

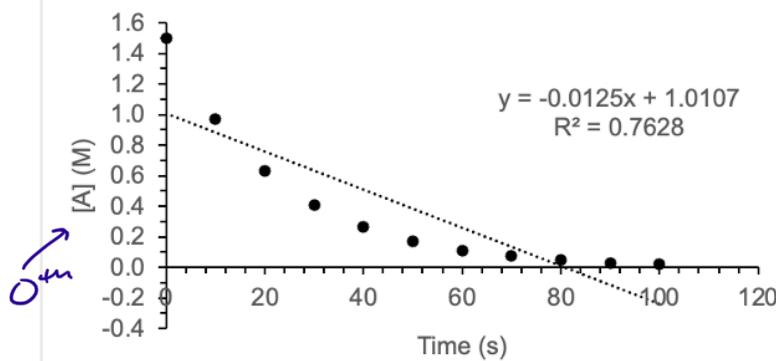
Kinetics

This worksheet should help you identify how we can use kinetics to understand chemical reactions. It is intended for you to work through it in order. (*Don't skip ahead.*)

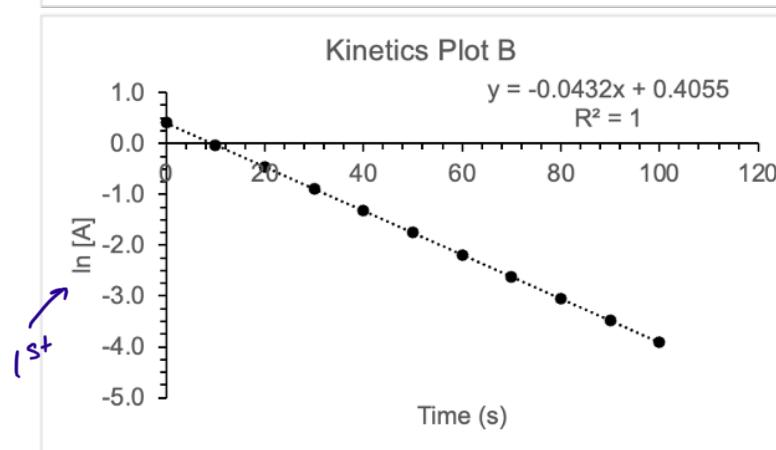


In order to find information about the reaction, you run a few experiments, resulting in the following data, where A represents O_3 .

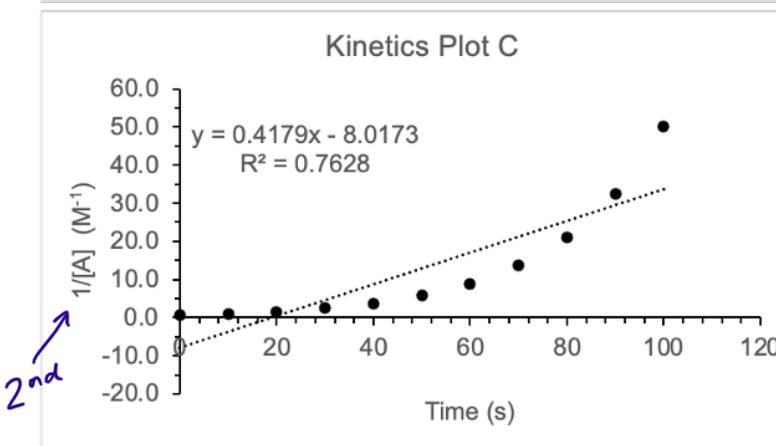
Kinetics Plot A



Kinetics Plot B



Kinetics Plot C



Time (s)	[A] (M)	$\ln[A]$	$1/[A] (\text{M}^{-1})$
0	1.500	0.405	0.667
10	0.974	-0.027	1.027
20	0.632	-0.459	1.582
30	0.410	-0.891	2.436
40	0.266	-1.323	3.753
50	0.173	-1.755	5.781
60	0.112	-2.187	8.904
70	0.073	-2.619	13.716
80	0.047	-3.051	21.127
90	0.031	-3.483	32.542
100	0.020	-3.915	50.126

Using the above data, answer the following questions:

What is the reaction order of O₃? How do you know?

Because only ln[O₃] vs time yields a linear plot, indicated by the dashed line fitting data points and an R² of 1, O₃ must be first order

What is the experimental rate law of the reaction?

$$\text{Rate} = k[\text{O}_3]$$

What is the rate constant (k) of the reaction?

The slope of the line tells us the value of k... 0.0432 s⁻¹
units for 1st order

We can check if this makes sense
Initial = 1.500
[1/2] = 0.75
This value comes between data points at 10s & 20s... So makes sense.

What is the half-life of O₃ in the reaction?

Because 1st order

$$t_{1/2} = \frac{0.693}{k}$$

$$t_{1/2} = \frac{0.693}{0.0432 \text{ s}^{-1}} = 16.0 \text{ s}$$

How long would it take for 90% of the initial concentration to be used up?

$$\ln[A] = -kt + \ln[A]_0$$

$$\ln[0.15] = -0.0432 \text{ s}^{-1} (t) + \ln[1.5]$$

$$-1.897 = -0.0432 \text{ s}^{-1} (t) + 0.4055$$

$$-2.303 = -0.0432 \text{ s}^{-1} (t)$$

$$53.3 \text{ s} = t$$

$$\text{Initial} = 1.500 \text{ M}$$

90% go away, so 10% left... 0.15 M

Makes sense if we look up 0.15 M in data table it comes between 50 & 60 s...

The reaction mechanism below has been proposed:

Step 1	$O_3(g) \rightarrow O_2(g) + O(g)$	Fast
Step 2	$O(g) + O_3(g) \rightarrow 2 O_2(g)$	Slow

What is the rate-determining step?

Step 2, because it is slow.

Are there any reaction intermediates? If so, what are they?

O is an intermediate because it is generated in the 1st step and then consumed in the 2nd step.

What is the rate law of the first reaction?

$$\text{Rate} = k_1 [O_3]$$

What is the rate law of the second reaction?

$$\text{Rate} = k_2 [O][O_3]$$

← overall rate law, so
need remove intermediate

What is the overall rate law?

$$\xrightarrow{1\text{st}} \text{Rate} = k_1 [O_3]$$

$$\xleftarrow{1\text{st}} \text{Rate} = k_1 [O][O_2]$$

$$k_1 [O_3] = k_{-1} [O][O_2]$$

$$\frac{k_1 [O_3]}{k_{-1} [O_2]} = [O]$$

$$\text{Rate} = k_2 [O][O_3]$$

$$\text{Rate} = k_2 \left(\frac{k_1 [O_3]}{k_{-1} [O_2]} \right) [O_3]$$

$$\text{Rate} = k \frac{[O_3]^2}{[O_2]}$$

Using your experimental data from #1, is the proposed mechanism valid? Why or why not?

No! A proposed mechanism must yield the same rate law as the experimental rate law, so this is not a valid mechanism.

$$T_2 > T_1 \text{ so } k_2 > k_1$$

Rate constants are dependent on temperature. The experiments from page 1 were completed at 250 °C. The experiments were repeated at 400 °C. If the activation energy is 76.0 kJ/mol, what is the rate of the second reaction?

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

$$T \text{ } ^\circ\text{C} \rightarrow K$$

$$\ln\left(\frac{k_2}{0.04325\text{s}^{-1}}\right) = \frac{76000 \text{ J/mol}}{8.314 \text{ J/molK}} \left(\frac{1}{523 \text{ K}} - \frac{1}{673 \text{ K}} \right)$$

$$e^{\ln\left(\frac{k_2}{0.04325\text{s}^{-1}}\right)} = 3.896$$

$$\frac{k_2}{0.04325\text{s}^{-1}} = 49.187$$

$$k_2 = 2.12 \text{ s}^{-1}$$

makes
sense
conceptually

Using all of the information from above and the knowledge that the reaction is exothermic, sketch an energy diagram.

