We know that half of the substance decomposes in a time equal to the half-life, \( t_{1/2} \). This leaves half of the compound. Half of what is left decomposes in a time equal to another half-life, so that only one quarter of the original compound remains. We see that 75% of the original compound has decomposed after two half–lives. Thus two half-lives equal one hour, or the half-life of the decay is 30 min.

\[
\begin{align*}
100\% \text{ starting compound} & \rightarrow t_{1/2} \rightarrow 50\% \text{ starting compound} \rightarrow t_{1/2} \rightarrow 25\% \text{ starting compound}
\end{align*}
\]

Using first order kinetics, we can solve for \( k \) using Equation (13.3) of the text, with \([A]_0 = 100\) and \([A] = 25\),

\[
\ln \frac{[A]}{[A]_0} = -kt
\]

\[
\ln \frac{25}{100} = -k(60 \text{ min})
\]

\[
k = \frac{-\ln(0.25)}{60 \text{ min}} = 0.023 \text{ min}^{-1}
\]

Then, substituting \( k \) into Equation (13.5) of the text, you arrive at the same answer for \( t_{1/2} \).

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

13.28 (a) For any first order reaction the rate constant can be found from the half–life using the following equation.

\[
k = \frac{0.693}{t_{1/2}}
\]

\[
k = \frac{0.693}{35.0 \text{ s}} = 0.0198 \text{ s}^{-1}
\]

(b) The time required for 95% of the phosphine to decompose can be found using the following equation.

\[
\ln \frac{[A]}{[A]_0} = -kt
\]

or

\[
t = \frac{1}{k} \ln \frac{[A]_0}{[A]}
\]

The value of \([A]\) after 95% of the reactant has decomposed is 0.0500\([A]_0\). Substitute the rate constant calculated in part (a) and \([A] = 0.0500[A]_0\) into the above equation to calculate the time required for 95% of the phosphine to decompose.

\[
t = \frac{1}{k} \ln \frac{[A]_0}{[A]} = \left( \frac{1}{0.0198 \text{ s}^{-1}} \right) \ln \frac{[A]_0}{0.0500[A]_0}
\]

\[
t = \frac{\ln 20.0}{0.0198 \text{ s}^{-1}} = 151 \text{ s}
\]
13.29 Since the reaction is known to be second-order, the relationship between reactant concentration and time is given by Equation (13.6) of the text. The problem supplies the rate constant and the initial (time = 0) concentration of NOBr. The concentration after 22 s can be found easily.

\[
\frac{1}{[\text{NOBr}]} = \frac{1}{[\text{NOBr}]_0} + kt
\]

\[
\frac{1}{[\text{NOBr}]} = \frac{1}{0.086 \, M} + (0.80 / M \cdot s)(22 \, s)
\]

\[
\frac{1}{[\text{NOBr}]} = 29 \, M^{-1}
\]

\[ [\text{NOBr}] = 0.034 \, M \]

If the reaction were first order with the same k and initial concentration, could you calculate the concentration after 22 s? If the reaction were first order and you were given the \( t_{1/2} \), could you calculate the concentration after 22 s?

13.71 (a) To determine the rate law, we must determine the exponents in the equation

\[
\text{rate} = k[\text{CH}_3\text{COCH}_3]^x[\text{Br}_2]^y[H^+]^z
\]

To determine the order of the reaction with respect to CH\(_3\)COCH\(_3\), find two experiments in which the [Br\(_2\)] and [H\(^+\)] are held constant. Compare the data from experiments (1) and (5). When the concentration of CH\(_3\)COCH\(_3\) is increased by a factor of 1.33, the reaction rate increases by a factor of 1.33. Thus, the reaction is first-order in CH\(_3\)COCH\(_3\).

To determine the order with respect to Br\(_2\), compare experiments (1) and (2). When the Br\(_2\) concentration is doubled, the reaction rate does not change. Thus, the reaction is zero-order in Br\(_2\).

To determine the order with respect to H\(^+\), compare experiments (1) and (3). When the H\(^+\) concentration is doubled, the reaction rate doubles. Thus, the reaction is first-order in H\(^+\).

The rate law is:

\[
\text{rate} = k[\text{CH}_3\text{COCH}_3][H^+]\]

(b) Rearrange the rate law from part (a), solving for k.

\[
k = \frac{\text{rate}}{[\text{CH}_3\text{COCH}_3][H^+]}\]

Substitute the data from any one of the experiments to calculate k. Using the data from Experiment (1),

\[
k = \frac{5.7 \times 10^{-5} \, M / s}{(0.30 \, M)(0.050 \, M)} = 3.8 \times 10^{-3} /M \cdot s\]

13.74 The rate expression for a third order reaction is:

\[
\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^3
\]

The units for the rate law are:

\[
\frac{M}{s} = kM^3\]

\[
k = M^{-2} \cdot s^{-1}\]
For a rate law, zero order means that the exponent is zero. In other words, the reaction rate is just equal to a constant; it doesn't change as time passes.

(a) The rate law would be:
\[ \text{rate} = k[A]^0 = k \]

The integrated zero-order rate law is: \([A] = -kt + [A]_0\). Therefore, a plot of \([A]\) versus time should be a straight line with a slope equal to \(-k\).

(b) \([A] = [A]_0 - kt\)

At \(t_{1/2}\), \([A] = [A]_0/2\). Substituting into the above equation:
\[
[A]_0/2 = [A]_0 - kt_{1/2}
\]
\[
t_{1/2} = \frac{[A]_0}{2k}
\]
\[
k = \frac{[A]_0}{2t_{1/2}}
\]

13.78 (a) Changing the concentration of a reactant has no effect on \(k\).
(b) If a reaction is run in a solvent other than in the gas phase, then the reaction mechanism will probably change and will thus change \(k\).
(c) Doubling the pressure simply changes the concentration. No effect on \(k\), as in (a).
(d) The rate constant \(k\) changes with temperature.
(e) A catalyst changes the reaction mechanism and therefore changes \(k\).
Mathematically, the amount left after ten half-lives is:

\[
\left(\frac{1}{2}\right)^{10} = 9.8 \times 10^{-4} = 0.098\%
\]

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

\[
k = \text{Slope} = 2.4 \times 10^7 /\text{M.s}
\]

First, solve for the rate constant, \(k\), from the half-life of the decay.

\[
\frac{t_{\frac{1}{2}}}{\tau} = \frac{2.44 \times 10^5 \text{ yr}}{k} \quad \Rightarrow \quad k = \frac{2.44 \times 10^5 \text{ yr}}{0.693} = 4.10 \times 10^{-6} \text{ yr}^{-1}
\]

Now, we can calculate the time for the plutonium to decay from \(5.0 \times 10^2 \text{ g}\) to \(1.0 \times 10^2 \text{ g}\) using the equation for a first-order reaction relating concentration and time.

\[
\ln \frac{[A]}{[A]_0} = -kt
\]

\[
\ln \frac{1.0 \times 10^2}{5.0 \times 10^2} = -(4.10 \times 10^{-6} \text{ yr}^{-1})t
\]

\[
1.6 = (4.10 \times 10^{-6} \text{ yr}^{-1})t
\]

\[
t = 3.9 \times 10^5 \text{ yr}
\]