

13.2 Consider the reaction: $2 \text{N}_2\text{O} (\text{g}) \rightarrow 2 \text{N}_2 (\text{g}) + \text{O}_2 (\text{g})$

A. Express the rate of the reaction with respect to each of the reactants and products.

B. In the first 10.0 s of the reaction, 0.018 mol of O_2 is produced in a reaction vessel with a volume of 0.250 L. What is the average rate of the reaction over this time interval?

C. Predict the rate of change in the concentration of N_2O over this time interval. In other words what is $\frac{\Delta[\text{N}_2\text{O}]}{\Delta t}$?

SOLUTION:

A.

$$\text{Rate} = \frac{-1 \Delta[\text{N}_2\text{O}]}{2 \Delta t}$$

$$\text{Rate} = \frac{+1 \Delta[\text{N}_2]}{2 \Delta t}$$

$$\text{Rate} = \frac{+1 \Delta[\text{O}_2]}{1 \Delta t}$$

B.

$$\text{Rate} = \frac{+1 \Delta[\text{O}_2]}{1 \Delta t} = \frac{\frac{0.018 \text{ mol } \text{O}_2}{0.250 \text{ L}} - 0 \text{ M initial}}{10 \text{ s}} = 7.2 \times 10^{-3} \frac{\text{M}}{\text{s}}$$

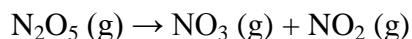
C.

$$\text{Rate} = \frac{-1 \Delta[\text{N}_2\text{O}]}{2 \Delta t} = 7.2 \times 10^{-3} \frac{\text{M}}{\text{s}}$$

$$\frac{-1 \Delta[\text{N}_2\text{O}]}{2 \Delta t} = 7.2 \times 10^{-3} \frac{\text{M}}{\text{s}}$$

$$\frac{\Delta[\text{N}_2\text{O}]}{\Delta t} = -1.44 \times 10^{-2} \frac{\text{M}}{\text{s}}$$

13.12 This reaction is first order in N_2O_5 :



The rate constant for the reaction at a certain temperature is 0.053 /s.

A. Calculate the rate of the reaction when $[\text{N}_2\text{O}_5] = 0.055 \text{ M}$.

B. What would the rate of the reaction be at the same concentration as in part a if the

reaction were second order? Zero order? (Assume the same numerical value for the rate constant with the appropriate units.)

SOLUTION:

$$A. \text{ Rate} = k[N_2O_5] = (0.053 \text{ s}^{-1})(0.055 \text{ M}) = 2.9 \times 10^{-3} \frac{M}{s}$$

$$B. \text{ Rate} = k[N_2O_5]^2 = (0.053 \text{ M}^{-1}\text{s}^{-1})(0.055 \text{ M})^2 = 1.6 \times 10^{-4} \frac{M}{s}$$

$$\text{Rate} = k[N_2O_5]^0 = (0.053 \text{ M s}^{-1})(0.055 \text{ M})^0 = 5.3 \times 10^{-2} \frac{M}{s}$$

13.16 Consider the data showing the initial rate of a reaction (A→products) at several different concentrations of A. What is the order of the reaction? Write a rate law for the reaction including the value of the rate constant, k.

[A] (M)	Initial Rate (M/s)
0.15	0.008
0.30	0.016
0.60	0.032

SOLUTION:

You can determine the order by inspection. When I double the [A] from 0.15 M to 0.30 M, the rate doubles from 0.008 M/s to 0.016 M/s. Same thing happens when I double it again from 0.30 M to 0.60 M, the rate doubles from 0.016 M/s to 0.032 M/s.

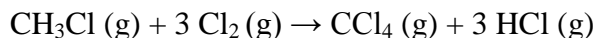
So, the reaction is first order in A.

$$\text{Rate} = k[A]$$

To determine k, I just plug in the values for the rate and [A]. I should average all 3, but since they are exact doublings, they will give exactly the same k.

$$\text{Rate} = 0.008 \frac{M}{s} = k[0.15 \text{ M}]$$
$$k = 5.3 \times 10^{-2} \text{ s}^{-1}$$

13.18 The data below were collected for the reaction:



[CH ₃ Cl] (M)	[Cl ₂] (M)	Initial Rate (M/s)
0.050	0.050	0.014
0.100	0.050	0.029
0.100	0.100	0.041
0.200	0.200	0.115

Write an expression for the reaction rate law and calculate the value of the rate constant, k. What is the overall order of the reaction?

SOLUTION: Again, it can be done by inspection but if you want to see the math:

$$\text{Rate} = k[\text{CH}_3\text{Cl}]^x[\text{Cl}_2]^y$$

I write the rate law for the first two experiments in the chart:

$$0.014 \frac{\text{M}}{\text{s}} = k[0.050 \text{ M}]^x[0.050 \text{ M}]^y$$

$$0.029 \frac{\text{M}}{\text{s}} = k[0.100 \text{ M}]^x[0.050 \text{ M}]^y$$

Then I divide the one equation by the other (left side divided by left side, right side divided by right side)

$$\frac{0.014 \frac{\text{M}}{\text{s}}}{0.029 \frac{\text{M}}{\text{s}}} = \frac{k[0.050 \text{ M}]^x[0.050 \text{ M}]^y}{k[0.100 \text{ M}]^x[0.050 \text{ M}]^y}$$

The k cancels as does the chlorine concentration

$$\begin{aligned} \frac{0.014 \frac{\text{M}}{\text{s}}}{0.029 \frac{\text{M}}{\text{s}}} &= \frac{[0.050 \text{ M}]^x}{[0.100 \text{ M}]^x} \\ 0.4828 &= (0.5)^x \end{aligned}$$

Take the ln of both sides:

$$\begin{aligned} \ln(0.4828) &= \ln(0.5)^x \\ \ln(0.4828) &= x \ln(0.5) \end{aligned}$$

$$x = \frac{\ln(0.48)}{\ln(0.5)} = 1.06 \approx 1$$

First order!

I do the same thing for second and third experiments.

$$0.041 \frac{M}{s} = k[0.100 M]^x [0.100 M]^y$$

$$0.029 \frac{M}{s} = k[0.100 M]^x [0.050 M]^y$$

Then I divide the one equation by the other (left side divided by left side, right side divided by right side)

$$\frac{0.041 \frac{M}{s}}{0.029 \frac{M}{s}} = \frac{k[0.100 M]^x [0.100 M]^y}{k[0.100 M]^x [0.050 M]^y}$$

The k cancels as does the chloroform concentration

$$\frac{0.041 \frac{M}{s}}{0.029 \frac{M}{s}} = \frac{[0.100 M]^y}{[0.050 M]^y}$$
$$1.414 = (2.0)^y$$

Take the ln of both sides:

$$\ln(1.414) = \ln(2.0)^y$$
$$\ln(1.414) = y \ln(2.0)$$

$$y = \frac{\ln(1.414)}{\ln(2.0)} = 0.499 \approx 0.5$$

So

$$\text{Rate} = k[CH_3Cl]^1 [Cl_2]^{0.5}$$

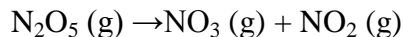
To get k, I just plug the data into the rate law:

[CH ₃ Cl] (M)	[Cl ₂] (M)	Initial Rate (M/s)	k (calc) $= \frac{\text{Rate}}{[\text{CH}_3\text{Cl}]^1[\text{Cl}_2]^{0.5}}$
0.050	0.050	0.014	1.25
0.100	0.050	0.029	1.30
0.100	0.100	0.041	1.30
0.200	0.200	0.115	1.29

The average k value is $1.28 \text{ M}^{-0.5}\text{s}^{-1}$

The total order of the rate law is one-and-one-half.

13.22 The data below show the concentration of N₂O₅ versus time for the reaction:



Time (s)	[N ₂ O ₅] (M)
0	1.0000
25	0.822
50	0.677
75	0.557
100	0.458
125	0.377
150	0.310
175	0.255
200	0.210

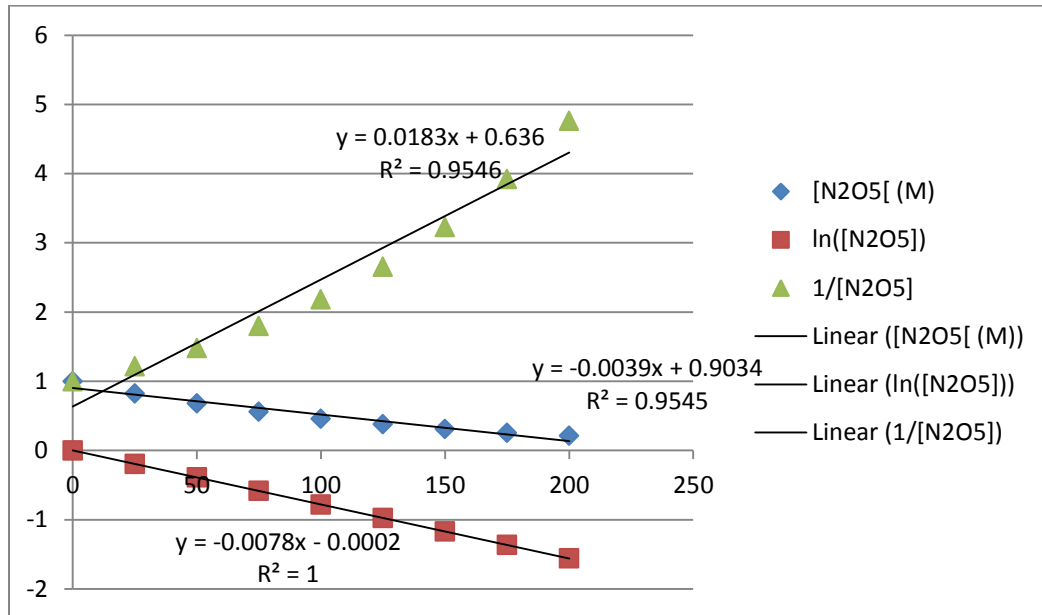
Determine the order of the reaction and the value of the rate constant. Predict the concentration of N₂O₅ at 250 s.

SOLUTION:

Integrated rate law problem. Easiest thing is to make the 3 graphs corresponding to 0, 1st, and 2nd order kinetics.

Time(s)	[N ₂ O ₅] (M)	ln([N ₂ O ₅])	1/[N ₂ O ₅]
0	1	0	1
25	0.822	-0.19601	1.216545
50	0.677	-0.39008	1.477105
75	0.557	-0.58519	1.795332
100	0.458	-0.78089	2.183406
125	0.377	-0.97551	2.65252

150	0.31	-1.17118	3.225806
175	0.255	-1.36649	3.921569
200	0.21	-1.56065	4.761905



The best straight line is the ln plot, so it is first order with $k=0.0078 \text{ s}^{-1}$.

Rate law:

$$\text{Rate} = (0.0078 \text{ s}^{-1})[\text{N}_2\text{O}_5]$$

Integrated Rate Law

$$\ln([\text{N}_2\text{O}_5])_t = - (0.0078 \text{ s}^{-1}) t - \ln([\text{N}_2\text{O}_5])_{t=0}$$

$$\ln([\text{N}_2\text{O}_5])_{t=250} = - (0.0078 \text{ s}^{-1}) (250 \text{ s}) - \ln(1)$$

$$\ln([\text{N}_2\text{O}_5])_{t=250} = -1.95$$

$$[\text{N}_2\text{O}_5] = e^{-1.95} = 0.142 \text{ M}$$

13.42 A reaction has a rate constant of 0.000122 /s at 27 C and 0.228 /s at 77 C.

- A. Determine the activation barrier for the reaction.
- B. What is the value of the rate constant at 17 C?

SOLUTION:

Arrhenius equation:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

I need E_a but it's the only thing I don't know:

$$\ln\left(\frac{0.000122 \text{ /s}}{0.228 \text{ /s}}\right) = \frac{-E_a}{8.314 \frac{\text{J}}{\text{mol K}}} \left(\frac{1}{300 \text{ K}} - \frac{1}{350 \text{ K}}\right)$$

$$\ln(5.35 \times 10^{-4}) = \frac{-E_a}{8.314 \frac{\text{J}}{\text{mol K}}} (4.762 \times 10^{-4})$$

$$E_a = 1.315 \times 10^5 \text{ J/mol}$$

B.

$$\ln\left(\frac{k}{0.228 \text{ /s}}\right) = \frac{-1.315 \times 10^5 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol K}}} \left(\frac{1}{290 \text{ K}} - \frac{1}{350 \text{ K}}\right) = (-1.582 \times 10^4)(5.911 \times 10^{-4})$$

$$\ln\left(\frac{k}{0.228}\right) = -9.35$$

$$\frac{k}{0.228} = e^{-9.35} = 8.68 \times 10^{-5}$$

$$k = 1.98 \times 10^{-5} \text{ /s}$$

13.54 The activation barrier for the hydrolysis of sucrose into glucose and fructose is 108 kJ/mol. If an enzyme increases the rate of the hydrolysis reaction by a factor of 1 million, how

much lower does the activation barrier have to be when sucrose is in the active site of the enzyme? (Assume that the frequency factors for the catalyzed and uncatalyzed reactions are identical and a temperature of 25 C.)

SOLUTION:

$$k = Ae^{\frac{-E_a}{RT}}$$

Same trick we used for the Arrhenius only this time the E_a isn't the same!

$$\ln k_1 = \frac{-E_{a1}}{RT} + \ln A$$

$$\ln k_2 = \frac{-E_{a2}}{RT} + \ln A$$

If we combine these two equations, we get:

$$\ln k_1 - \ln k_2 = \frac{-E_{a1}}{RT} + \ln A - \left(\frac{-E_{a2}}{RT} + \ln A \right)$$

The $\ln A$ still cancels, but I'm left with:

$$\ln k_1 - \ln k_2 = \frac{-E_{a1}}{RT} + \frac{E_{a2}}{RT}$$

If the catalyzed rate is 10^6 times the uncatalyzed, then $k_1 = 10^6 k_2$

$$\begin{aligned} \ln(10^6 k_2) - \ln k_2 &= \frac{-E_{a1}}{RT} + \frac{E_{a2}}{RT} = \frac{1}{RT} (E_{a2} - E_{a1}) \\ &= \frac{1}{\left(8.314 \frac{J}{mol K}\right) (298 K)} \left(108 \times \frac{10^3 J}{mol} - E_{a1}\right) \end{aligned}$$

$$\ln(10^6) + \ln(k_2) - \ln k_2 = \frac{1}{\left(8.314 \frac{J}{mol K}\right) (298 K)} \left(108 \times \frac{10^3 J}{mol} - E_{a1}\right)$$

$$\ln(10^6) = \left(4.036 \times 10^{-4} \frac{mol}{J}\right) \left(108 \times \frac{10^3 J}{mol} - E_{a1}\right)$$

$$13.816 = 43.589 - 4.036 \times 10^{-4} \frac{mol}{J} E_{a1}$$

$$E_{a1} = 7.38 \times 10^4 \text{ J/mol or } 73.8 \text{ kJ/mol}$$

13.62 Cyclopropane (C_3H_6) reacts to form propene (C_3H_6) in the gas phase. The reaction is first order in cyclopropane and has a rate constant of $5.87 \times 10^{-4} \text{ /s}$ at 485 C. If a 2.5 L reaction vessel initially contains 722 torr of cyclopropane at 485 C, how long will it take for the partial pressure of cyclopropane to drop below 100 torr?

SOLUTION:

1st order rate law, so:

$$\text{Rate} = k[\text{C}_3\text{H}_6]$$

1st order integrated rate law is:

$$\ln([\text{C}_3\text{H}_6]_{\text{time}}) = -kt + \ln([\text{C}_3\text{H}_6]_{\text{initial}})$$

For gases, the atm is proportional to the molarity:

$$P = (n/V)RT = MRT$$

So you can actually just use pressures!

$$\ln(100 \text{ torr}) = -(5.87 \times 10^{-4} \text{ /s}) t + \ln(722 \text{ torr})$$

$$4.605 = -5.87 \times 10^{-4} t + 6.58$$

$$-1.97 = -5.87 \times 10^{-4} t$$

$$t = 3364 \text{ s}$$