ChemE 2200 – Chemical Kinetics Lecture 2

Today:

Rate equations from experimental data; concentration vs. time.

- method of initial rates.
- isolation method.
- integrated rate equations.
- method of half lives.

Defining Question:

" How to best assess graphically an empirical fit to experimental data?"

Reading for Today's Lecture:

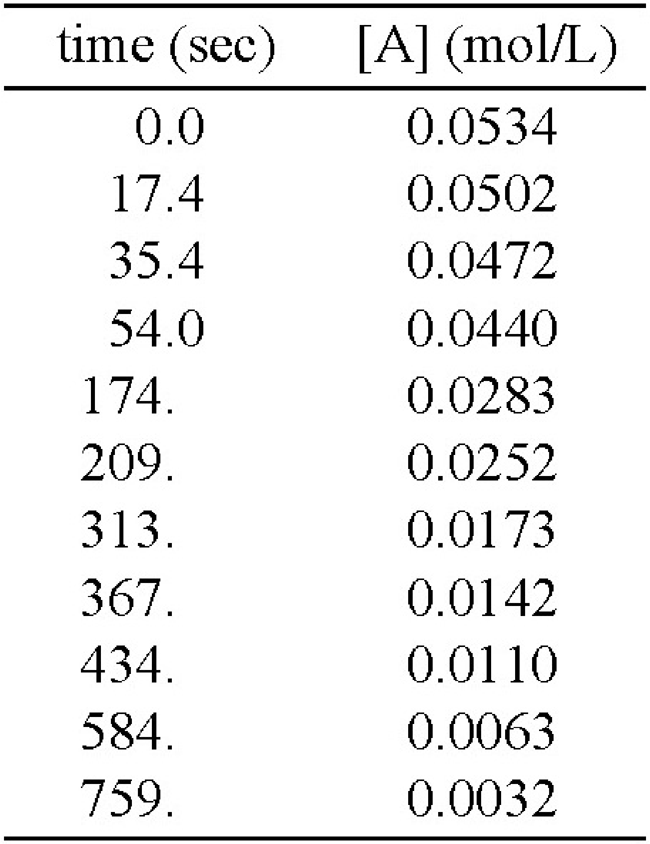
McQuarrie & Simon, Chp 28.2-28.4.

Reading for Kinetics Lecture 3:

McQuarrie & Simon, Chp 28.7.

Rate Equations from Experimental Data

$A \rightarrow P$ irreversible



time (sec)	[A] (mol/L)
0.0	0.0534
17.4	0.0502
35.4	0.0472
54.0	0.0440
174.	0.0283
209.	0.0252
313.	0.0173
367.	0.0142
434.	0.0110
584.	0.0063
759.	0.0032

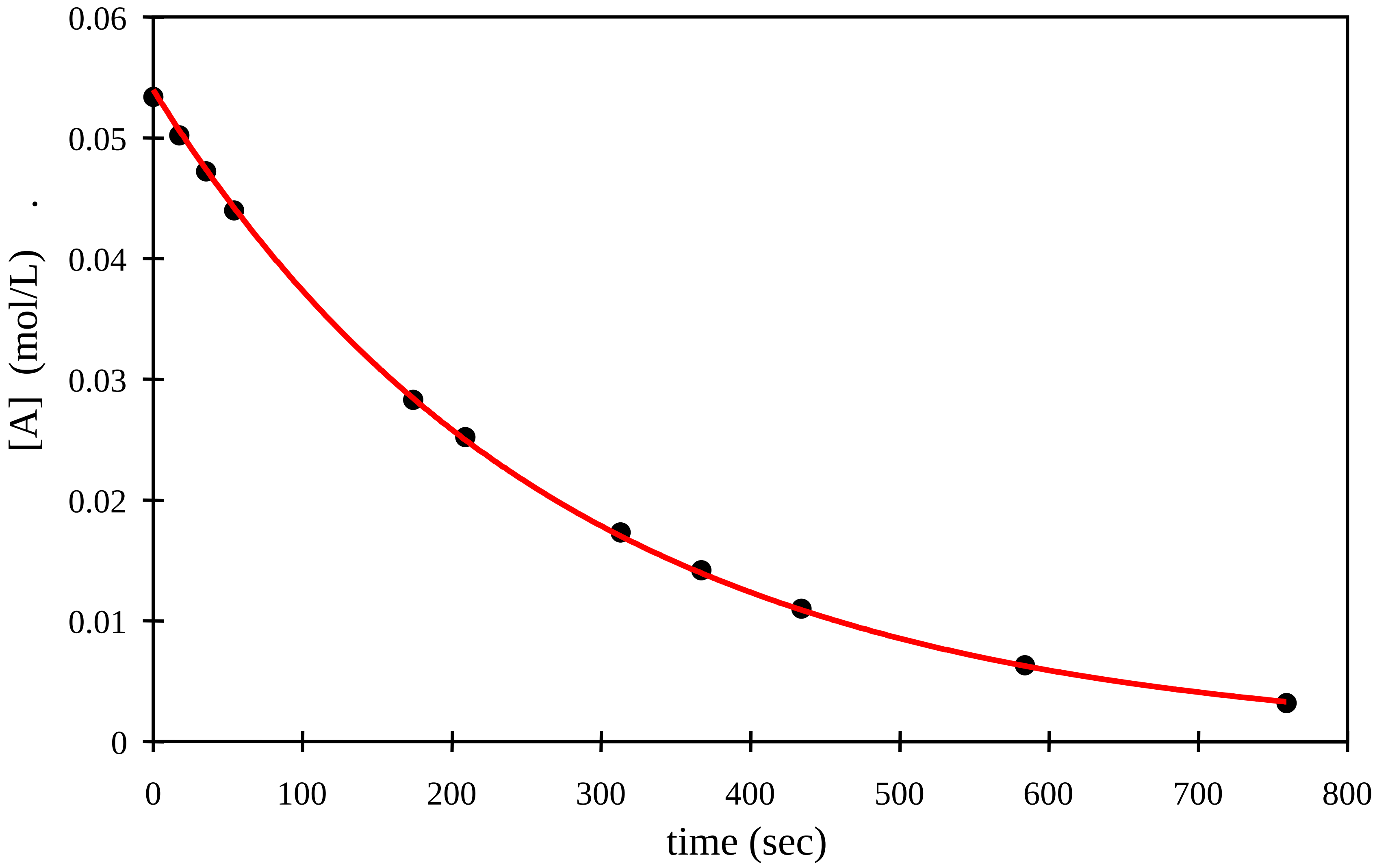
rate equation?

assume $$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^{a}$$

$a = ?$

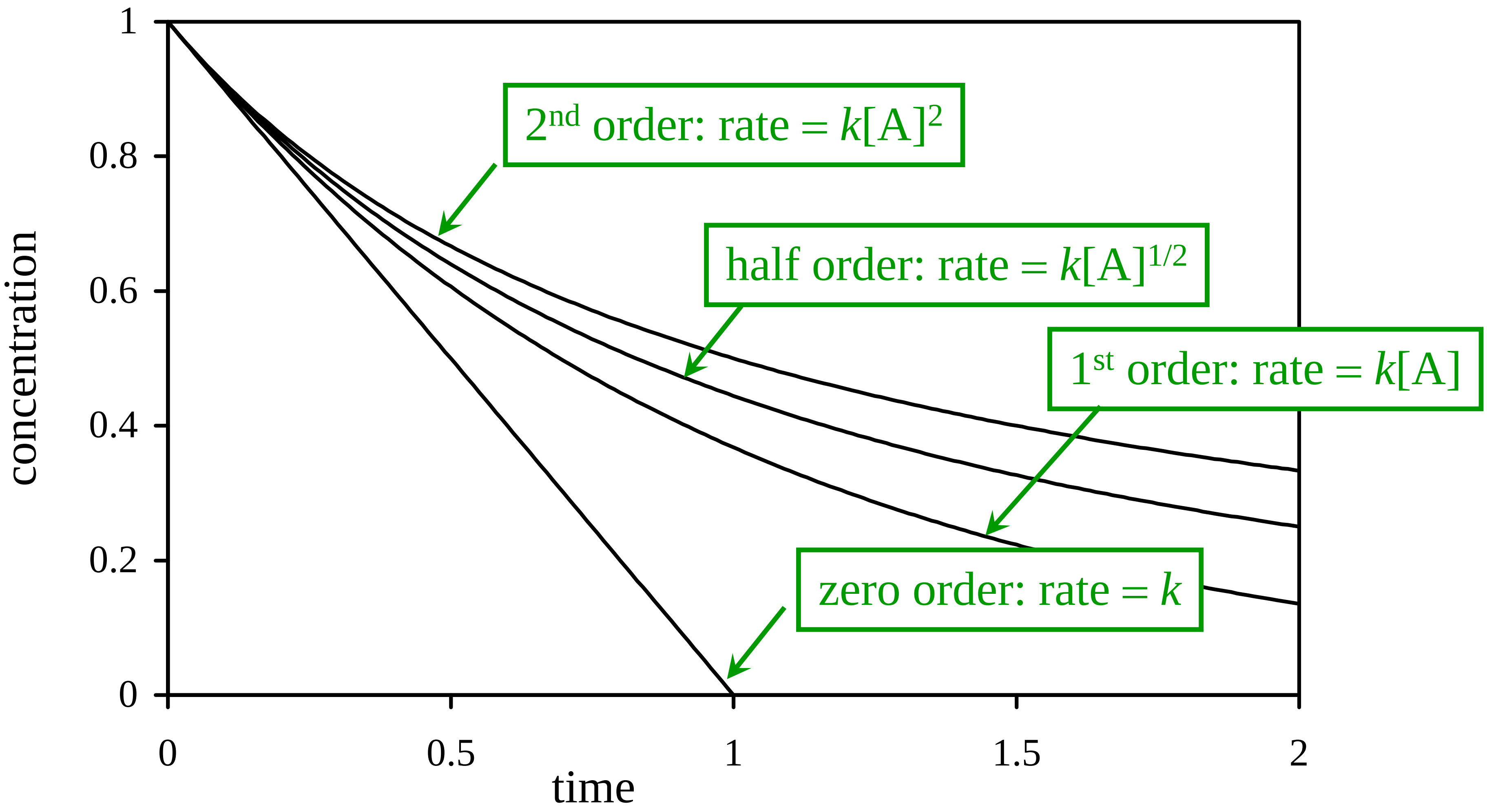
usually $a = 0, 1/2, 1, 3/2, \text{ or } 2$

Rate Equations from Experimental Data



How to Find Reaction Order?

Guess "*a*" and fit a line to the data?



Reaction Order?

Better to plot the data as a straight line.

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^{a}$$

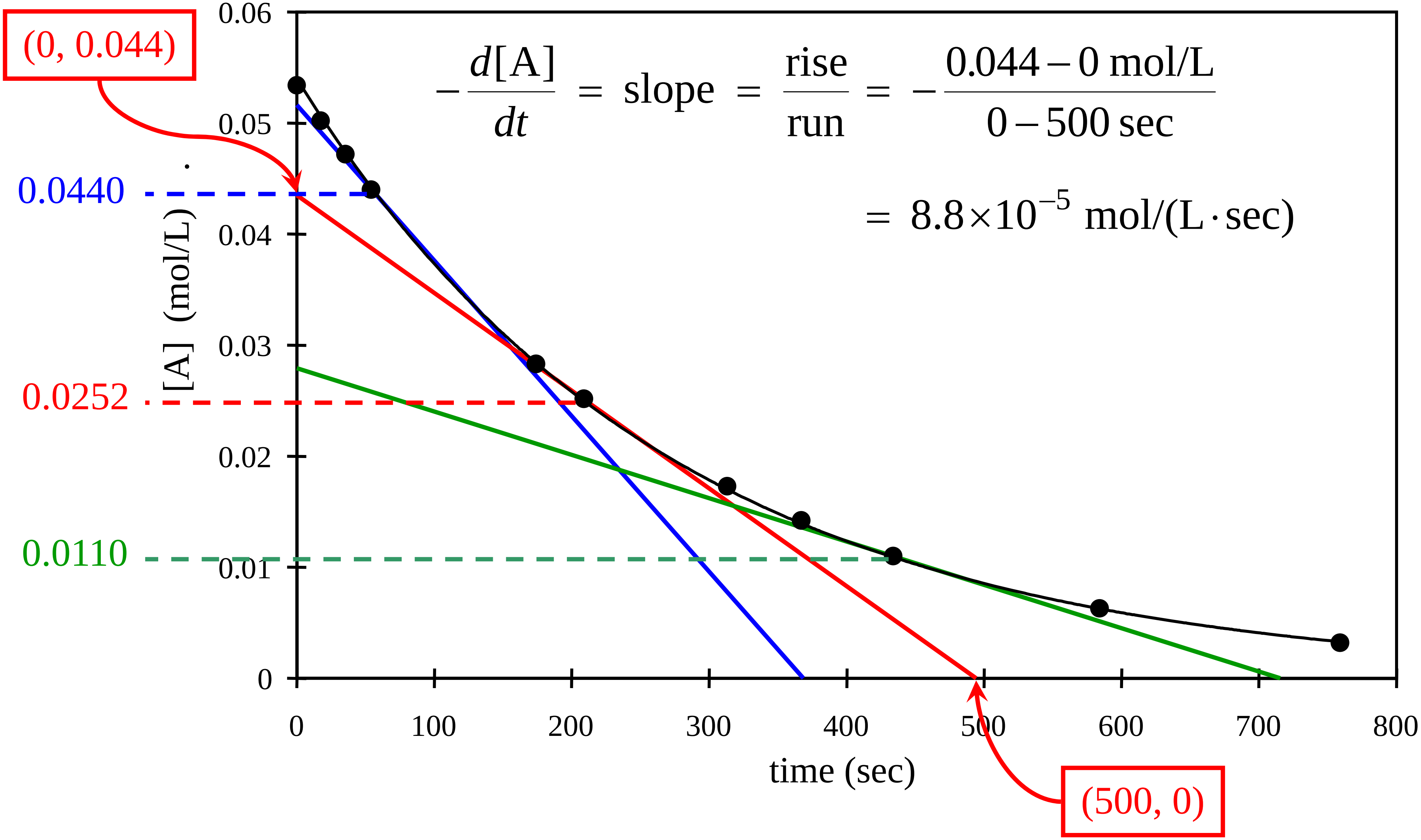
$$\log_{10}\left(-\frac{d[\mathrm{A}]}{dt}\right) = \log_{10}\left(k[\mathrm{A}]^{a}\right)$$

$$\underbrace{\boxed{\log_{10}\left(-\frac{d[\mathrm{A}]}{dt}\right)}}_{y} = \underbrace{\boxed{a}}_{\text{slope}}\,\underbrace{\boxed{\log_{10}[\mathrm{A}]}}_{x} + \underbrace{\boxed{\log_{10} k}}_{\text{intercept}}$$

equation for a
straight line on
a log-log plot

How to convert concentration vs. time to rate vs. concentration?

Measure slopes!



$$-\frac{d[\mathrm{A}]}{dt} = \text{slope} = \frac{\text{rise}}{\text{run}} = -\frac{0.044 - 0\ \text{mol/L}}{0 - 500\ \text{sec}}$$

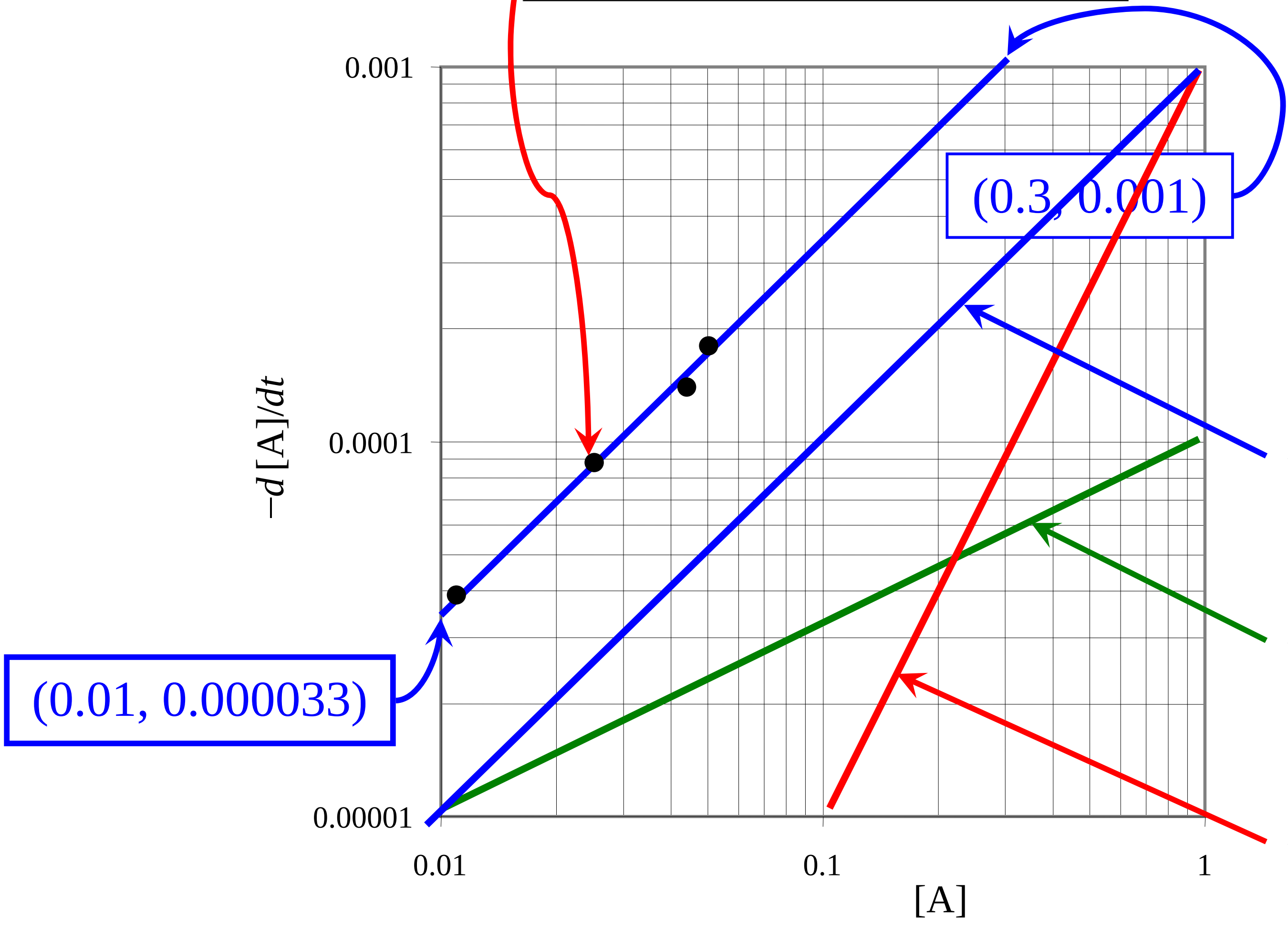
$$= 8.8\times 10^{-5}\ \text{mol/(L}\cdot\text{sec)}$$

Method of Initial Rates

[A] (mol/L)	$-d[A]/dt$ (mol/L/sec)
0.0502	1.8×10^{-4}
0.0440	1.4×10^{-4}
0.0252	8.8×10^{-5}
0.0110	3.9×10^{-5}

$$\text{slope} = \frac{\text{rise}}{\text{run}}$$

$$\cancel{= \frac{0.001 - 0.000033}{0.3 - 0.01} = 0.003 \approx 0}$$



$$= \frac{\log_{10} 0.001 - \log_{10} 0.000033}{\log_{10} 0.3 - \log_{10} 0.01}$$

$$= \frac{1.48}{1.48} = 1$$ *Reasonable?*

$$\frac{\text{rise}}{\text{run}} = \frac{2\ \text{decades}}{2\ \text{decades}} = 1$$

$$\frac{\text{rise}}{\text{run}} = \frac{1\ \text{decade}}{2\ \text{decades}} = \frac{1}{2}$$

$$\frac{\text{rise}}{\text{run}} = \frac{2\ \text{decades}}{1\ \text{decade}} = 2$$

Isolation Method

More than one reactant? Isolate the effects of [A].

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{P}$$

B is in excess.

time (sec)	[A] (mol/L)	[B] (mol/L)
0	1.0	100.0
1	0.9	99.9
3	0.8	99.8
10	0.6	99.6

$[\mathrm{B}] \approx [\mathrm{B}]_0$

[B] is ~constant

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^a[\mathrm{B}]^b \approx k[\mathrm{A}]^a[\mathrm{B}]_0^b = k'[\mathrm{A}]^a \quad \text{where } k' = k[\mathrm{B}]_0^b$$

Integrated Rate Equations: First-Order Reactions

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^{1}$$

separate …

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

important:
add integration limits

and integrate.

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]} = \int_0^t -k\,dt$$

$$\ln\frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -kt$$

$$2.303\,\log_{10}\frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -kt$$

equation for a straight line

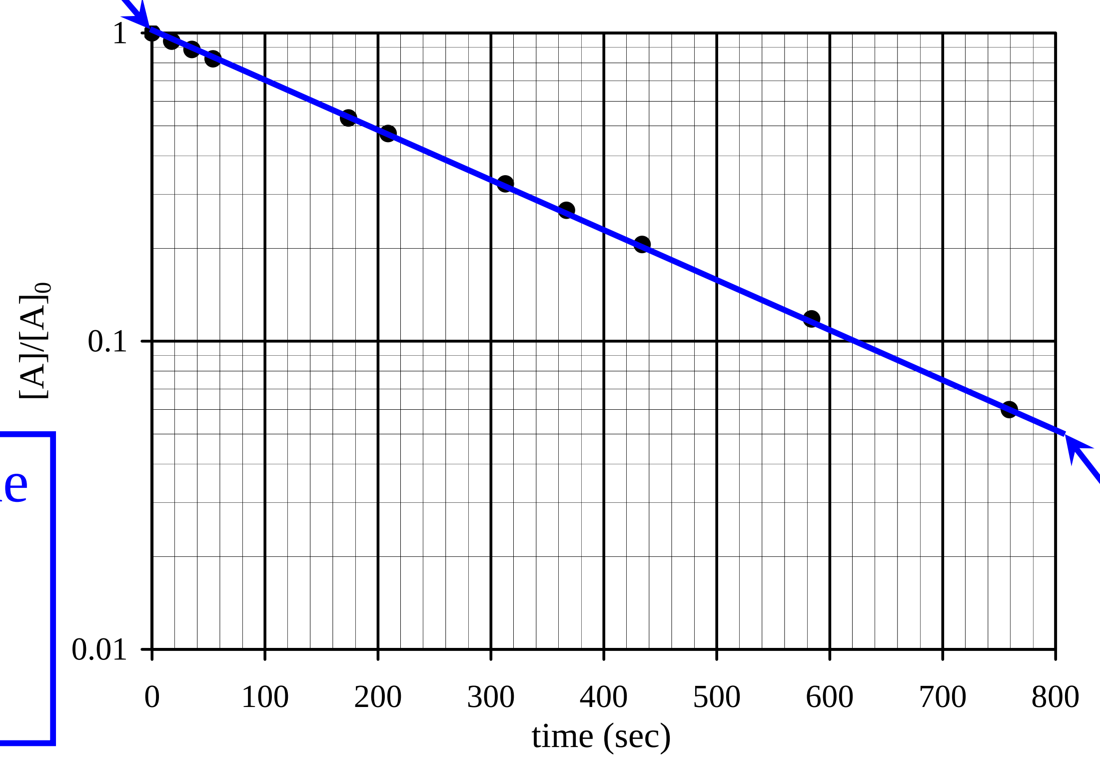
plot $\frac{[\mathrm{A}]}{[\mathrm{A}]_0}$ vs. t on semilog paper.

Integrated Rate Equations: First-Order Reactions, A → P

time (sec)	[A] (mol/L)	$[A]/[A]_0$
0.0	0.0534	1.000
17.4	0.0502	0.940
35.4	0.0472	0.884
54.0	0.0440	0.824
174.	0.0283	0.530
209.	0.0252	0.472
313.	0.0173	0.324
367.	0.0142	0.266
434.	0.0110	0.206
584.	0.0063	0.118
759.	0.0032	0.060

$$\boxed{2.303 \log_{10} \frac{[A]}{[A]_0} = -kt}$$

(0, 1)



(800, 0.052)

straight line confirms 1^{st}-order reaction

$$\text{slope} = \frac{-k}{2.303} = \frac{\text{rise}}{\text{run}}$$

$$= \frac{\log_{10} 0.052 - \log_{10} 1}{800 - 0}$$

$$= -0.0016/\text{sec}$$

$$k = 0.0037/\text{sec}$$

Integrated Rate Equations: Second-Order Reactions

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^2$$

separate and integrate.

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = \int_0^t -k\,dt$$

$$-\left(\frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_0}\right) = -kt$$

$$\boxed{\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt}$$

equation for a straight line

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{1 + kt[\mathrm{A}]_0}$$

$$\boxed{\text{plot } \frac{1}{[\mathrm{A}]} \text{ vs. } t.}$$

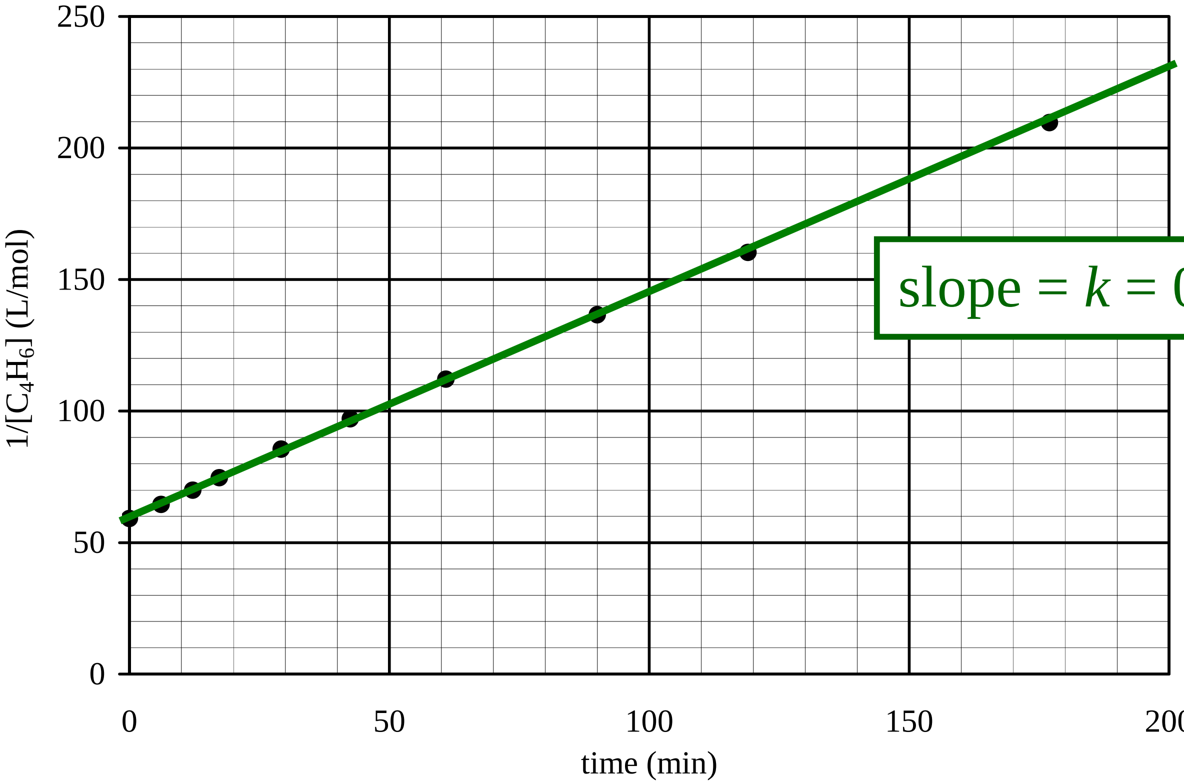
Integrated Rate Equations: Second-Order Reactions, 2A → P

Example: Dimerization of Butadiene

$$2C_4H_6 \rightarrow C_8H_{12}$$

time (min)	$[C_4H_6]$ (mol/L)	$1/[C_4H_6]$
0.0	0.0169	59.2
6.1	0.0155	64.5
12.2	0.0143	69.9
17.3	0.0134	74.6
29.2	0.0117	85.5
42.5	0.0103	97.1
60.9	0.00892	112.1
90.0	0.00732	136.6
119.0	0.00624	160.3
177.0	0.00477	209.6

$$\boxed{\frac{1}{[A]} = \frac{1}{[A]_0} + kt}$$



slope = k = 0.86 L/(mol·min)

straight line confirms 2nd-order reaction

Integrated Rate Equations: Half Lives

$t_{½}$ ≡ the time for a reactant concentration to decrease to ½ its initial value

First-Order Reaction:

$$\ln\frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -kt$$

substitute $[\mathrm{A}] = ½[\mathrm{A}]_0$
at $t = t_{½}$

$$\ln\frac{½[\mathrm{A}]_0}{[\mathrm{A}]_0} = -kt_{½}$$

$$t_{½} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

If $t_{½}$ is independent of [A],
reaction is first order and irreversible.

Integrated Rate Equations: Half Lives

$t_{1/2} \equiv$ the time for a reactant concentration to decrease to ½ its initial value

Second-Order Reaction:

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{1 + kt[\mathrm{A}]_0}$$

substitute $[\mathrm{A}] = \frac{1}{2}[\mathrm{A}]_0$
at $t = t_{1/2}$

$$\tfrac{1}{2}[\mathrm{A}]_0 = \frac{[\mathrm{A}]_0}{1 + kt_{1/2}[\mathrm{A}]_0}$$

$$t_{1/2} = \frac{1}{k[\mathrm{A}]_0}$$

Plot $t_{1/2}$ vs. $1/[\mathrm{A}]_0$. If line is straight,
reaction is second order and irreversible.

Integrated Rate Equations: Half Lives

n^{th} Order Reaction:

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^n$$

need an integrated equation.

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]^n} = \int_0^t -k\,dt$$

$$-\frac{1}{n-1}\left(\frac{1}{[\mathrm{A}]^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right) = -kt$$

substitute $[\mathrm{A}] = ½[\mathrm{A}]_0$ at $t = t_{½}$

$$t_{½} = \frac{2^{n-1}-1}{(n-1)k[\mathrm{A}]_0^{n-1}}$$

okay for $n = 1$?

L'Hôpital!

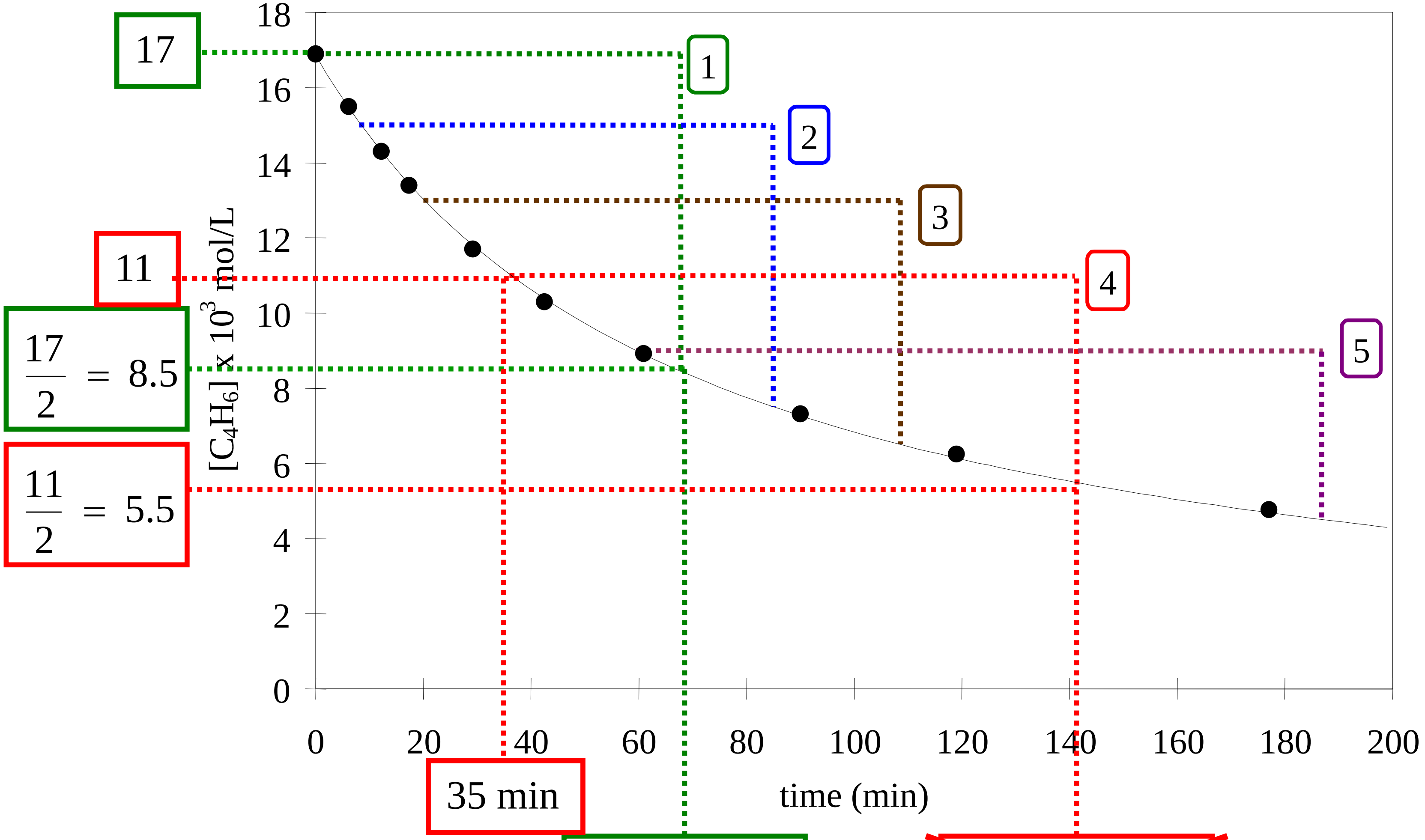
$$\log_{10} t_{½} = \log_{10}\left[\frac{2^{n-1}-1}{(n-1)k[\mathrm{A}]_0^{n-1}}\right]$$

$$\underbrace{\boxed{\log_{10} t_{½}}}_{y} = \underbrace{(1-n)}_{\text{slope}}\underbrace{\boxed{\log_{10}[\mathrm{A}]_0}}_{x} + \underbrace{\log_{10}\left[\frac{2^{n-1}-1}{(n-1)k}\right]}_{\text{intercept}}$$

straight line!

Integrated Rate Equations: Half Lives

Dimerization of Butadiene: $2C_4H_6 \rightarrow C_8H_{12}$



$t_{1/2}$ = 68 min

~~$t_{1/2}$ = 140 min~~

$t_{1/2}$ = 140 – 35 = 105 min

Integrated Rate Equations: Half Lives

Dimerization of Butadiene: $2C_4H_6 \rightarrow C_8H_{12}$

	$[C_4H_6]$	$t_{1/2}$
1	0.0169	68 min
2	0.015	77
3	0.013	87
4	0.011	105
5	0.009	128

$$\text{slope} = \frac{\text{rise}}{\text{run}}$$

$$= \frac{\log_{10}(1000) - \log_{10}(12)}{\log_{10}(0.0012) - \log_{10}(0.1)}$$

$$= \frac{1.92}{-1.92} = -1$$

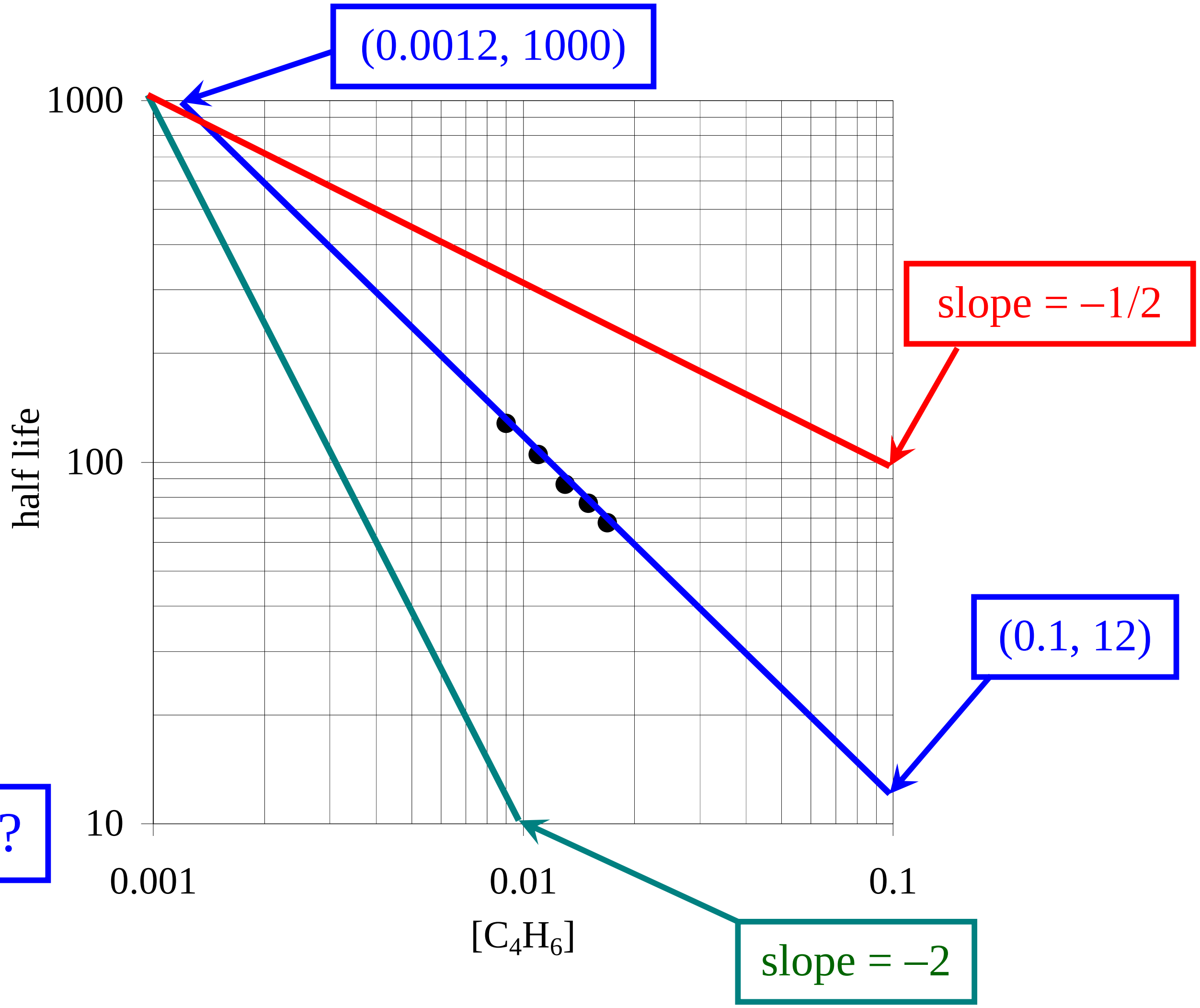
reasonable?

~~$\therefore\ n\ =\ \text{reaction order}\ =\ -1$~~

$$1 - n = -1$$

$$n = 2$$

$$\boxed{\therefore\ n\ =\ \text{reaction order}\ =\ 2}$$



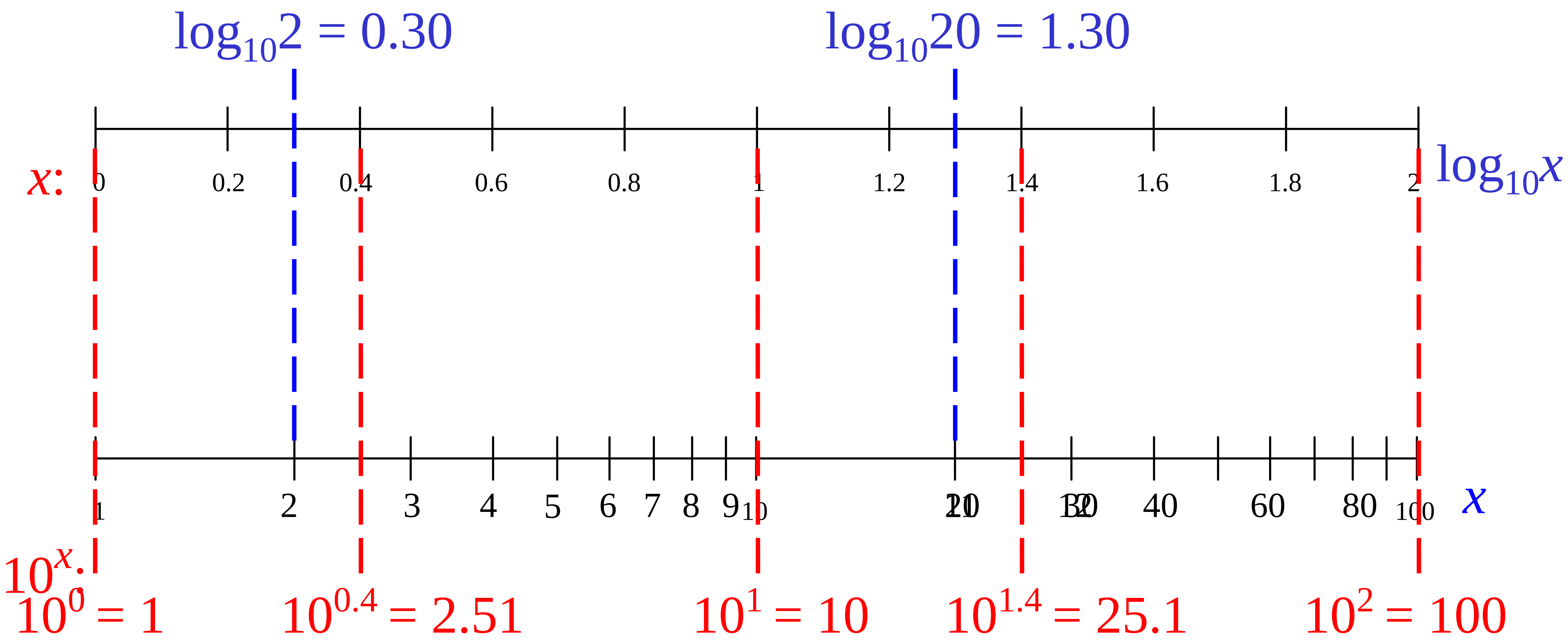
(0.0012, 1000)

slope = –1/2

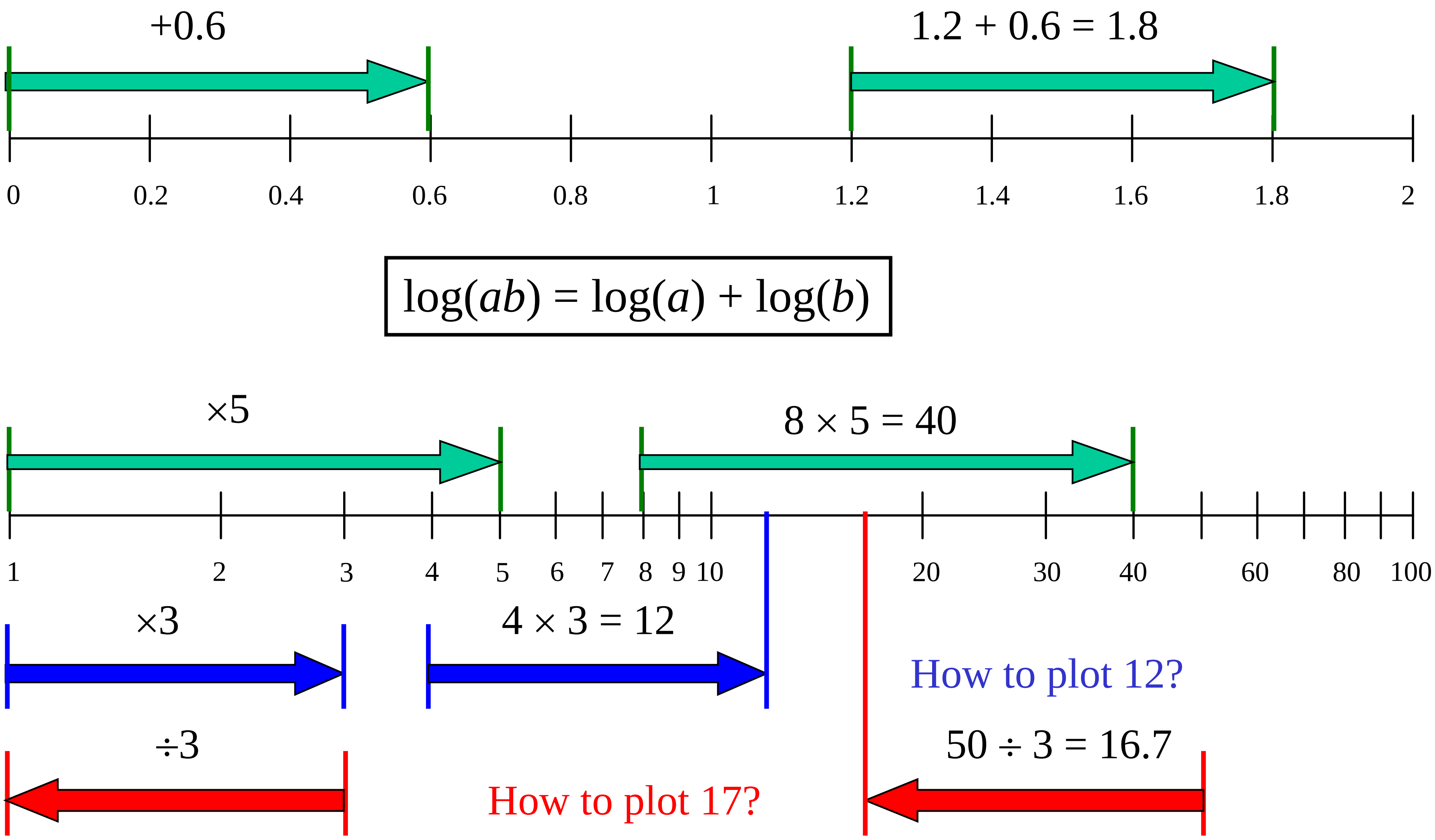
(0.1, 12)

slope = –2

Logarithmic Scales



Logarithmic Scales



$$\boxed{\log(ab) = \log(a) + \log(b)}$$

How to plot 12?

How to plot 17?

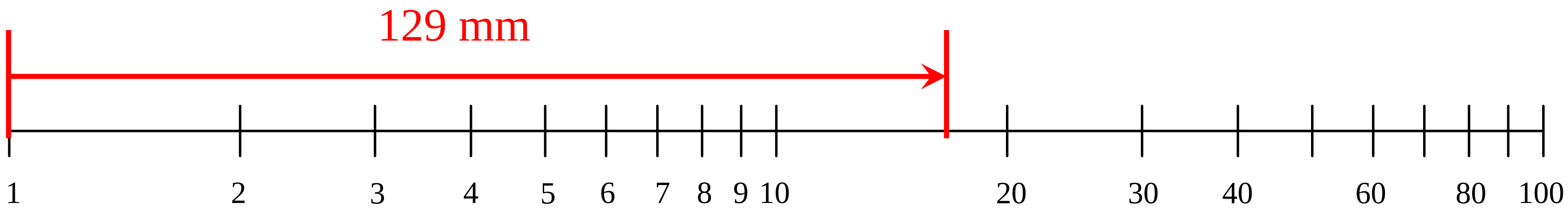
Logarithmic Scales

Another method to plot numbers.

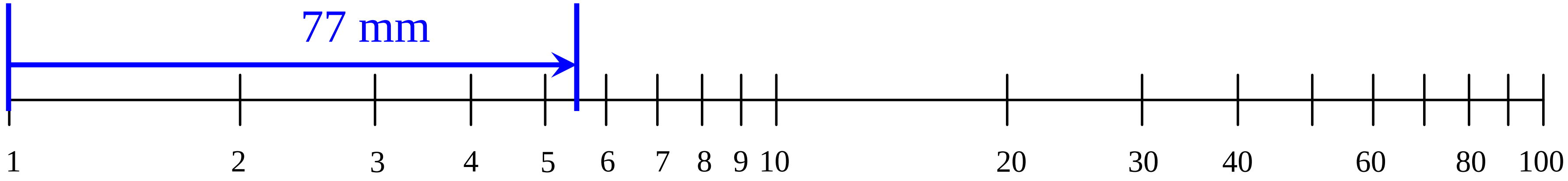
distance from 1 to 10 = 105 mm
distance from 1 to 17 = x mm

$$\frac{\log_{10} 17}{\log_{10} 10} = \frac{x}{105\text{ mm}}$$

$$x = (\log_{10} 17)(105\text{ mm}) = 129\text{ mm}$$



A method to read numbers.



distance from 1 to 10 = 105 mm
distance from 1 to x = 77 mm

$$\frac{\log_{10} x}{\log_{10} 10} = \frac{77\text{ mm}}{105\text{ mm}}$$

$$x = 10^{77/105} = 5.4$$

Prelim 1 2025 Statistics

A-J Front of 245 Olin
K-Z Back of 245 Olin

Mean: 85 / 120 (71%)
Std. Deviation: 21

Solution is posted.

Problem 1: 14 ± 4 / 20 (70%)

Problem 2: 16 ± 9 / 30 (52%)

Problem 3: 20 ± 6 / 25 (80%)

Problem 4: 14 ± 6 / 20 (70%)

Problem 5: 22 ± 6 / 25 (86%)