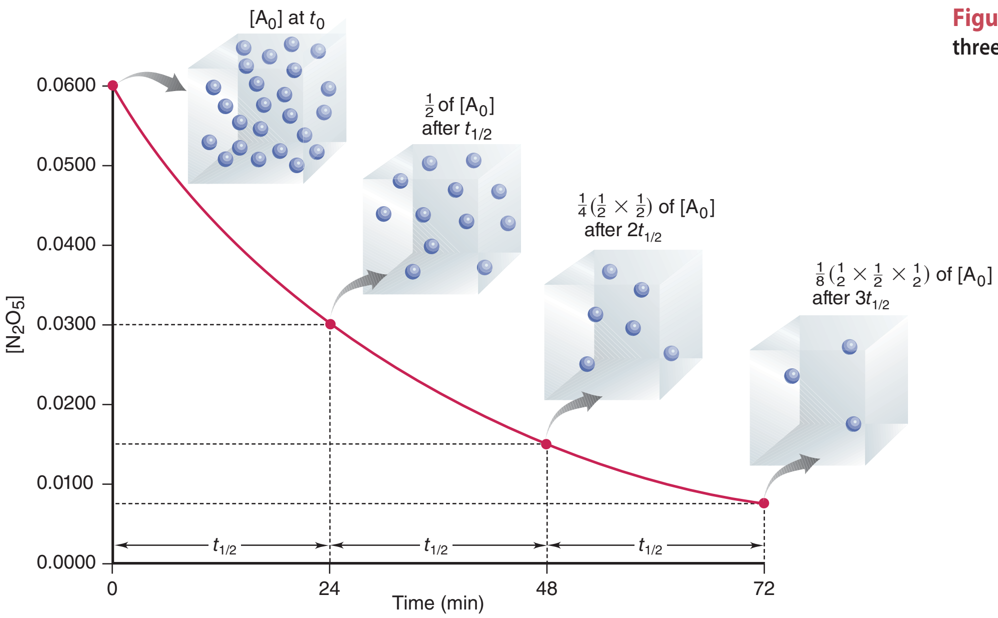

Figure 16.12 A plot of $[N_2O_5]$ vs. time for three reaction half-lives.

Reaction Half-Life

The **half-life ($t_{1/2}$)** of a reaction is the time it takes for the reactant concentration to reach *half its initial value.* A half-life has time units appropriate for the specific reaction and is characteristic of that reaction at a given temperature. For example, at 45°C, the half-life for the decomposition of N_2O_5, which we know is first order, is 24.0 min. Therefore, if we start with, say, 0.0600 mol/L of N_2O_5 at 45°C, 0.0300 mol/L will have reacted after 24 min (one half-life), and 0.0300 mol/L will remain; after 48 min (two half-lives), 0.0150 mol/L will remain; after 72 min (three half-lives), 0.0075 mol/L will remain, and so forth (Figure 16.12). The mathematical expression for the half-life depends on the overall order of the reaction.

First-Order Reactions We can derive an expression for the half-life of a first-order reaction from the integrated rate law, which is

$$\ln \frac{[A]_0}{[A]_t} = kt$$

By definition, after one half-life, $t = t_{1/2}$, and $[A]_t = \frac{1}{2}[A]_0$. Substituting and canceling $[A]_0$ gives

$$\ln \frac{\cancel{[A]_0}}{\frac{1}{2}\cancel{[A]_0}} = kt_{1/2} \qquad \text{or} \qquad \ln 2 = kt_{1/2}$$

Then, solving for $t_{1/2}$, we have

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \qquad \text{(first-order process; rate} = k[A]) \qquad \textbf{(16.7)}$$

Notice that $t_{1/2}$ *and* k *are inversely proportional*. Thus, a fast reaction, one with a relatively large rate constant, has a short half-life, and a slow reaction, one with a small rate constant, has a long half-life:

$$k\uparrow,\ t_{1/2}\downarrow \qquad \text{and} \qquad k\downarrow,\ t_{1/2}\uparrow$$

Because no concentration term appears, *for a first-order reaction, the time it takes to reach one-half the starting concentration is a constant and, thus, independent of reactant concentration.*

Decay of an unstable, radioactive nucleus is an example of a first-order process that does not involve a *chemical* change. For example, the half-life for the decay of uranium-235 is 7.1×10^8 years. Thus, a sample of ore containing uranium-235 will have half the original mass of uranium-235 after 7.1×10^8 years: a sample containing 1 kg will contain 0.5 kg of uranium-235, a sample containing 1 mg will contain 0.5 mg, and so forth. (We discuss radioactive decay thoroughly in Chapter 24.)