Differential Rate Laws vs. Integrated Rate Laws

- Differential rate law: *Rate* vs. concentration

- Integrated rate law: concentration vs. time

Integrated Rate Law for a First-Order Reaction

- For a reaction, A 6 products, which is first-order in A, we can write the differential rate law

$$Rate = \frac{-d[A]}{dt} = k[A]$$

- Consider the change in concentration of A from its initial value $[A]_o$ to its value $[A]$ at some later time t. By integral calculus it can be shown

$$-\ln\left(\frac{[A]}{[A]_o}\right) = kt \quad\Rightarrow\quad \ln\left(\frac{[A]}{[A]_o}\right) = -kt$$

L   This expression is the *first-order integrated rate law* equation.

U   Another way of writing this expression:

$$\ln\left(\frac{[A]_o}{[A]}\right) = kt$$

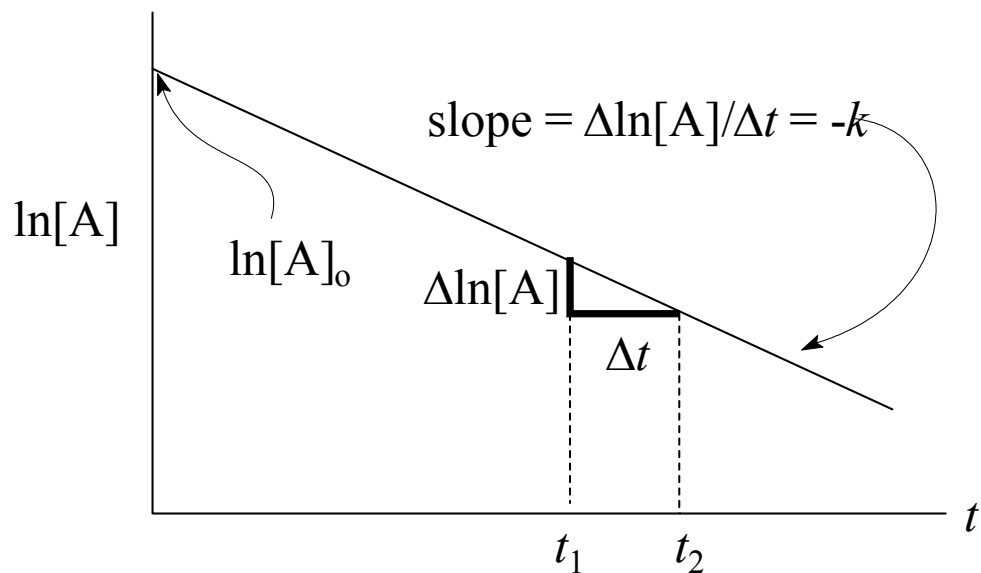# Linear Form of the First-Order Integrate Rate Law

$$\ln\left(\frac{[A]}{[A]_o}\right) = -kt$$

- Expanding the logarithm and rearranging:

$$\ln[A] = -kt + \ln[A]_o$$

- This is a straight-line equation:

$$y = mx + b$$

Half-Life of a First-Order Reaction

L   For any reaction we define the ***half-life*** as that time required for the concentrations of a reactant to diminish to half of what its value was at some initial time.

If $t = t_{1/2}$ Y $[A] = \frac{1}{2}[A]_o$.

Relationship Between $t_{1/2}$ and k

Substituting into the first-order integrated rate law expression at time $t_{1/2}$, when $[A] = \frac{1}{2}[A]_o$:

$$\ln\left(\frac{[A]_o}{[A]}\right) = \ln\left(\frac{[A]_o}{\frac{1}{2}[A]_o}\right) = kt_{1/2}$$
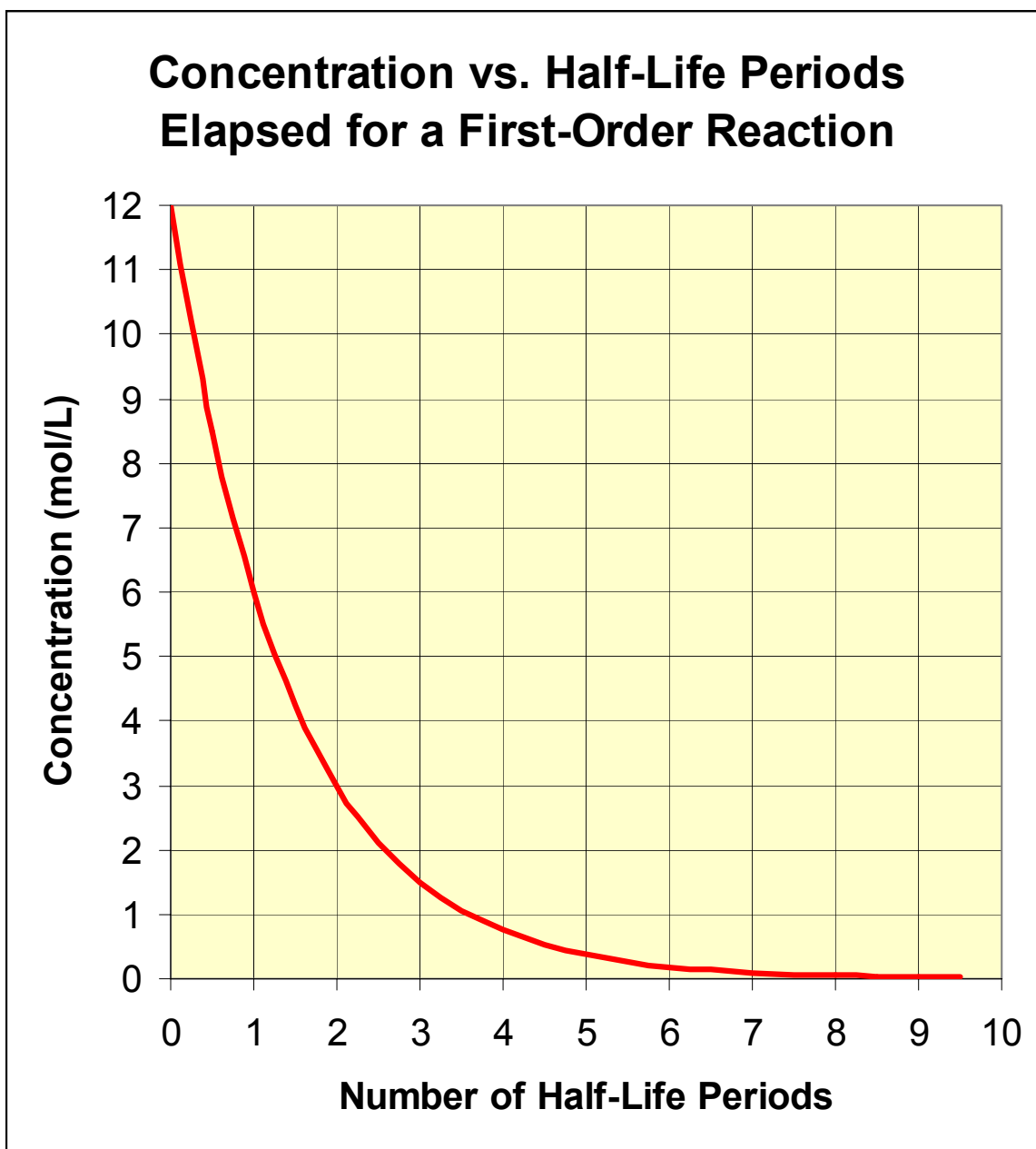
$$\ln 2 = kt_{1/2}$$

$$0.693 = kt_{1/2}$$

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

Concentration vs. Time in Half-Lives

L   After each $t_{1/2}$ period, there is half as much reactant as what was present at the beginning of the half-life period.

Concentration vs. Half-Life Periods Elapsed for a First-Order Reaction

Concentration vs. Time in Half-Life Periods
General Equation for a First-Order Reaction

Let h be the number of half-life periods elapsed:

$$h = \frac{t}{t_{1/2}}$$

Then, at time t the concentration of A as a function of its initial concentration $[A]_o$ is

$$[A] = [A]_o(1/2)^h$$

L   The value of h does not have to be an integer. 7

Nuclear Decay

L   Radioactive decay is a first-order process.

$$Rate = A = \lambda N$$

   where A = decay rate (activity)
            λ = decay constant (analogous to k)
            N = number of radioactive atoms

L   The following equations can be defined in analogy with the general integrated rate equation and half-life equations for a first-order reaction:

$$\ln (N_t/N_o) = -\lambda t \qquad\qquad t_{1/2} = 0.693/\lambda$$

$$N_t = N_o(\tfrac{1}{2})^h \qquad\qquad A_t = A_o(\tfrac{1}{2})^h$$

Important Terms and Equations
for First-Order Reactions

Terms

$[A]$ = concentration of A at some elapsed time, t

$[A]_o$ = concentration of A at an initial point in the reaction, at time $t = 0$

k = rate constant for the reaction, in units of $(\text{time})^{-1}$

$t_{1/2}$ = half-life period; time required for the concentration of A to fall to half the value it had at the beginning of the half-life period; i.e. time it takes for $[A] = \frac{1}{2}[A]_o$

h = number of half-life periods elapsed = $t/t_{1/2}$

Important Terms and Equations
for First-Order Reactions

Equations

Differential rate law (*Rate* vs. concentration):

$$Rate = k[A]$$

Integrated rate law (concentration vs. time):

$$\ln \frac{[A]_o}{[A]} = kt \qquad\qquad \ln \frac{[A]}{[A]_o} = -kt$$

$$\ln[A] = -kt + \ln[A]_o$$

A plot of ln[A] vs. time is a straight line whose slope is -k and whose intercept is ln [A]$_o$.

Half-life:

$$[A] = [A]_o(\tfrac{1}{2})^h$$

$$t_{1/2} = 0.693/k$$

Important Terms and Equations
for Radioactive Decay

Terms

N_t = number of radioactive atoms at some elapsed time, t

N_o = number of radioactive atoms at an initial point, at time $t = 0$

λ = decay constant in units of (time)$^{-1}$ (analogous to k)

A = decay activity in units of disintegrations per time per gram (analogous to *Rate*)

$t_{1/2}$ = half-life period; time required for N_t to fall to half the value it had at the beginning of the half-life period; i.e. time it takes for $N_t = \frac{1}{2}N_o$

h = number of half-life periods elapsed = $t/t_{1/2}$

Important Terms and Equations
for Radioactive Decay

Equations

Radioactive decay law (analogous to differential rate law):

$$A = \lambda N$$

Time dependence of N (analogous to integrated rate law):

$$\ln\frac{N_o}{N_t} = \lambda t \qquad\qquad \ln\frac{N_t}{N_o} = -\lambda t$$

$$\ln N_t = -\lambda t + \ln N_o$$

A plot of $\ln N_t$ vs. time is a straight line whose slope is $-\lambda$ and whose intercept is $\ln N_o$.

Half-life:

$$N_t = N_o(\tfrac{1}{2})^h \qquad \text{and} \qquad A_t = A_o(\tfrac{1}{2})^h$$

$$t_{1/2} = 0.693/\lambda$$