

Chapter 15: Chemical Kinetics; 10, 12, 13, 16, 18, 22, 26, 27, 31, 37, 38

Reaction Rates

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10. The coefficients in the balanced reaction relate the rate of disappearance of reactants to the rate of production of products. From the balanced reaction, the rate of production of P_4 will be 1/4 the rate of disappearance of PH_3 and the rate of production of H_2 will be 6/4 the rate of disappearance of PH_3 . By convention, all rates are given as positive values.

$$\text{Rate} = -\frac{\Delta[PH_3]}{\Delta t} = \frac{-(-0.0048 \text{ mol}/2.0 \text{ L})}{s} = 2.4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\frac{\Delta[P_4]}{\Delta t} = -\frac{1}{4} \frac{\Delta[PH_3]}{\Delta t} = 2.4 \times 10^{-3}/4 = 6.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\frac{\Delta[H_2]}{\Delta t} = -\frac{6}{4} \frac{\Delta[PH_3]}{\Delta t} = 6(2.4 \times 10^{-3})/4 = 3.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

12. a. The units for rate are always $\text{mol L}^{-1} \text{ s}^{-1}$. b. $\text{Rate} = k$; k has units of $\text{mol L}^{-1} \text{ s}^{-1}$.

c. $\text{Rate} = k[A]$, $\frac{\text{mol}}{\text{L s}} = k \left(\frac{\text{mol}}{\text{L}} \right)$ d. $\text{Rate} = k[A]^2$, $\frac{\text{mol}}{\text{L s}} = k \left(\frac{\text{mol}}{\text{L}} \right)^2$

k must have units of s^{-1} .

k must have units $\text{L mol}^{-1} \text{ s}^{-1}$.

e. $\text{L}^2 \text{ mol}^{-2} \text{ s}^{-1}$

13. $\text{Rate} = k[\text{Cl}]^{1/2}[\text{CHCl}_3]$, $\frac{\text{mol}}{\text{L s}} = k \left(\frac{\text{mol}}{\text{L}} \right)^{1/2} \left(\frac{\text{mol}}{\text{L}} \right)$; k must have units of $\text{L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$.

Rate Laws from Experimental Data: Initial Rates Method

16. a. $\text{Rate} = k[\text{I}]^x[\text{S}_2\text{O}_8^{2-}]^y$, $\frac{12.5 \times 10^{-6}}{6.25 \times 10^{-6}} = \frac{k(0.080)^x(0.040)^y}{k(0.040)^x(0.040)^y}$, $2.00 = 2.0^x$, $x = 1$

$$\frac{12.5 \times 10^{-6}}{6.25 \times 10^{-6}} = \frac{k(0.080)^x(0.040)^y}{k(0.080)^x(0.020)^y}, 2.00 = 2.0^y, y = 1; \text{Rate} = k[\text{I}][\text{S}_2\text{O}_8^{2-}]$$

b. For the first experiment:

$$\frac{12.5 \times 10^{-6} \text{ mol}}{\text{L s}} = k \left(\frac{0.080 \text{ mol}}{\text{L}} \right) \left(\frac{0.040 \text{ mol}}{\text{L}} \right), k = 3.9 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$$

The other values are:

Initial Rate (mol L ⁻¹ s ⁻¹)	k (L mol ⁻¹ s ⁻¹)
12.5 × 10 ⁻⁶	3.9 × 10 ⁻³
6.25 × 10 ⁻⁶	3.9 × 10 ⁻³
6.25 × 10 ⁻⁶	3.9 × 10 ⁻³
5.00 × 10 ⁻⁶	3.9 × 10 ⁻³
7.00 × 10 ⁻⁶	3.9 × 10 ⁻³

$$k_{\text{mean}} = 3.9 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$$

18. a. $\text{Rate} = k[\text{Hb}]^x[\text{CO}]^y$

Comparing the first two experiments, [CO] is unchanged, [Hb] doubles, and the rate doubles. Therefore, $x = 1$ and the reaction is first order in Hb. Comparing the second and third experiments, [Hb] is unchanged, [CO] triples and the rate triples. Therefore, $y = 1$ and the reaction is first order in CO.

b. $\text{Rate} = k[\text{Hb}][\text{CO}]$

c. From the first experiment:

$$0.619 \mu\text{mol L}^{-1} \text{ s}^{-1} = k (2.21 \mu\text{mol/L})(1.00 \mu\text{mol/L}), k = 0.280 \text{ L } \mu\text{mol}^{-1} \text{ s}^{-1}$$

The second and third experiments give similar k values, so $k_{\text{mean}} = 0.280 \text{ L } \mu\text{mol}^{-1} \text{ s}^{-1}$.

d. $\text{Rate} = k[\text{Hb}][\text{CO}] = \frac{0.280 \text{ L}}{\mu\text{mol s}} \times \frac{3.36 \mu\text{mol}}{\text{L}} \times \frac{2.40 \mu\text{mol}}{\text{L}} = 2.26 \mu\text{mol L}^{-1} \text{ s}^{-1}$

Integrated Rate Laws

22. a. Since the $1/[A]$ vs time plot was linear, then the reaction is second order in A. The slope of the $1/[A]$ vs. time plot equals the rate constant k . Therefore, the rate law, the integrated rate law and the rate constant value are:

$$\text{Rate} = k[A]^2; \quad \frac{1}{[A]} = kt + \frac{1}{[A]_0}; \quad k = 3.60 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$$

- b. The half-life expression for a second order reaction is: $t_{1/2} = \frac{1}{k[A]_0}$

$$\text{For this reaction: } t_{1/2} = \frac{1}{3.60 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1} \times 2.80 \times 10^{-3} \text{ mol/L}} = 9.92 \times 10^3 \text{ s}$$

Note: We could have used the integrated rate law to solve for $t_{1/2}$ where $[A] = (2.80 \times 10^{-3} / 2) \text{ mol/L}$.

- c. Since the half-life for a second order reaction depends on concentration, then we must use the integrated rate law to solve.

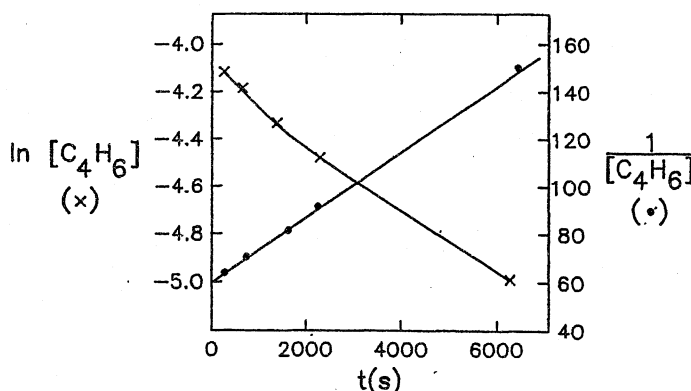
$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}, \quad \frac{1}{7.00 \times 10^{-4} \text{ M}} = \frac{3.60 \times 10^{-2} \text{ L}}{\text{mol s}} \times t + \frac{1}{2.80 \times 10^{-3} \text{ M}}$$

$$1.43 \times 10^3 - 357 = 3.60 \times 10^{-2} t, \quad t = 2.98 \times 10^4 \text{ s}$$

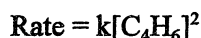
26. The first assumption to make is that the reaction is first order. For a first order reaction, a graph of $\ln [C_4H_6]$ vs. t should yield a straight line. If this isn't linear, then try the second order plot of $1/[C_4H_6]$ vs. t . The data and the plots follow.

Time	195	604	1246	2180	6210 s
$[C_4H_6]$	1.6×10^{-2}	1.5×10^{-2}	1.3×10^{-2}	1.1×10^{-2}	$0.68 \times 10^{-2} \text{ M}$
$\ln [C_4H_6]$	-4.14	-4.20	-4.34	-4.51	-4.99
$1/[C_4H_6]$	62.5	66.7	76.9	90.9	147 M^{-1}

Note: To reduce round off error, we carried extra sig. figs. in the data points.



The natural log plot is not linear, so the reaction is not first order. Since the second order plot of $1/[C_4H_6]$ vs. t is linear, then we can conclude that the reaction is second order in butadiene. The differential rate law is:



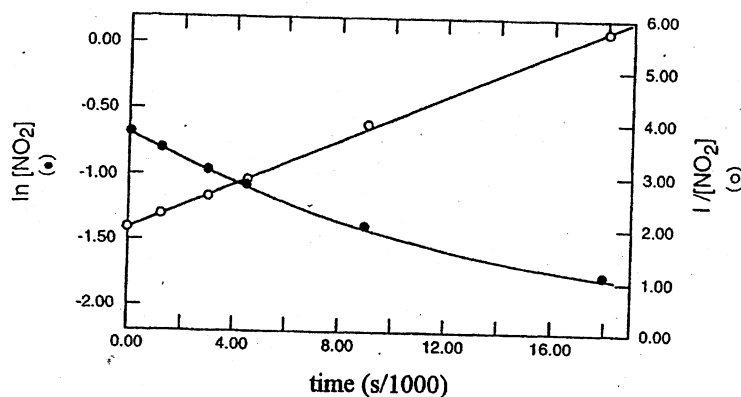
For a second order reaction, the integrated rate law is: $\frac{1}{[C_4H_6]} = kt + \frac{1}{[C_4H_6]_0}$

The slope of the straight line equals the value of the rate constant. Using the points on the line at 1000. and 6000. s:

$$k = \text{slope} = \frac{144 \text{ L/mol} - 73 \text{ L/mol}}{6000. \text{ s} - 1000. \text{ s}} = 1.4 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$$

27. Assume the reaction is first order and see if the plot of $\ln [NO_2]$ vs. time is linear. If this isn't linear, try the second order plot of $1/[NO_2]$ vs. time. The data and plots follow.

Time (s)	$[NO_2]$ (M)	$\ln [NO_2]$	$1/[NO_2]$ (M^{-1})
0	0.500	-0.693	2.00
1.20×10^3	0.444	-0.812	2.25
3.00×10^3	0.381	-0.965	2.62
4.50×10^3	0.340	-1.079	2.94
9.00×10^3	0.250	-1.386	4.00
1.80×10^4	0.174	-1.749	5.75



The plot of $1/[NO_2]$ vs. time is linear. The reaction is second order in NO_2 . The differential rate law and integrated rate law are: $\text{Rate} = k[NO_2]^2$ and $\frac{1}{[NO_2]} = kt + \frac{1}{[NO_2]_0}$.

The slope of the plot $1/[NO_2]$ vs. t gives the value of k . Using a couple points on the plot:

$$\text{slope} = k = \frac{\Delta y}{\Delta x} = \frac{(5.75 - 2.00) M^{-1}}{(1.80 \times 10^4 - 0) s} = 2.08 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$$

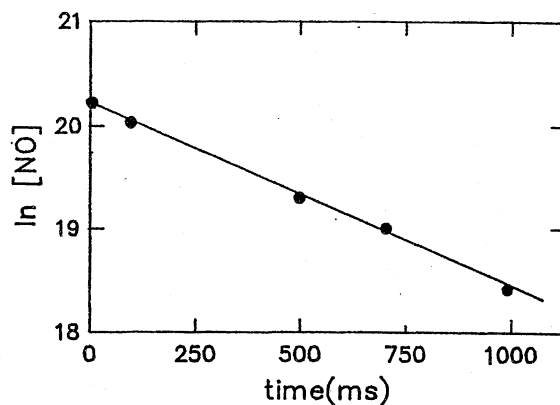
To determine $[NO_2]$ at 2.70×10^4 s, use the integrated rate law where $1/[NO_2]_0 = 1/0.500 M = 2.00 M^{-1}$.

$$\frac{1}{[NO_2]} = kt + \frac{1}{[NO_2]_0}, \quad \frac{1}{[NO_2]} = \frac{2.08 \times 10^{-4} \text{ L}}{\text{mol s}} \times 2.70 \times 10^4 \text{ s} + 2.00 M^{-1}$$

$$\frac{1}{[NO_2]} = 7.62, \quad [NO_2] = 0.131 M$$

31. a. We check for first order dependence by graphing $\ln [\text{concentration}]$ vs. time for each set of data. The rate dependence on NO is determined from the first set of data since the ozone concentration is relatively large compared to the NO concentration, so it is effectively constant.

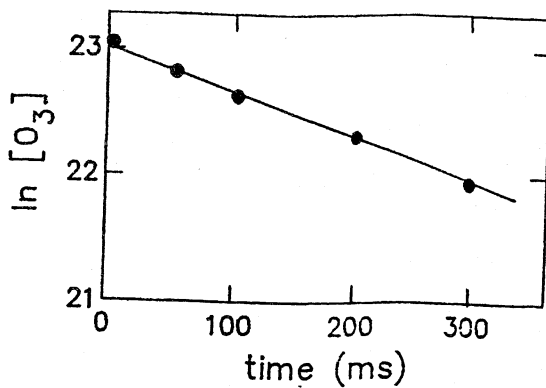
time (ms)	[NO] (molecules/cm ³)	$\ln [\text{NO}]$
0	6.0×10^8	20.21
100.	5.0×10^8	20.03
500.	2.4×10^8	19.30
700.	1.7×10^8	18.95
1000.	9.9×10^7	18.41



Since $\ln [\text{NO}]$ vs. t is linear, the reaction is first order with respect to NO.

We follow the same procedure for ozone using the second set of data. The data and plot are:

time (ms)	[O ₃] (molecules/cm ³)	$\ln [\text{O}_3]$
0	1.0×10^{10}	23.03
50.	8.4×10^9	22.85
100.	7.0×10^9	22.67
200.	4.9×10^9	22.31
300.	3.4×10^9	21.95



The plot of $\ln [\text{O}_3]$ vs. t is linear. Hence, the reaction is first order with respect to ozone.

- b. Rate = $k[\text{NO}][\text{O}_3]$ is the overall rate law.
 c. For NO experiment, Rate = $k'[\text{NO}]$ and $k' = -(\text{slope from graph of } \ln [\text{NO}] \text{ vs. } t)$.

$$k' = -\text{slope} = -\frac{18.41 - 20.21}{(1000. - 0) \times 10^{-3} \text{ s}} = 1.8 \text{ s}^{-1}$$

37. a. If the reaction is 38.5% complete, then 38.5% of the original concentration is consumed, leaving 61.5%.

$$[A] = 61.5\% \text{ of } [A]_0 \text{ or } [A] = 0.615 [A]_0; \ln \left(\frac{[A]}{[A]_0} \right) = -kt, \ln \left(\frac{0.615 [A]_0}{[A]_0} \right) = -k(480. \text{ s})$$

$$\ln(0.615) = -k(480. \text{ s}), -0.486 = -k(480. \text{ s}), k = 1.01 \times 10^{-3} \text{ s}^{-1}$$

b. $t_{1/2} = (\ln 2)/k = 0.6931/1.01 \times 10^{-3} \text{ s}^{-1} = 686 \text{ s}$

c. 25% complete: $[A] = 0.75 [A]_0; \ln(0.75) = -1.01 \times 10^{-3} (t), t = 280 \text{ s}$

75% complete: $[A] = 0.25 [A]_0; \ln(0.25) = -1.01 \times 10^{-3} (t), t = 1.4 \times 10^3 \text{ s}$

Or, we know it takes $2 \times t_{1/2}$ for reaction to be 75% complete. $t = 2 \times 686 \text{ s} = 1370 \text{ s}$

95% complete: $[A] = 0.05 [A]_0; \ln(0.05) = -1.01 \times 10^{-3} (t), t = 3 \times 10^3 \text{ s}$

For ozone experiment, Rate = $k''[O_3]$ and $k'' = -(\text{slope from } \ln [O_3] \text{ vs. } t)$.

$$k'' = -\text{slope} = -\frac{(21.95 - 23.03)}{(300. - 0) \times 10^{-3} \text{ s}} = 3.6 \text{ s}^{-1}$$

- d. From NO experiment, Rate = $k[NO][O_3] = k'[NO]$ where $k' = k[O_3]$.

$$k' = 1.8 \text{ s}^{-1} = k(1.0 \times 10^{14} \text{ molecules/cm}^3), k = 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$

We can check this from the ozone data. Rate = $k''[O_3] = k[NO][O_3]$ where $k'' = k[NO]$.

$$k'' = 3.6 \text{ s}^{-1} = k(2.0 \times 10^{14} \text{ molecules/cm}^3), k = 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$

Both values of k agree.

38. Successive half-lives increase in time for a second order reaction. Therefore, assume reaction is second order in A.

$$t_{1/2} = \frac{1}{k[A]_0}, k = \frac{1}{t_{1/2}[A]_0} = \frac{1}{10.0 \text{ min } (0.10 \text{ M})} = 1.0 \text{ L mol}^{-1} \text{ min}^{-1}$$

a. $\frac{1}{[A]} = kt + \frac{1}{[A]_0} = \frac{1.0 \text{ L}}{\text{mol min}} \times 80.0 \text{ min} + \frac{1}{0.10 \text{ M}} = 90. \text{ M}^{-1}, [A] = 1.1 \times 10^{-2} \text{ M}$

- b. 30.0 min = 2 half-lives, so 25% of original A is remaining.

$$[A] = 0.25(0.10 \text{ M}) = 0.025 \text{ M}$$