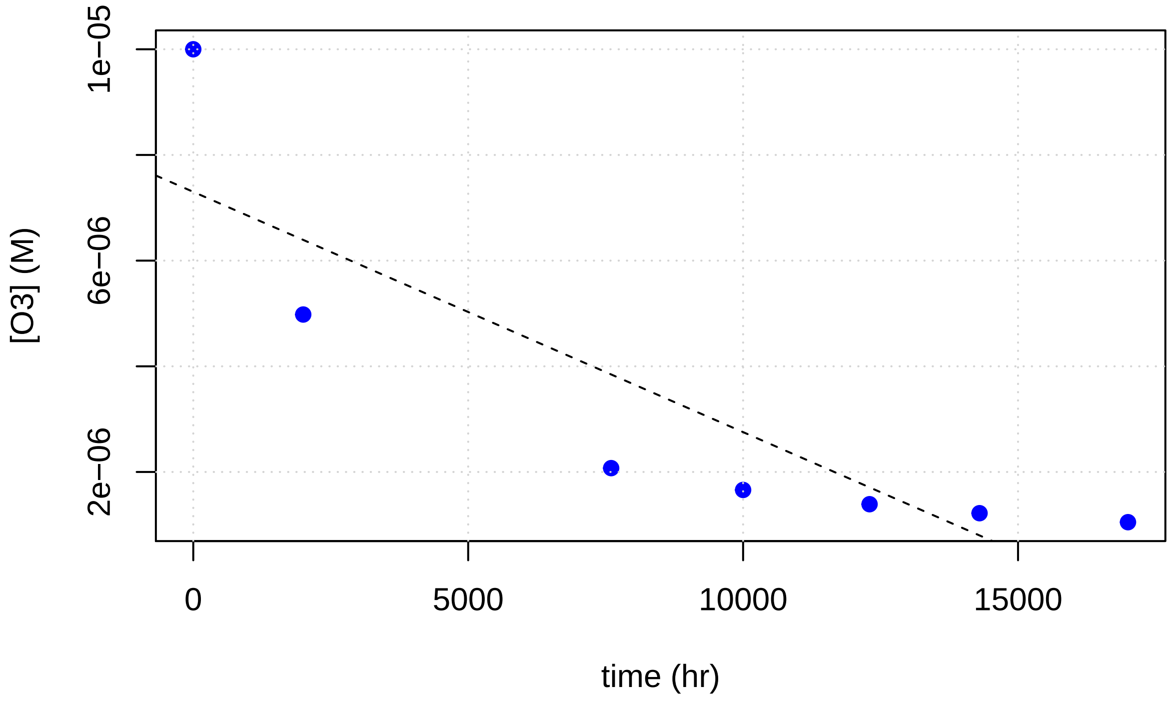


Linear regression suggests that the relationship is not a straight-line; thus, we next try plotting the $\ln[\text{CH}_2\text{Cl}_2]$ vs time

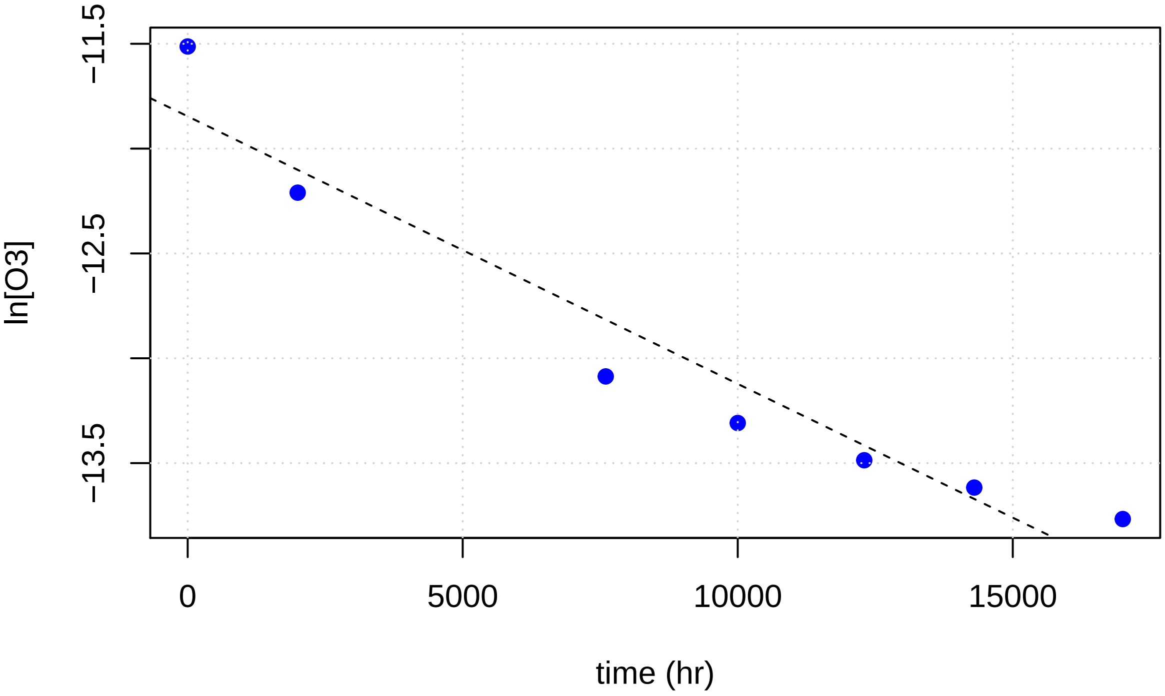


Linear regression suggests that this relationship is a straight-line, indicating that the reaction is first order with respect to SO_2Cl_2. The slope of the regression line gives the rate constant, which is 2.20e-05 s^{-1}.

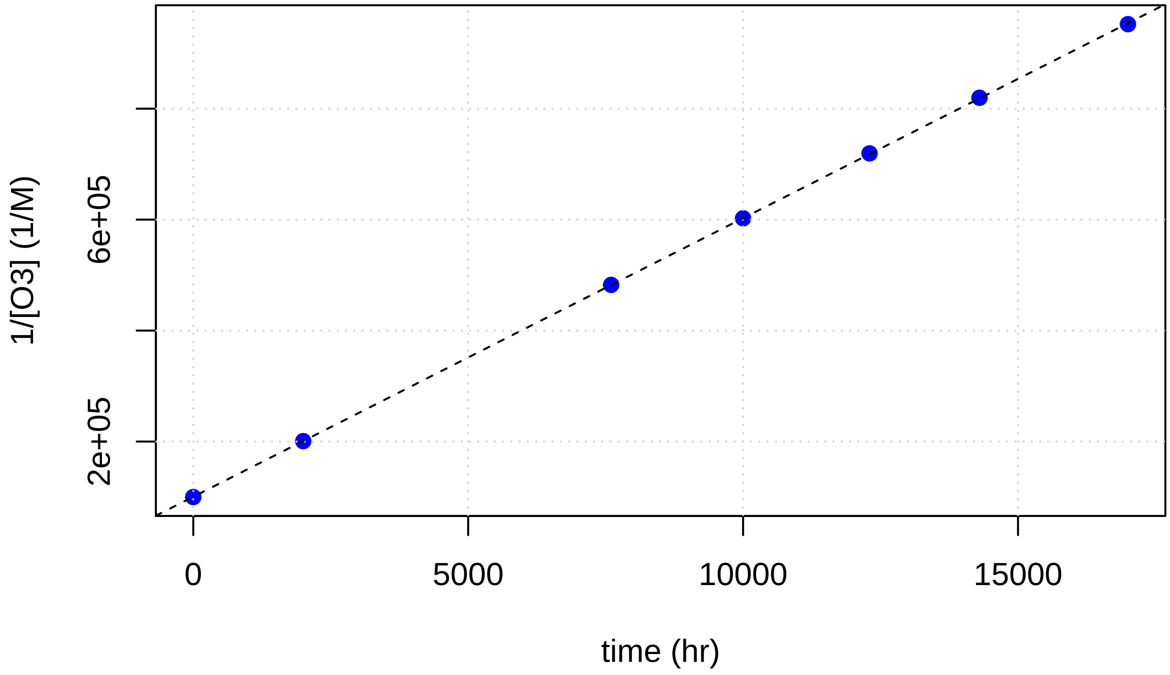
17.34: To determine the reaction's rate law, we first try plotting the $[O_3]$ vs. time



Linear regression suggests that the relationship is not a straight-line; thus, we next try plotting the $\ln[CH_2Cl_2]$ vs time



Linear regression suggests that the relationship is not a straight-line; thus, we next try plotting the $[CH_2Cl_2]^{-1}$ vs time



Linear regression suggests that this relationship is a straight-line, indicating that the reaction is second order with respect to O_3. The slope of the regression line gives the rate constant, which is 5.02e+01 M^{-1} hr^{-1}.

17.46: With a half-life of 42 days for a first-order process, the rate constant is

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{42 \text{ d}} = 0.0165 \text{ d}^{-1}$$

To find the time to achieve 1/64th of the original dose, we use the integrated equation for a first-order reaction where the initial concentration is 64 and the final concentration is 1; thus

$$\ln(1) = \ln(64) - (0.0165 \text{ d}^{-1}) \times t$$

and solve for time obtaining $t = 252$ d.

17.60: Beginning with the Arrhenius equation at each tempeature, we have at 30°C or 303 K

$$k_{303} = A \times e^{-E_a/(8.314 \times 303)}$$

and we have at 37°C or 310 K

$$k_{310} = A \times e^{-E_a/(8.314 \times 310)}$$

Dividing the second equation by the first equation gives

$$\frac{k_{310}}{k_{303}} = 1.47 = \frac{e^{-E_a/(8.314 \times 310)}}{e^{-E_a/(8.314 \times 303)}}$$

Note that the term A is dropped as it appears in both the numerator and the denominator. Taking the ln of both sides of this equation gives

$$\ln(1.47) = -\frac{E_a}{8.314 \times 310} + \frac{E_a}{8.314 \times 303}$$

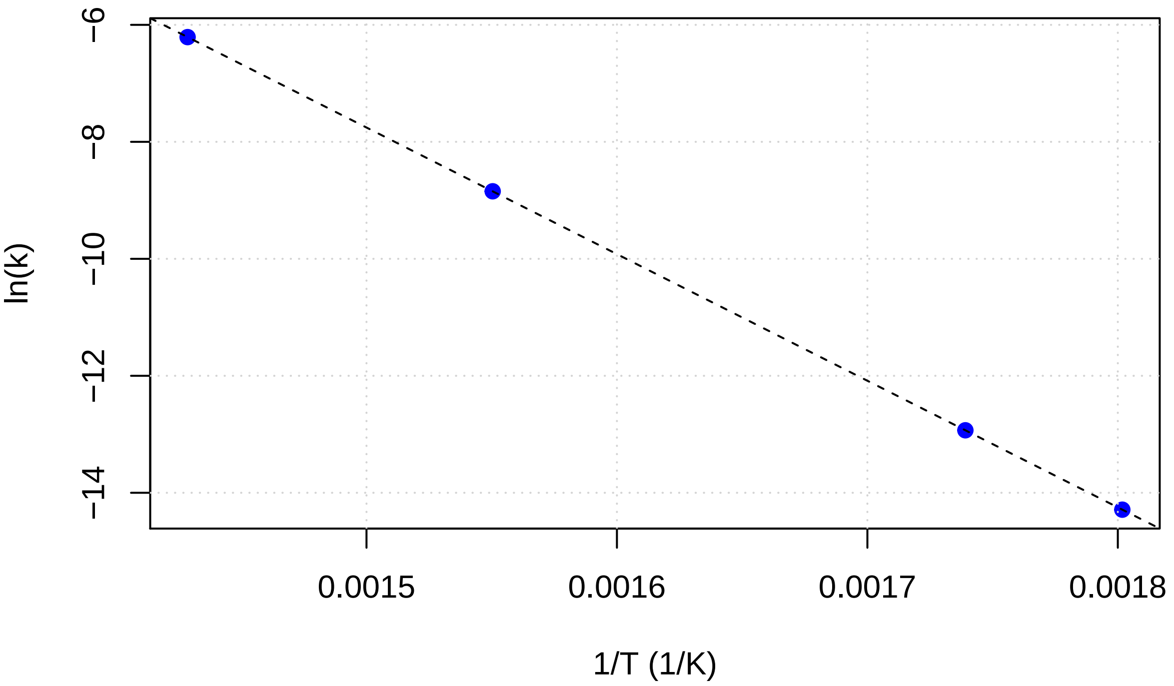
$$0.3853 = -\frac{E_a}{2577.34} + \frac{E_a}{2519.14}$$

$$0.3853 = 8.964 \times 10^{-6} \times E_a$$

$$E_a = 42,980 \text{ J/mol}$$

or 43.0 kJ/mol.

17.62: To find the activation energy, E_a, we plot $\ln k$ as a function of T^{-1}, which should give a straight-line with a slope equal to $-E_a/R$.



The slope of the line is -2.16e+04, which, after multiplying by $-R = 8.314$ J/mol•K and, converting to kJ, gives $E_a =$ -180 kJ/mol.

17.68: If we do not have information about the reaction's mechanism, then we cannot use the reaction's stoichiometry to determine reaction orders. If the net reaction has a one-step mechanism, then the rate law follows from this elementary reaction and the rate law is $R = k[\mathrm{A}][\mathrm{B}]$; thus, doubling the concentration of A doubles the rate.

17.72: For an elementary reaction, the rate law includes each reactant's concentration raised to a power that matches its stoichiometry; thus, for (a) we have $R = k[\mathrm{O_3}]$, for (b) we have $R = k[\mathrm{O_3}][\mathrm{Cl}]$, for (c) we have $R = k[\mathrm{ClO}][\mathrm{O}]$, for (d) we have $R = k[\mathrm{O_3}][\mathrm{NO}]$, and for (e) we have $R = k[\mathrm{NO_2}][\mathrm{O}]$.

17.74: For (a), from the first two experiments, we see that doubling the concentration of H_2 while holding constant the concentration of NO doubles the initial rate; thus, we know that the reaction is first-order in H_2. From the last two experiments, we see that doubling the concentration of NO while holding constant the concentration of H_2 increases the rate by a factor of four, which means the reaction is second-order in NO. For (b), the results from (a) give the rate law as

$$R = k[\mathrm{NO}]^2[\mathrm{H_2}]$$

For (c), the rate constant is, using data from the first experiment

$$k = \frac{R}{[\mathrm{NO}]^2[\mathrm{H_2}]} = \frac{1.8 \times 10^{-4}\ \mathrm{M/min}}{(0.0060\ \mathrm{M})^2(0.0010\ \mathrm{M})} = 5.0 \times 10^3\ \mathrm{M^{-2}min^{-1}}$$

For (d), we just use the reaction's stoichiometry. If we consume half of the H_2, then its concentration decreases by 0.0010 mol/L, which means the concentration of NO_2 also decreases by 0.0010 mol/L (given the 2:2 stoichiometric ratio), decreasing from 0.0060 to 0.0050 mol/L. For (e), the rds cannot be the first step because if it is, the rate law cannot depend on the concentration of H_2. If we assume that the second step is the rds, then its rate law is

$$R = k[\mathrm{N_2O_2}][\mathrm{H_2}]$$

If we assume the first step is in rapid equilibrium, then the concentration of N_2O_2 is found using the equilibrium constant for the reaction

$$K = \frac{[\mathrm{N_2O_2}]}{[\mathrm{NO}]^2}$$

$$[\mathrm{N_2O_2}] = K \times [\mathrm{NO}]^2$$

Substituting back gives

$$R = k[\mathrm{N_2O_2}][\mathrm{H_2}] = k \times K \times [\mathrm{NO}]^2[\mathrm{H_2}]$$

which matches the rate law.