Chemical Kinetics

Why study kinetics?

Average Rate

- Δ concentration of reactant or product over a period of time
- [reactants] ↓ over time
- [products] ↑ over time

Relative Reaction Rates

The Rate Law

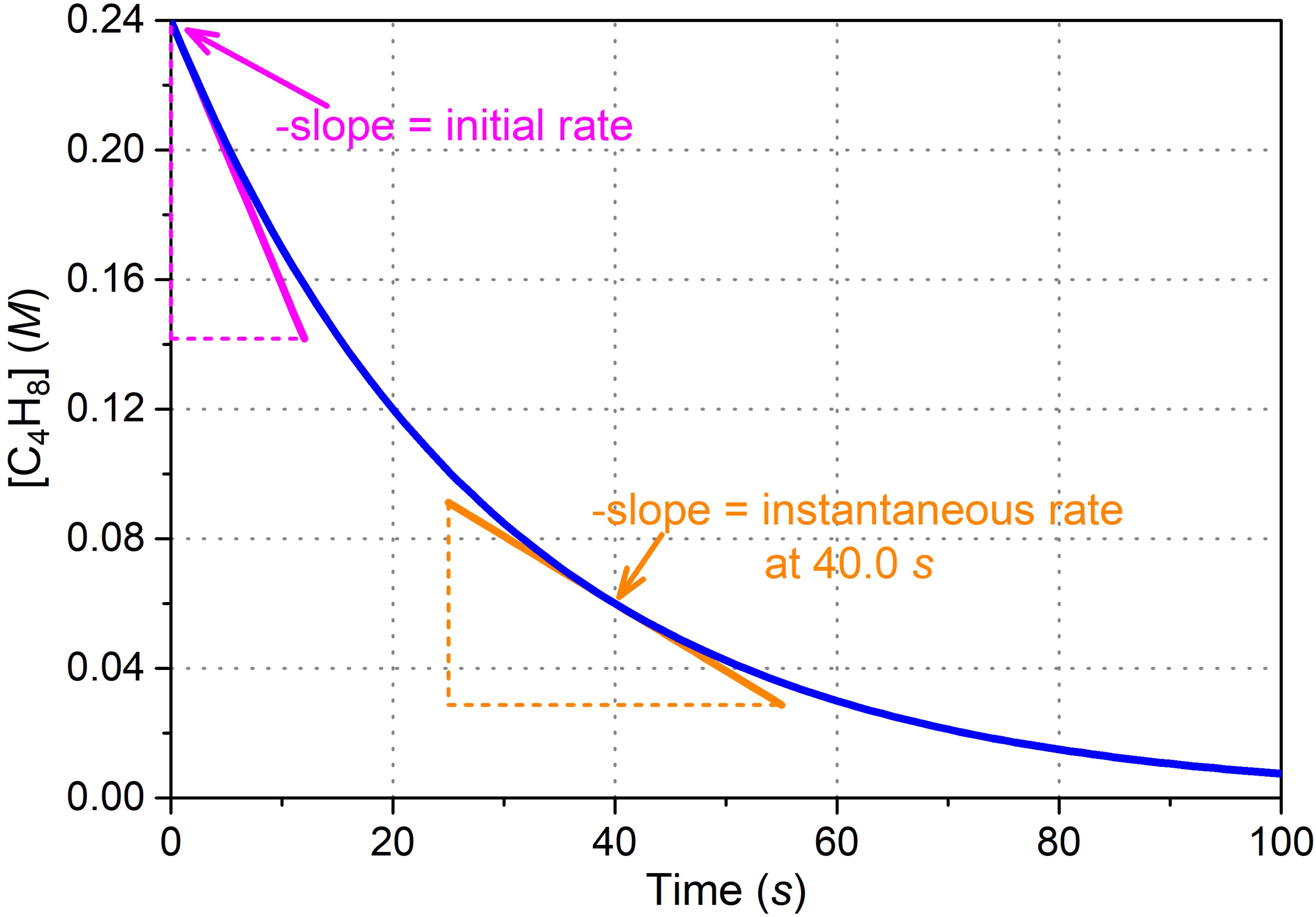
- A rate law describes a relationship between the rate of a reaction and the concentration of its reactants
- The rate law *must* be determined experimentally!

For a reaction A + B → products

rate = $k[A]^m[B]^n$

Finding the Rate Law: Method of Initial Rates

- Measure initial rate (at t = 0)
- Vary concentrations of reactants and determine the initial rate

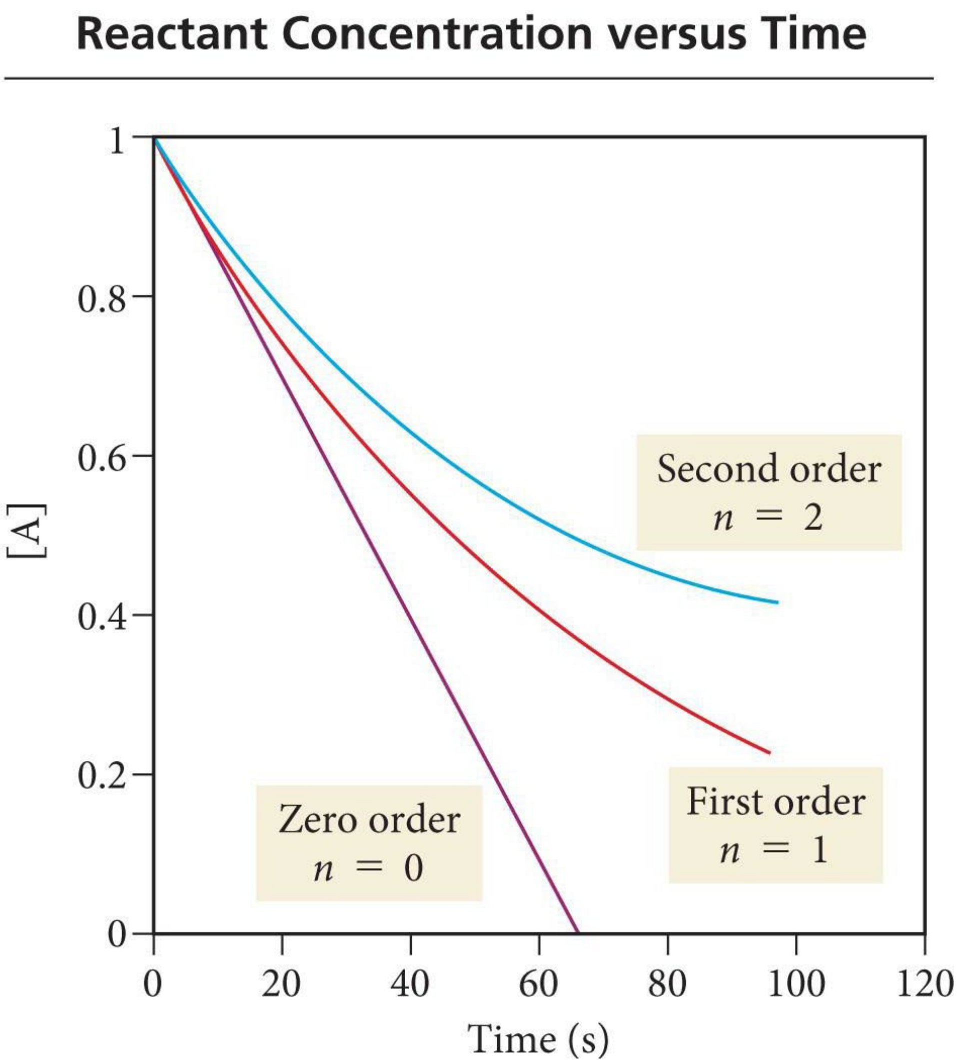


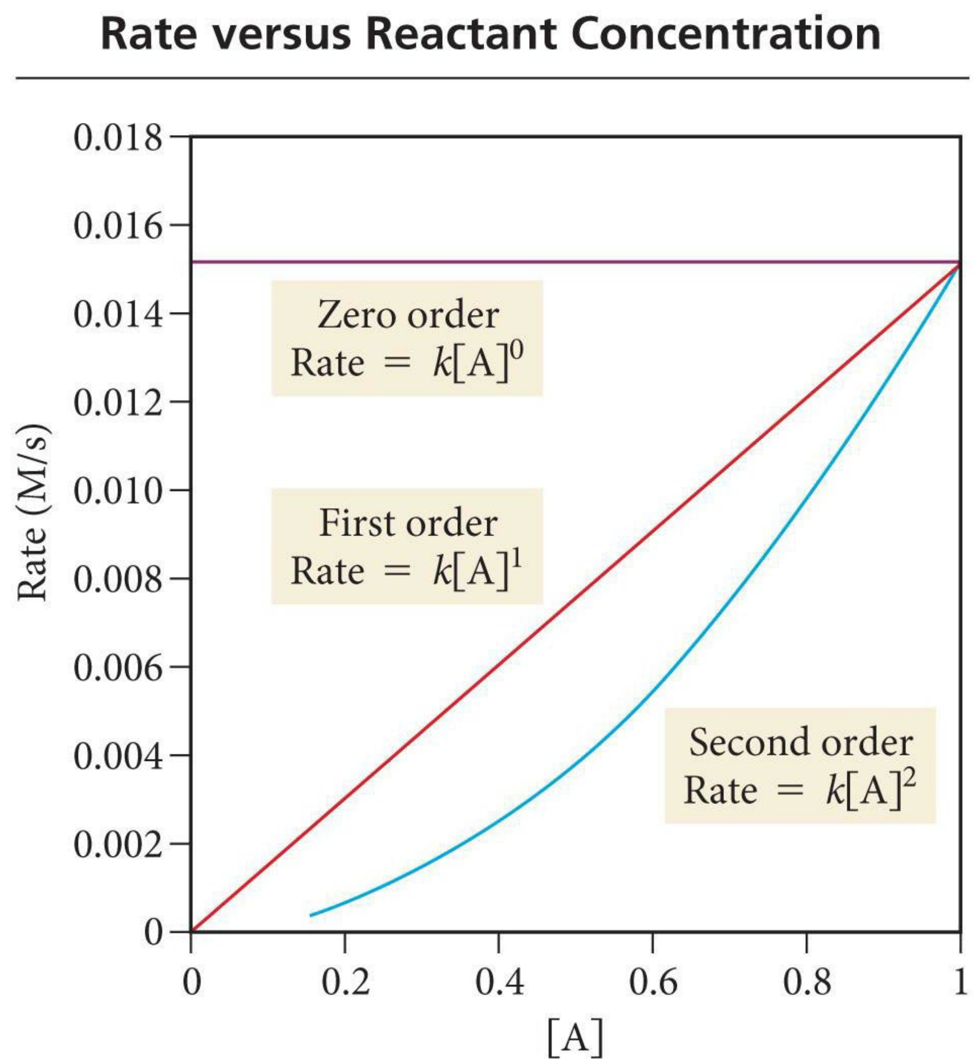
Determining the rate law and Rate Constant of a Reaction

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

$[NO_2]$ (M)	[CO] (M)	Initial Rate (M/s)
0.10	0.10	0.0021
0.20	0.10	0.0082
0.20	0.20	0.0083
0.40	0.10	0.033

Reactant Concentration versus Time
A - Products





Integrated Rate Laws

- Applying calculus to integrate the differential rate law gives another equation showing the relationship between the concentration of A and the time of the reaction; this is called the integrated rate law.

Order	Rate	Integrated Rate Law
0	$r = k[A]^0 = k$	$[A]_t = -kt + [A]_o$
1	$r = k[A]$	$\ln [A]_t = -kt + \ln [A]_o$
2	$r = k[A]^2$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_o}$

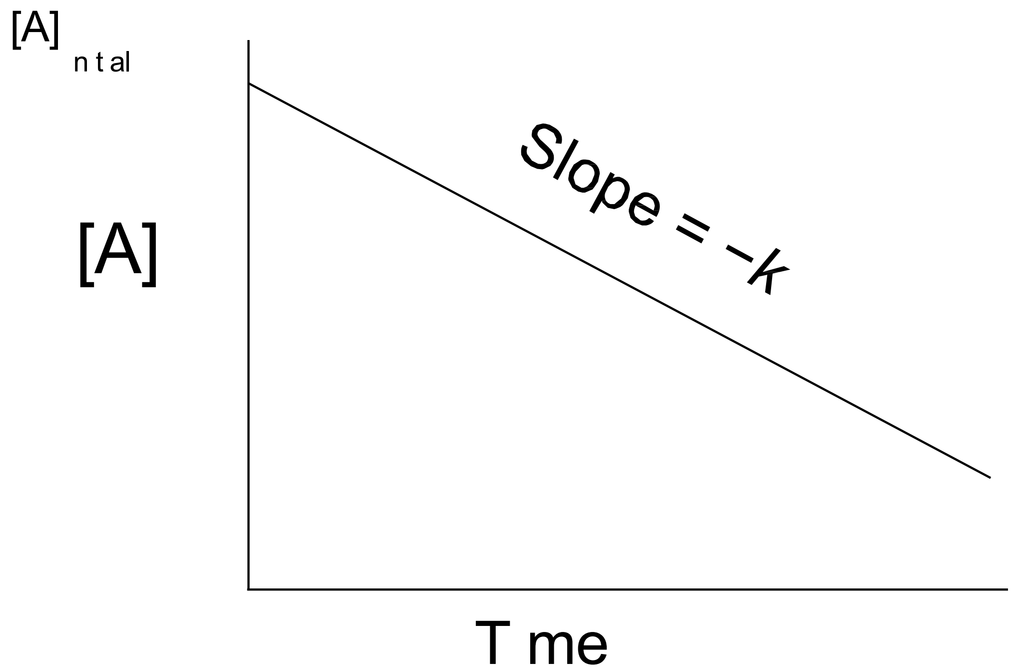
- How can we use graphical methods to determine the reaction order with respect to A?

Using integrated rate law

- Given data , prepare 3 kinetics plots
- Determine order of reaction and rate constant
- Graphing by hand in lecture , we will use excel for data analysis for kinetics labs
- Excel versus graphing by hand?

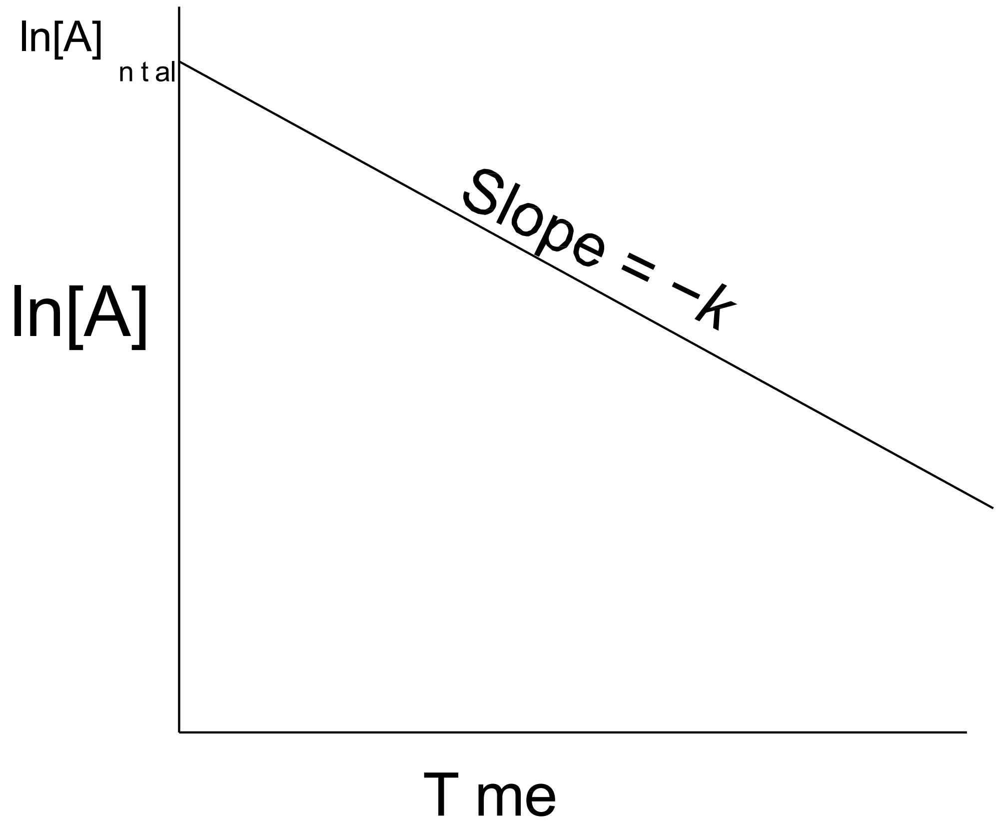
Zero Order Reactions

$[A] = -kt + [A_o]$



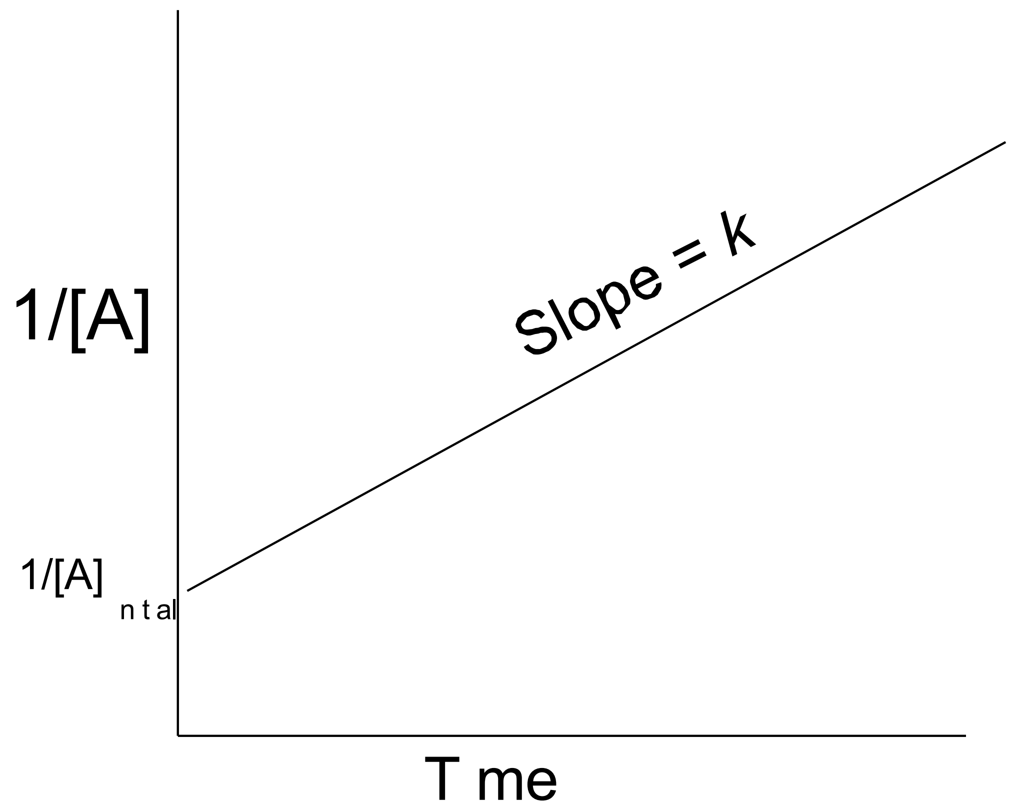
First-Order Integrated Rate Law

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



Second-Order Integrated Rate Law

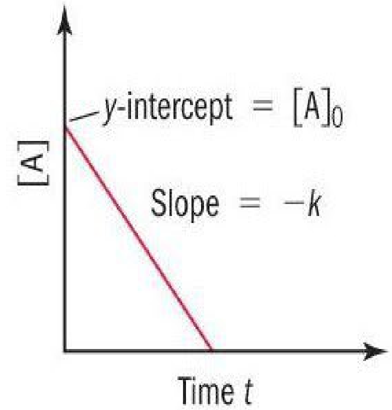
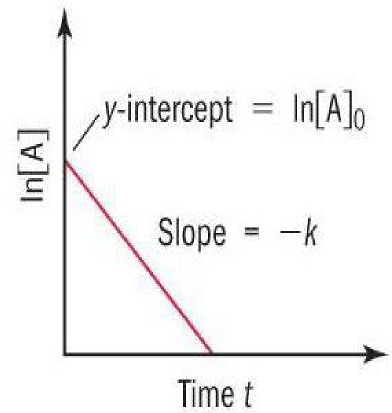
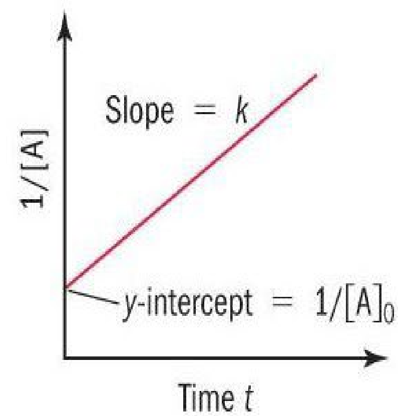
$1/[A] = kt + 1/[Ao]$



Time (min)	$[CH_3CN]$, (M)
0	1
5	0.794
15	0.501
20	0.393
25	0.316

Determine the reaction order and the rate constant with respect to CH_3CN

TABLE 13.2 Rate Law Summary Table

Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	Rate $= k[A]^0$	$M \cdot s^{-1}$	$[A]_t = -kt + [A]_0$		$t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k}\frac{[A]_0}{2}$
1	Rate $= k[A]^1$	s^{-1}	$\ln[A]_t = -kt + \ln[A]_0$ $\ln\frac{[A]_t}{[A]_0} = -kt$		$t_{1/2} = \frac{0.693}{k} = \frac{1}{k}(0.693)$
2	Rate $= k[A]^2$	$M^{-1} \cdot s^{-1}$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$		$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k}\frac{1}{[A]_0}$

Suppose that the half-life of steroids taken by an athlete is 42 days.
Assuming that the steroids biodegrade by a first-order process,
how long would it take for 1/64 of the initial dose to remain in the athlete's body