A particular reactant decomposes with a half-life of 107 s when its initial concentration is 0.360 M . The same reactant decomposes with a half-life of 217 s when its initial concentration is $\mathbf{0 . 1 7 8} \mathrm{M}$. Calculate the rate constant ( $k$ ) and reaction order?

## Answer:

The reaction is not first-order because the half-life of a first-order reaction is independent of the initial concentration:
$\mathrm{t}^{1} / 2=(\ln (2)) / k$
That leaves zero-order and second-order to test.

For a zero-order reaction, the half-life is given by the expression: $\mathrm{t}^{1 / 2}=\left([\mathrm{A}]^{0}\right) / 2 \mathrm{k}$
Calculate k for the two conditions given:
(a) 139 s when its initial concentration is 0.293 M
$\mathrm{t} 1 / 2=\left([\mathrm{A}]^{0}\right) / 2 \mathrm{k}$
$139 \mathrm{~s}=(0.293 \mathrm{M}) / 2 \mathrm{k}$
$\mathrm{k}=(0.293 \mathrm{M}) / 2)^{*}\left(1 /(139 \mathrm{~s})=1.05 \times 10^{-3} \mathrm{~mol} / \mathrm{L} \cdot \mathrm{s}\right.$
(b) 231 s when its initial concentration is 0.176 M
$t^{1} / 2=\left([A]^{0}\right) / 2 k$
$231 \mathrm{~s}=(0.176 \mathrm{M}) / 2 \mathrm{k}$
$\mathrm{k}=(0.176 \mathrm{M}) / 2)^{*}\left(1 /(231 \mathrm{~s})=3.81 \times 10^{-4} \mathrm{~mol} / \mathrm{L} \cdot \mathrm{s}\right.$
The values of $k$ are different, so that rules out zero-order.

For a second-order reaction, the half-life is given by the expression: $\left.t^{1 / 2}=1 /\left(\left(k^{*}\right)[A]^{0}\right)\right)$
Calculate k for the two conditions given:
(a) 139 s when its initial concentration is 0.293 M
$\left.\mathrm{t}^{1} / 2=1 /\left(\left(k^{*}\right)[\mathrm{A}]^{0}\right)\right)$
$139 \mathrm{~s}=1 /\left(\mathrm{k}^{*}(0.293 \mathrm{M})\right)$
$\mathrm{k}=1 /\left((0.293 \mathrm{M})^{*}(139 \mathrm{~s})\right)=2.46 \times 10^{-2} \mathrm{~L} / \mathrm{mol} \cdot \mathrm{s}$
(b) 231 s when its initial concentration is 0.176 M
$\left.t 1 / 2=1 /\left(\left(k^{*}\right)[A]^{0}\right)\right)$
$231 \mathrm{~s}=1 /\left(\mathrm{k}^{*}(0.176 \mathrm{M})\right)$
$\mathrm{k}=1 /\left((0.176 \mathrm{M})^{*}(231 \mathrm{~s})\right)=2.46 . \times 10^{-2} \mathrm{~L} / \mathrm{mol} \cdot \mathrm{s}$
The values of $k$ are the same, so the reaction is second-order, and $k=2.46 . \times 10^{-2} \mathrm{~L} / \mathrm{mol} \cdot \mathrm{s}$.

