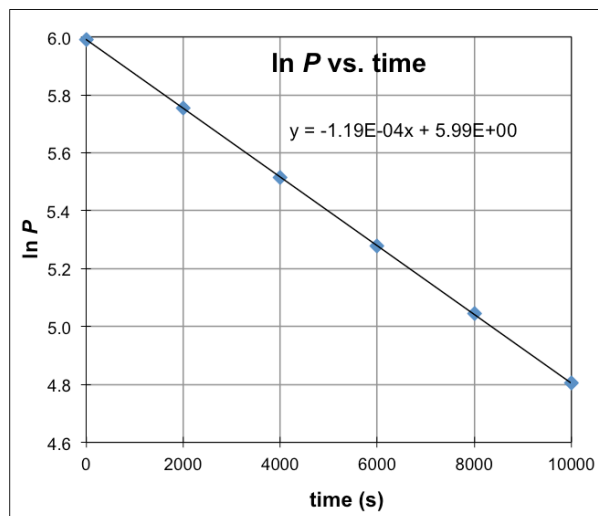


- 21 Cyclobutane decomposes to ethene according to the equation $C_4H_8(g) \rightarrow 2C_2H_4(g)$. Determine the order of the reaction and the rate based on the following pressures at 430°C at constant volume.

Time (s)	$P_{C_4H_8}$ (mmHg)
0	400
2.000	316
4.000	248
6.000	196
8.000	155
10.000	122

The graph of $\ln P$ vs. time is linear, so the reaction is 1st order with slope = $-k$

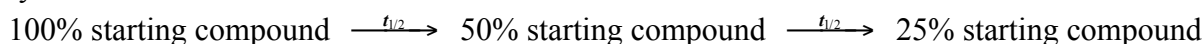
$$k = 1.19 \times 10^{-4} \text{ s}^{-1}$$



- 24 Define half life and write the equation relating half-life to k for a first-order reaction. Half-life is the time required for the concentration of a reactant to decrease to half of its initial concentration.

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

- 27 What is the half-life of a compound if 75 percent of a given sample decomposes in 60 min? Assume 1st order kinetics. We see that 75% of the original compound has decomposed meaning that 25% remains, which is two half-lives. Thus two half-lives equal one hour, or the half-life of the decay is 30 min:

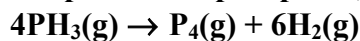


Alternately, using first order kinetics (assume we don't have an exact multiple of 0.5), we can solve for k using Equation (13.3), with $[A]_0 = 100$ and $[A] = 25$:

$$\ln \frac{[A]_t}{[A]_0} = -kt; \ln \frac{25}{100} = -k(60 \text{ min}); k = -\frac{\ln(0.25)}{60 \text{ min}} = 0.023 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.023 \text{ min}^{-1}} = 30 \text{ min}$$

- 28 The decomposition of phosphine, PH_3 , into phosphorus and hydrogen is first order:



The half-life is 35.0 s at 680°C.

(a) Calculate the first-order rate constant.

$$k = \frac{0.693}{t_{1/2}}; k = \frac{0.693}{35.0 \text{ s}} = 0.0198 \text{ s}^{-1}$$

(b) Calculate the time required for 95% of the phosphine to decompose.

Since we initially have 100% of the compound and 95% has reacted, then (100% – 95%), or 5% remains. Thus, the ratio of the percentages will be equal to the ratio of the actual concentrations; that is, $[A]_t/[A]_0 = 5\%/100\%$, or 0.05/1.00:

$$\ln \frac{[A]_t}{[A]_0} = -kt; \ln \frac{(0.05)}{(1.00)} = -(0.0198 \text{ s}^{-1})t; t = -\frac{\ln(0.0500)}{0.0198 \text{ s}^{-1}} = \mathbf{151 \text{ s}}$$

29 The rate constant for the second-order reaction, $2\text{NOBr(g)} \rightarrow 2\text{NO(g)} + \text{Br}_2\text{(g)}$, is $0.80/M \cdot s$ at 10°C

(a) For a starting concentration of $0.086M$, calculate the concentration of NOBr at 22 s.

$$\frac{1}{[\text{NOBr}]_t} = kt + \frac{1}{[\text{NOBr}]_0} = (0.80/M \cdot s)(22s) + \frac{1}{0.086 M} = 29 M^{-1}$$

$$[\text{NOBr}] = \mathbf{0.034 M}$$

30 The rate constant for the second-order reaction, $2\text{NO}_2\text{(g)} \rightarrow 2\text{NO(g)} + \text{O}_2\text{(g)}$, is $0.54/M \cdot s$ at 300°C . How long would it take for the concentration of NO_2 to decrease from $0.62M$ to $0.28M$?

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt; \frac{1}{0.28} = \frac{1}{0.62} + 0.54t; t = \mathbf{3.6 \text{ s}}$$

94 Chlorine oxide (ClO), decays rapidly at room temperature: $2\text{ClO(g)} \rightarrow \text{Cl}_2\text{(g)} + \text{O}_2\text{(g)}$. From the following data, determine the reaction order and calculate the rate constant for the reaction.

Time (s)	$[\text{ClO}] (M)$	$1/[\text{ClO}] (M^{-1})$
0.12×10^{-3}	8.49×10^{-6}	1.18×10^5
0.96×10^{-3}	7.10×10^{-6}	1.41×10^5
2.24×10^{-3}	5.79×10^{-6}	1.73×10^5
3.20×10^{-3}	5.20×10^{-6}	1.92×10^5
4.00×10^{-3}	4.77×10^{-6}	2.10×10^5

Reaction is **second-order** because a plot of $1/[\text{ClO}]$ vs. time is a straight line. The slope of the line equals the rate constant, k .

$$k = \text{Slope} = \mathbf{2.4 \times 10^7 /M \cdot s}$$

