

14-74 (a) The following table gives the half-lives

	1st half-life	2nd half-life	3rd half-life
zeroth order	227 s	114 s	57 s
first order	315 s	315 s	315 s
second order	227 s	455 s	680 s

The entries in the first two columns are read from the graph in the problem by noting that the concentration of A falls from 1.0 to 0.5 M during the first half-life and from 0.5 to 0.25 M during the second half-life. The entries in the third column come from extrapolation of the trends: for a zeroth-order reaction, each successive half-life is shorter by a factor of 2; for a first-order reaction, each half-life equals the previous one; for a second-order reaction each half-life is longer by a factor of 2. Some of the results can be confirmed by looking at the graph.

(b) The problem states that the rate constant is numerically the same for all three cases. It is easiest to estimate this value for the zeroth-order case because the rate of zeroth-order reactions remains constant from first to last. The rate equals the negative of the slope of the black line (the negative sign comes in because A is a reactant). Using the line from time zero to 454 s gives

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{(0 - 1) \text{ mol L}^{-1}}{(454 - 0) \text{ s}} = 0.00220 \text{ mol L}^{-1} \text{ s}^{-1}$$

For a zeroth-order reaction the rate is a constant—the rate constant:  $\text{rate} = k$ . Therefore,

$$k_{\text{zero}} = \boxed{0.0022 \text{ mol L}^{-1} \text{ s}^{-1}}$$

For the first-order and second-order cases, only the units differ:

$$k_{\text{first}} = \boxed{0.0022 \text{ s}^{-1}} \quad \text{and} \quad k_{\text{second}} = \boxed{0.0022 \text{ L mol}^{-1} \text{ s}^{-1}}$$

(c) Substitute  $t = 300 \text{ s}$  and the original concentration of A into the appropriate equation for the dependence of the concentrations on time:

$$\begin{aligned} \text{zero} \quad [A] &= [A]_0 - kt = 1.0 \text{ mol L}^{-1} - (0.0022 \text{ mol L}^{-1} \text{ s}^{-1})(300 \text{ s}) \\ &= \boxed{0.34 \text{ mol L}^{-1}} \\ \text{first} \quad [A] &= [A]_0 e^{-kt} = (1.0 \text{ mol L}^{-1}) \exp((-0.0022 \text{ s}^{-1})(300 \text{ s})) \\ &= \boxed{0.52 \text{ mol L}^{-1}} \\ \text{second} \quad \frac{1}{[A]} &= 2kt + \frac{1}{[A]_0} = 2(0.0022 \text{ L mol}^{-1} \text{ s}^{-1})(300 \text{ s}) + 1.0 \text{ L mol}^{-1} \\ &= 2.32 \text{ L mol}^{-1} \quad [A] = \boxed{0.43 \text{ mol L}^{-1}} \end{aligned}$$

(d) The second-order reaction starts out fast because its rate depends on the square of the concentration of A. As A is used up, this value drops rapidly and the second-order reaction slows down rapidly. In contrast, the zeroth-order reaction continues at the same rate until the very last supply of A is used up.