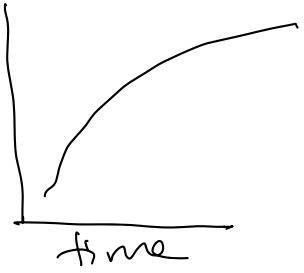
Chemical Kinetics

Why study kinetics?

Average Rate

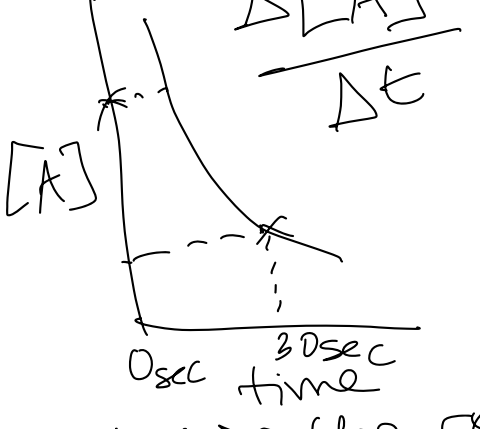
$A \rightarrow B$

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



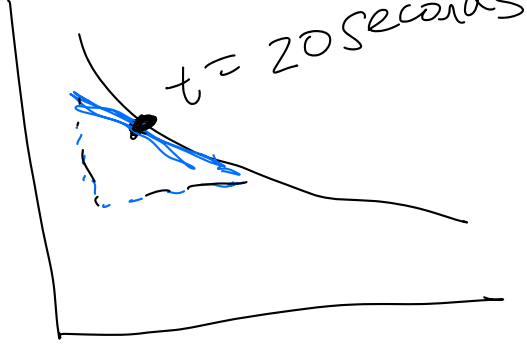
instantaneous rate

$$\frac{\Delta[A]}{\Delta t}$$



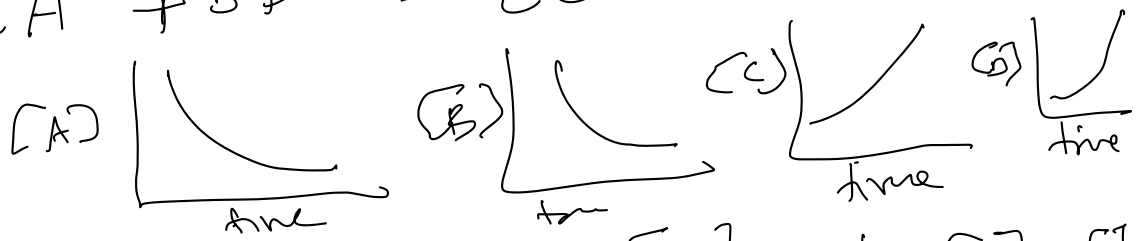
What is the rxn. rate over 30 sec

[A]



Relative Reaction Rates → average rates

$$aA + bB \rightarrow cC + dD$$



$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = +\frac{1}{c}\frac{\Delta[C]}{\Delta t} = +\frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

example:

$$2H_2O_{2(aq)} \rightarrow 2H_2O_{(\ell)} + O_{2(g)}$$

the average rate for the disappearance of hydrogen peroxide is $-3.00 \times 10^{-2} \frac{M}{h}$, what is the average rate of appearance for oxygen?

$\frac{\Delta[A]}{\Delta t}$ $\frac{M}{\text{seconds, minutes or hours}}$

$$-\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = +\frac{1}{1}\frac{\Delta[O_2]}{\Delta t}$$

$$-\frac{1}{2} \times \left(-3.00\times10^{-2}\frac{M}{h}\right) = \frac{\Delta[O_2]}{\Delta t}$$

$1.5\times10^{-2}\frac{M}{h}$ for appearance of oxygen

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

rate law constant

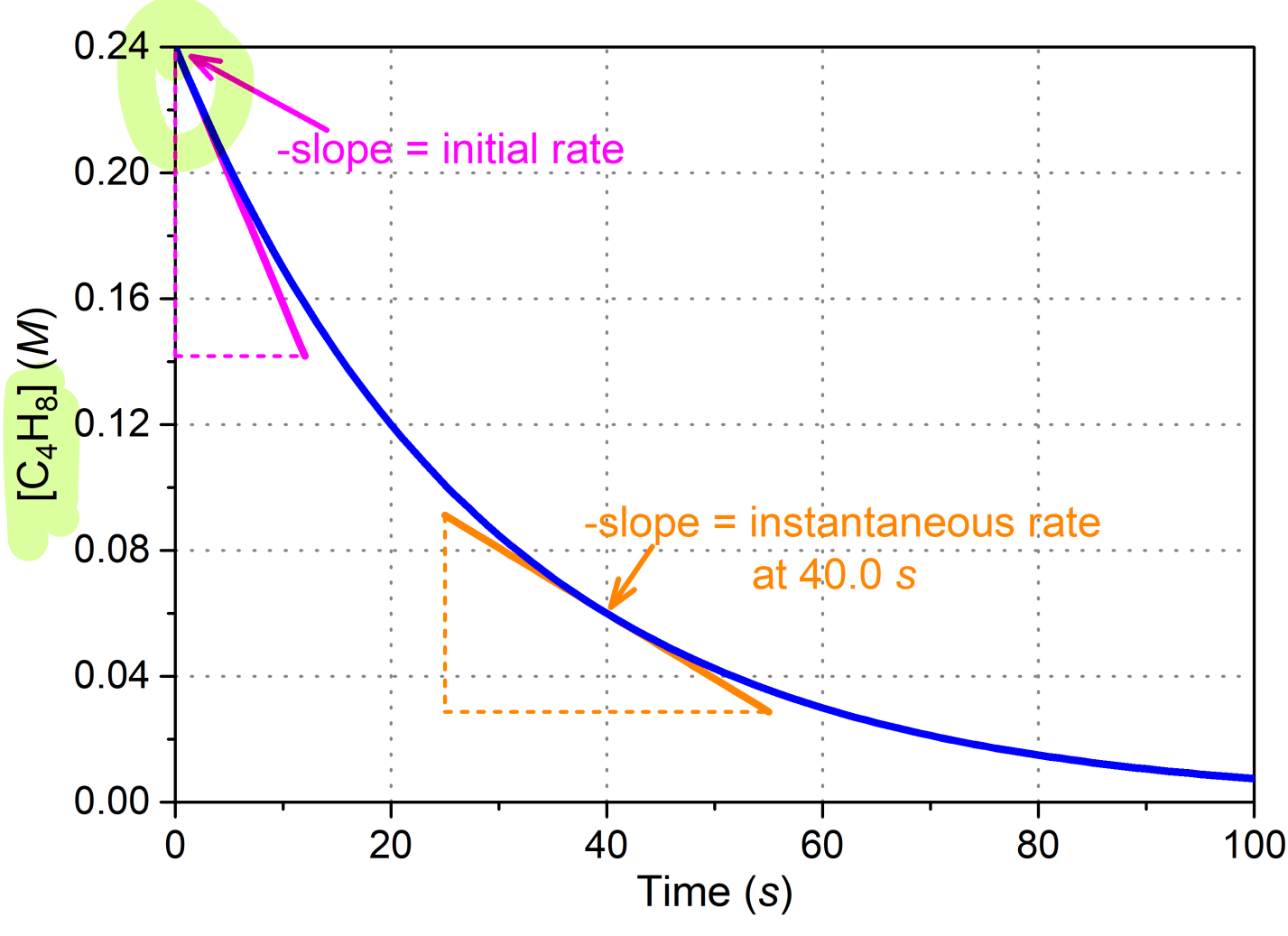
reaction rate

"m" is the order of the reaction with respect to A

"n" is the order of the reaction with respect to B

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

$$\text{rate} = k[NO_2]^m[CO]^n$$

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{k[NO_2]^m_{exp2}[CO]^n_{exp2}}{k[NO_2]^m_{exp1}[CO]^n_{exp1}}$$

$$\frac{0.0082}{0.0021} = \frac{(0.2)^m \cancel{(0.10)^n}}{(0.10)^m \cancel{(0.10)^n}}$$

$$4 = 2^m \qquad 2^m = 4$$

$$m = 2$$

$$\text{rate} = k[NO_2]^2[O_3]^n$$

$$\text{double } [NO_2]$$

$$\text{rate} \times 4$$

$$\frac{\text{rate } 3}{\text{rate } 2} = \frac{k[NO_2]^2[O]^n}{k[NO_2]^2[O]^n}$$

exp 2

$$\frac{0.0083}{0.0082} = \frac{1.[0.2]^n}{[0.1]^n}$$

$$1 = 2^n$$

$n = 0$

zero order with respect to O

$$\text{rate} = k[NO_2]^2$$

Find rate constant, k

$$\text{rate} = k[NO_2]^2$$

exp #1

$$0.0021 \frac{M}{s} = k(0.10\,M)^2$$

$$0.052 \frac{M \times 1}{s\,M^2} = k \times 0.10 \frac{M^2}{M^2}$$

$$\frac{M}{s} \times \frac{1}{M^2}$$

$$k = 0.21\ M^{-1} s^{-1}$$

A → products

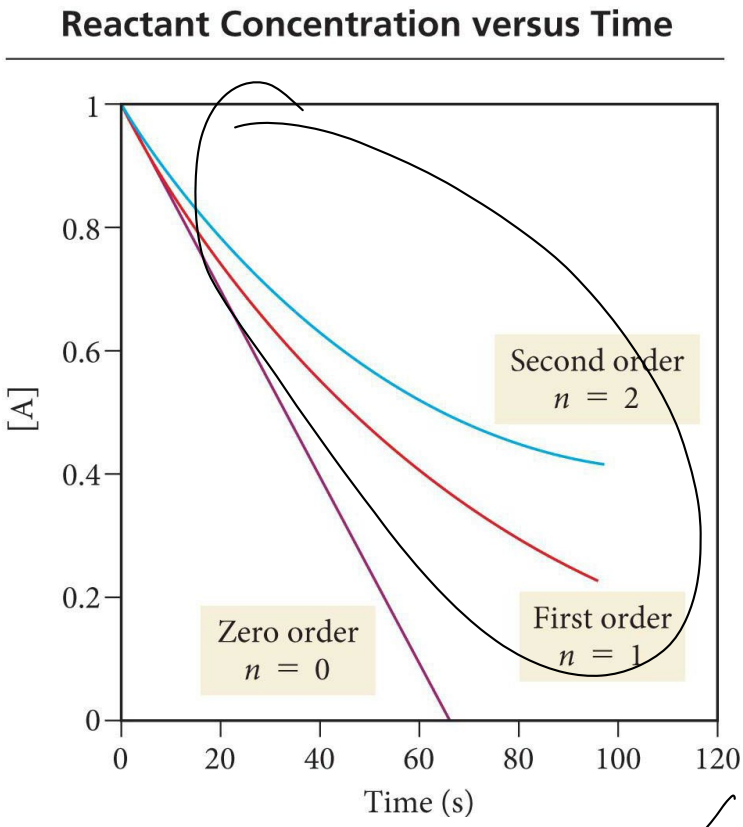
How do we measure [A] over time in lab?

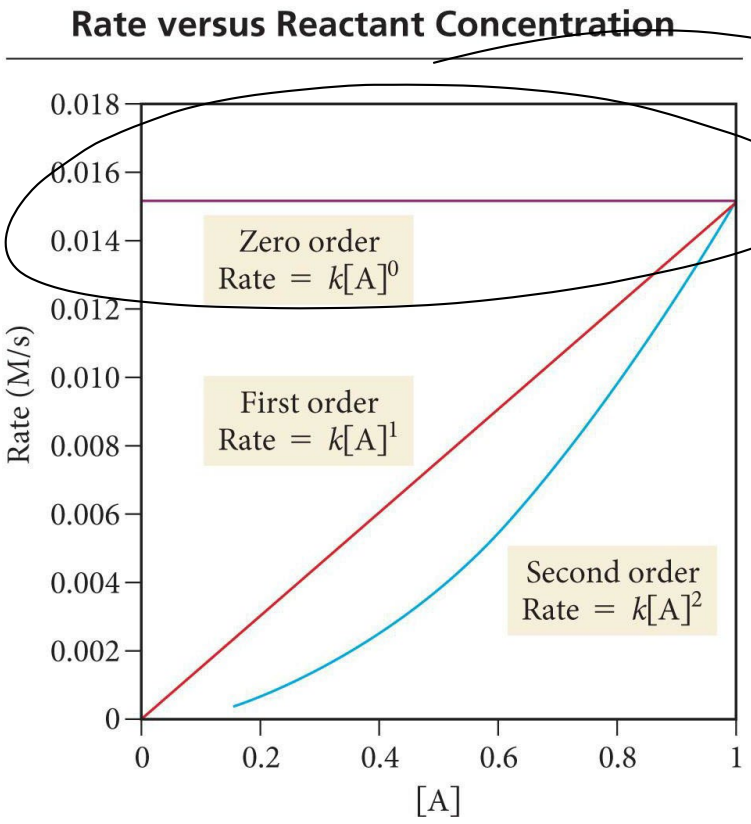
Beer's Law

$A = \varepsilon c l$

- A: absorbance
- ε: ? (unique to each molecule)
- c: concentration
- l: path length (1 cm)

Reactant Concentration versus Time
A - Products





rate = [A]^0 = rate

A → products

differential rate law

$$\text{rate} = k[A]^m$$

rate define as

$$\frac{\Delta[A]}{\Delta t} = k[A]^m$$

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	$r = k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$

y

y ← $\ln [A]_t$

y ← $\frac{1}{[A]_t}$

x is time

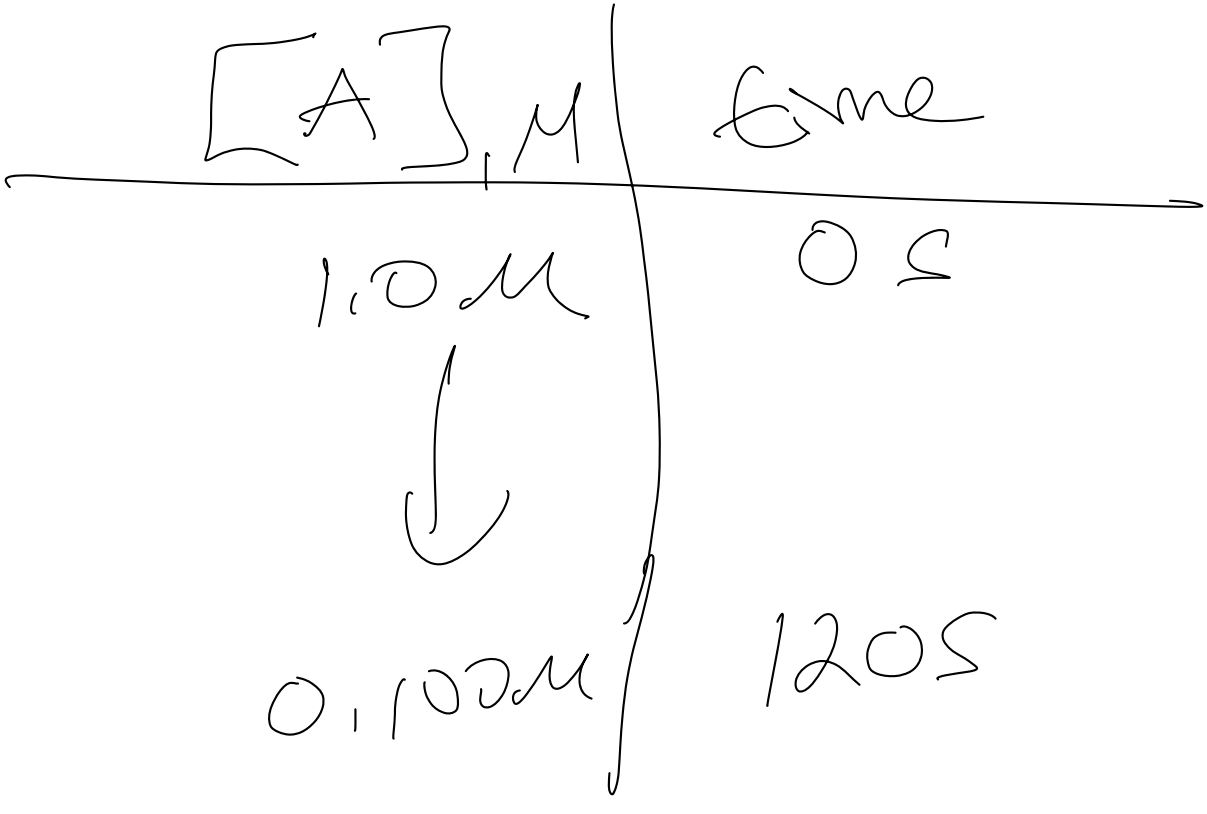
	slope
0	$-k$
1	$-k$
2	k

$y = mx + b$

$[A]_o$ initial concentration

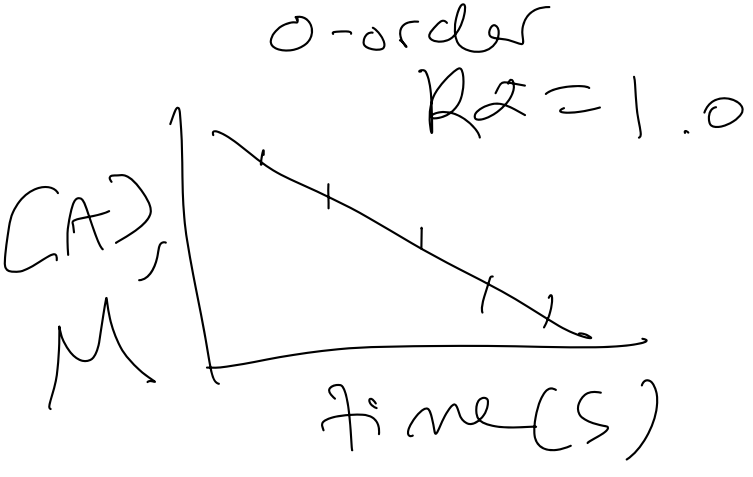
$[A]_t$ concentration at the time given in the problem

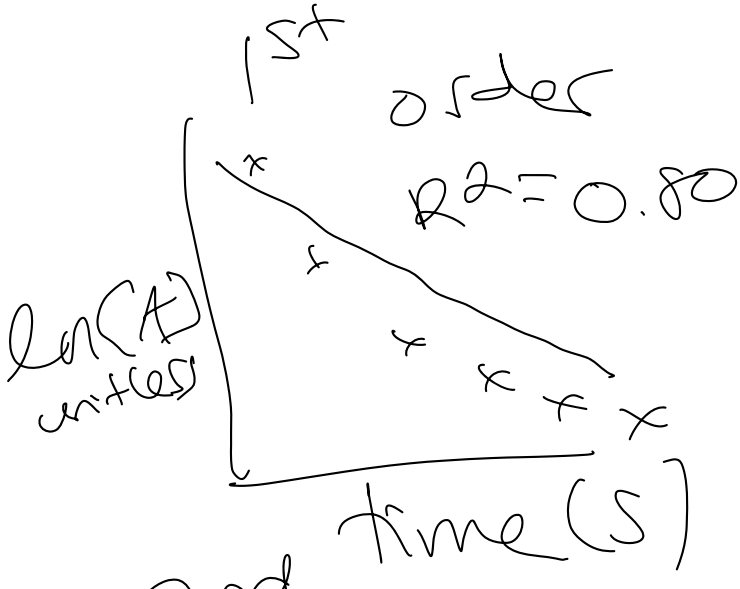
- How can we use graphical methods to determine the reaction order with respect to A?

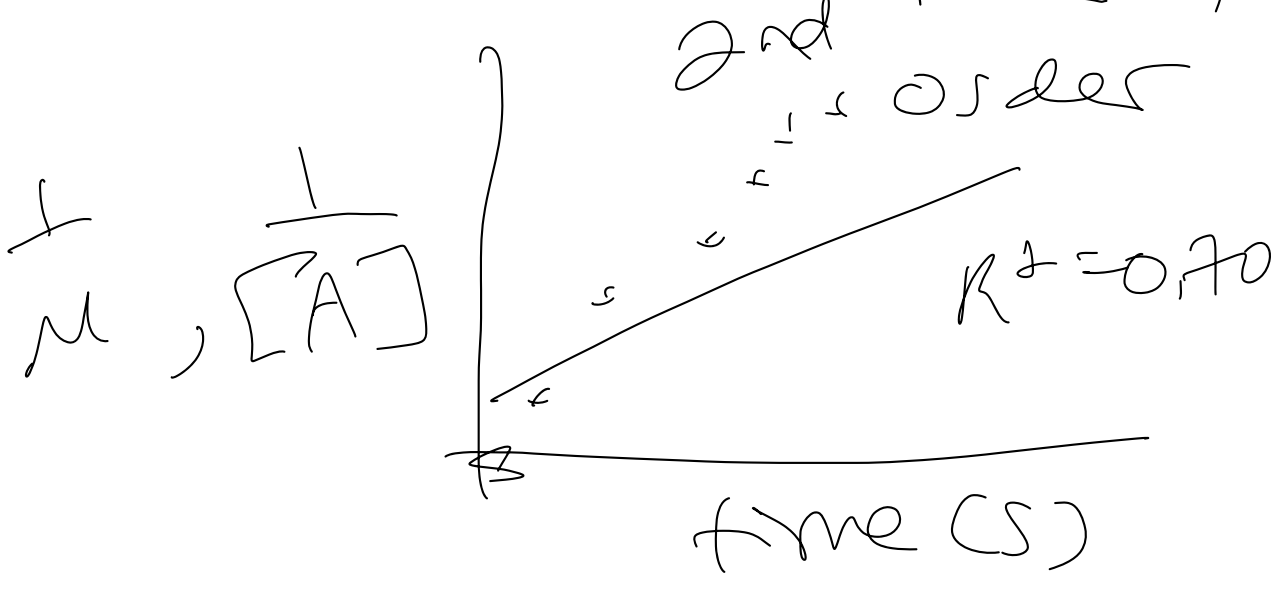


Using integrated rate law

- 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?

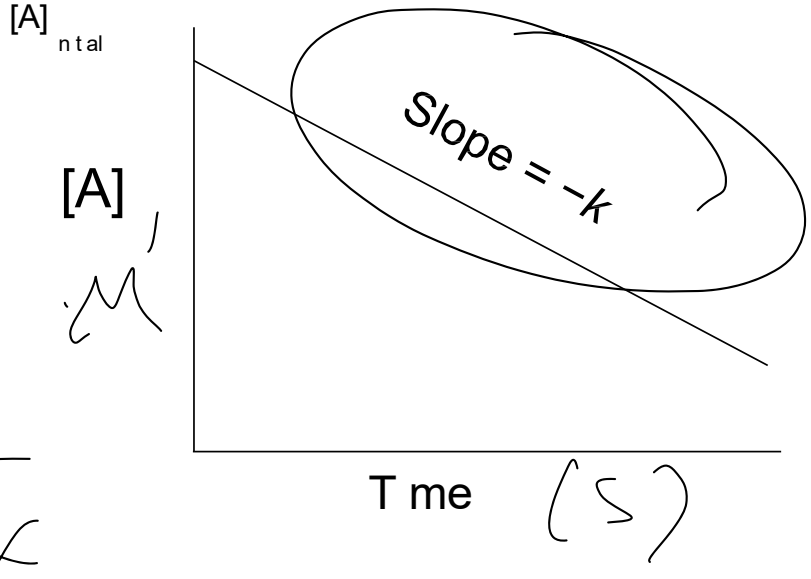






Zero Order Reactions

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

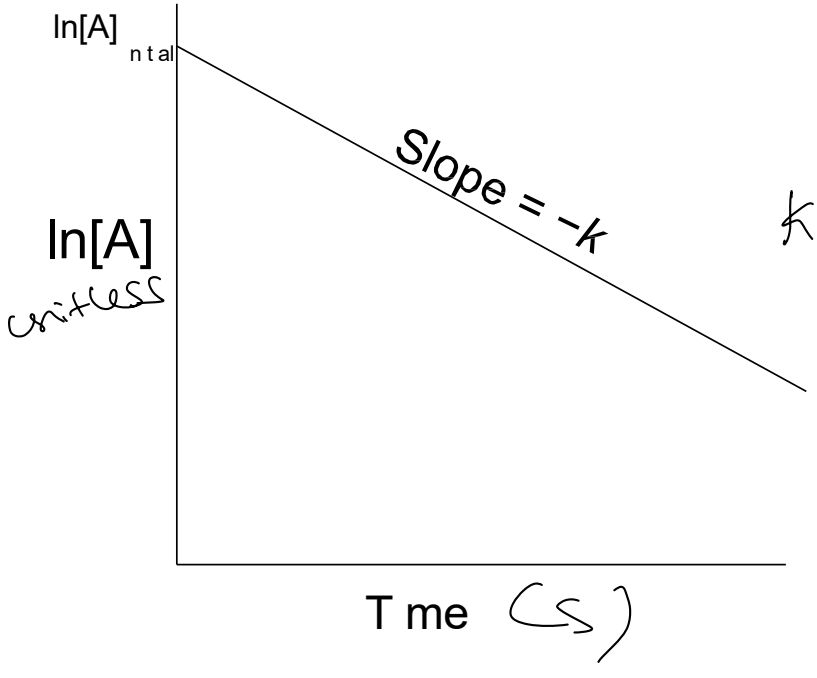


$\text{slope} = \frac{\Delta y}{\Delta x}$

$K = \frac{M}{s}$

First-Order Integrated Rate Law

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



k units

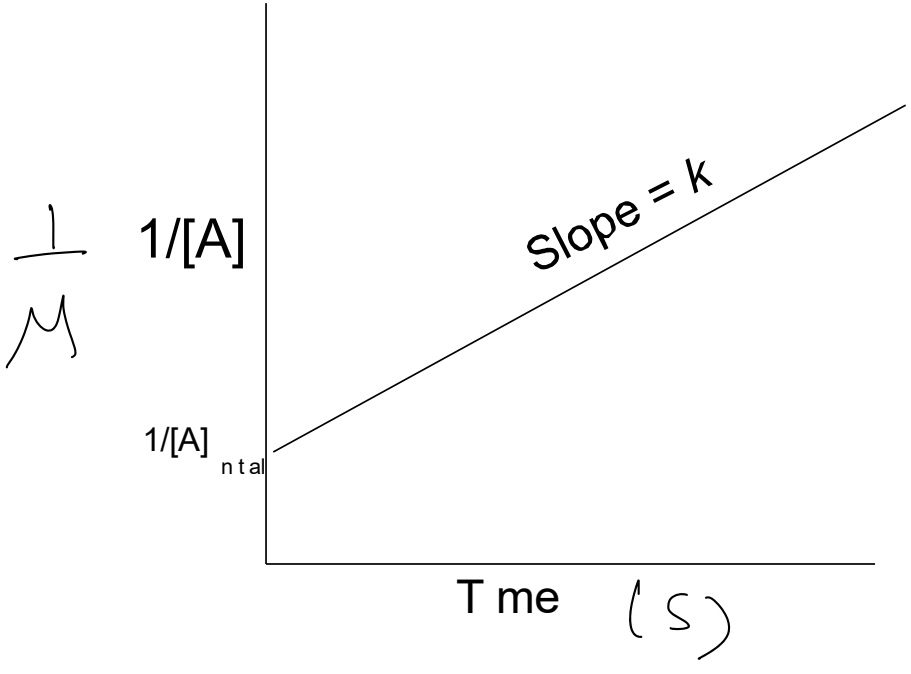
1 or sec^{-1}

sec

s^{-1}

Second-Order Integrated Rate Law

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



$\frac{1}{M}$

K unit $M^{-1} s^{-1}$

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

2nd → no

0
5

20
25

1
1.25] 0.05

2.54
3.16] 0.124

$$rate = K[CH_3CN]^1$$

$$rate = 0.043\ min^{-1}[CH_3CN]^1$$

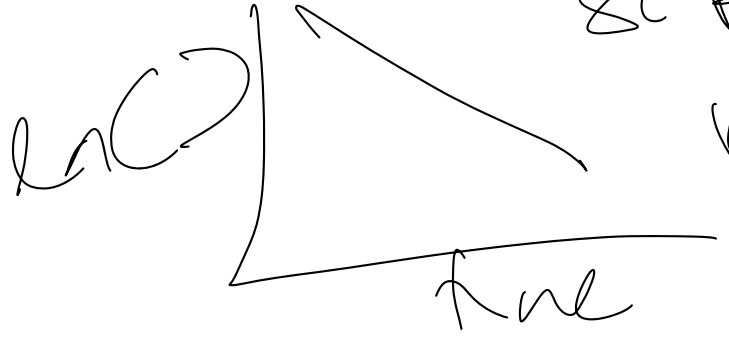
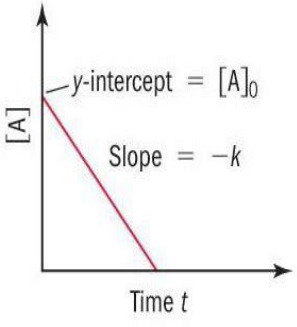
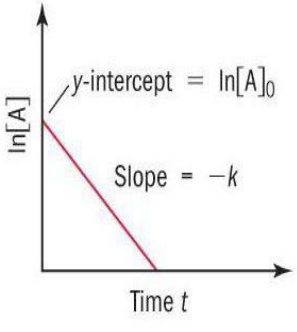
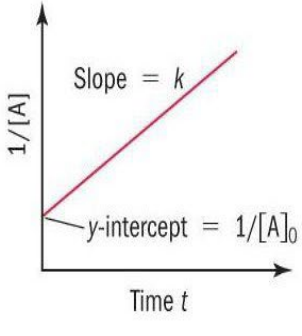


TABLE 13.2 Rate Law Summary Table

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 $= k[A]^2$	$M^{-1} \cdot s^{-1}$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$		$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k}\frac{1}{[A]_0}$

all radioisotopes & most drugs products

① $\ln(a \cdot b) = \ln a + \ln b$

② $\ln\left(\frac{a}{b}\right) = \ln a - \ln b$

③ $\ln a^{x} = x \ln a$

$8 = (2.5)^{m}$

$\ln 8 = \ln 2.5^{m}$

$$\frac{\ln 8}{\ln 2.5} = n \qquad \frac{\ln 2.5}{\ln 2.5}$$

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

$$t_{1/2} = 42 \text{ days}$$

1st order kinetics

$$\ln[A]_t = -kt + \ln[A]_0$$

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

① $k = \frac{0.693}{t_{1/2}}$

$k = \frac{0.693}{42 \text{ days}} = 0.0165 \text{ day}^{-1}$

$t = 2$

② $\ln[A]_t - \ln[A]_0 = -kt$

$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$

$\frac{1}{64}$ remains of the steroid

$$[A]_0 = 1$$

$$[A]_t = 0.0156$$

$$\ln\left(\frac{0.0156}{1}\right) = -0.0165\,day^{-1}(t)$$

$$\frac{-4.16}{-0.0165\,day^{-1}} = \frac{-0.0165\,day^{-1}(t)}{-0.0165\,day^{-1}}$$

$$\rightarrow 252\ days$$

$$\frac{1}{2^n} = \frac{1}{64}$$

$$n = 6$$

$$6 \times 42 \text{ days} = 252 \text{ days}$$