

Chapter 3 in the text provides different types of reaction rate models and discusses how to determine which model to select given concentration vs. time data. This is presented by linearizing the models and using statistics to determine which model fits the data best.

The main skill/knowledge you should obtain from this chapter is the ability to determine which rate model fits a set of data the best using regression statistics.

# Analyzing rate data

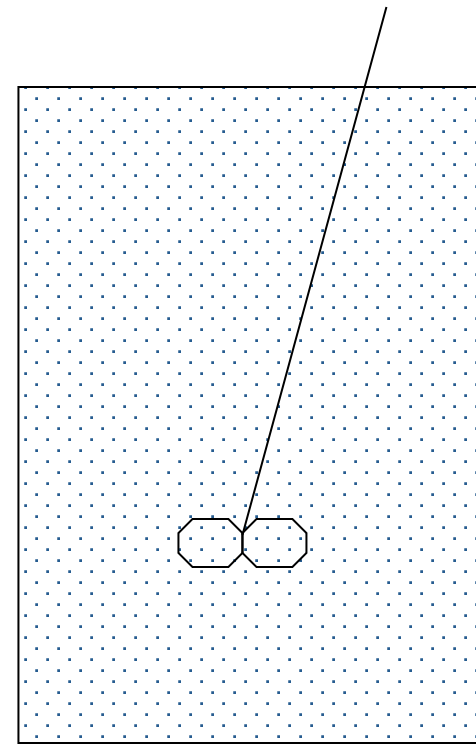
Given you can measure the concentration vs. time for a chemical reaction in the lab/factory, how do you develop a reaction rate model to describe the reaction?

There are 2 methods to do this, using integral and differential techniques, based on a constant volume/density batch reactor.

(Note: A constant volume reactor is simple a closed system at fixed volume, in which reactants are charged at  $t=0$  and the reaction proceeds vs. time.)

# Constant Volume Batch Reactor

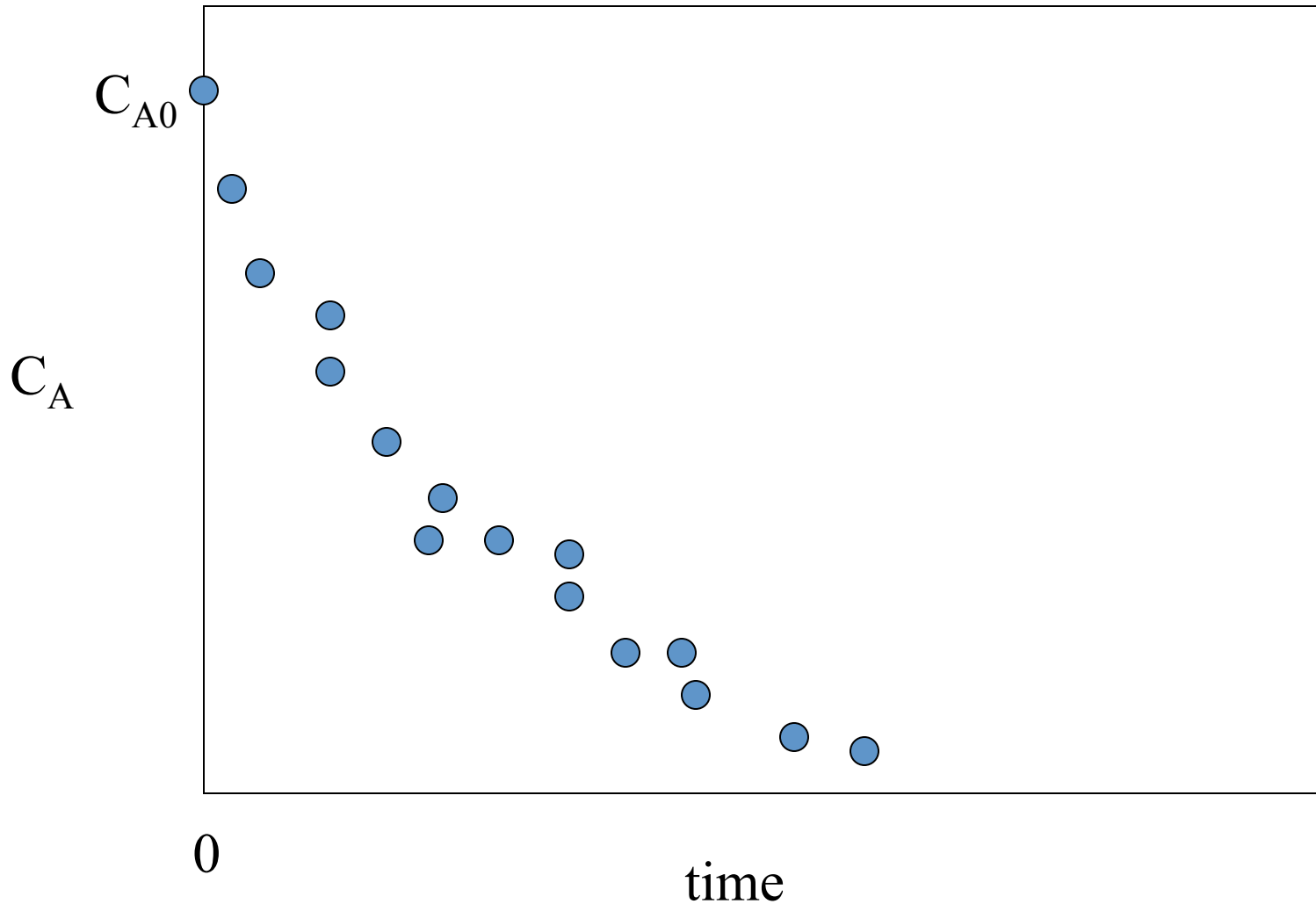
- Fixed volume/density
- well-mixed
- homogeneous gas or liquid phase
- Assume ideal gas behavior



$$\begin{aligned} r_i &= (1/V)(dN_i/dt) = (d[N_i/V]/dt) = dC_i/dt \quad \{\text{liquids}\} \\ &= (1/RT)(dp_i/dt) \quad \{\text{for ideal gas}\} \end{aligned}$$

Assume you have measured the concentration of some reactant A vs. time in a fixed volume batch reactor at constant temperature.

How can you use this data to establish a reaction rate model?



## Integral rate data analysis (develop model, see if it fits data)

Let's assume an elementary, first order, unimolecular decomposition model,



the reaction rate equation for this model would be:

$$-r_A = -dC_A/dt = k \cdot C_A$$

with the initial condition that  $C_A = C_{A0}$  at  $t = 0$

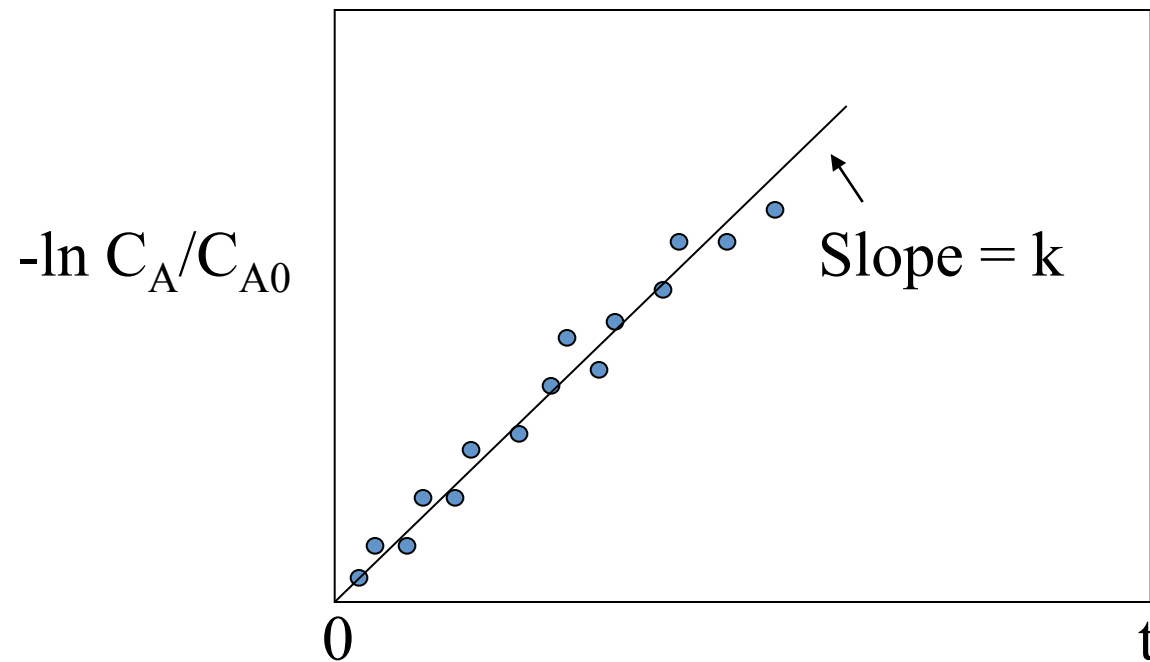
Integrating this equation by simply separating variables yields:

$$\begin{aligned} -r_A &= -dC_A/dt = k \cdot C_A \\ -\int dC_A / C_A &= \int k dt \end{aligned}$$

$$-\ln (C_A / C_{A0}) = kt$$

Note that this is a unimolecular reaction, so A basically decomposes into products

Plotting the data values as  $-\ln (C_A/ C_{A0})$  vs.  $t$  would show a straight line through the data, whose statistical goodness of fit would indicate the validity of the model



The basic idea behind rate data analysis using the integral method is to:

1. Setup a rate equation based on a hypothesized elementary reaction model
2. Integrate the model to obtain  $f(C) = kt$
3. Examine the plot of  $f(C)$  vs.  $t$  with the data for linearity, which would indicate a valid reaction model



# Constant Volume Batch Reactor

## Integral data analysis

Integrate the rate equation and plot

$$-r_A = -dC_A/dt = k \cdot f(C)$$

$$-dC_A/f(C) = k dt$$

$$-\int dC_A/f(C) = \int k dt = k \int dt = kt$$

If the rate equation is correct, this plot of  $-\int dC_A/f(C)$  vs.  $t$  should give a straight line with slope  $k$

# Linear regression for fitting functions to data

## Linearized models

Evaluate different linearized models for best fit of  $f(C)$  vs.  $t$ , using visual and objective regression parameters ( $r$  and  $SE$ )

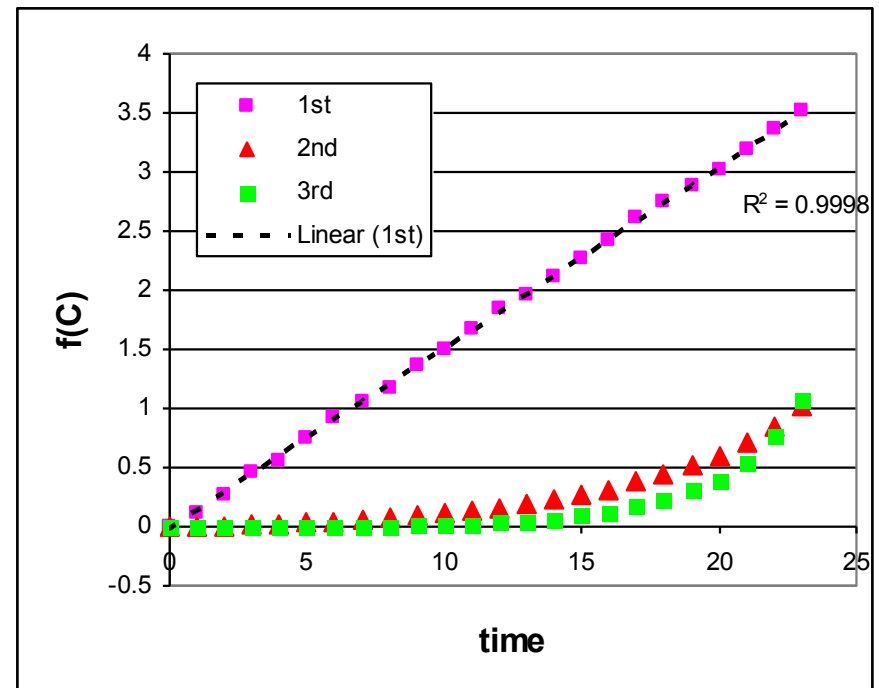
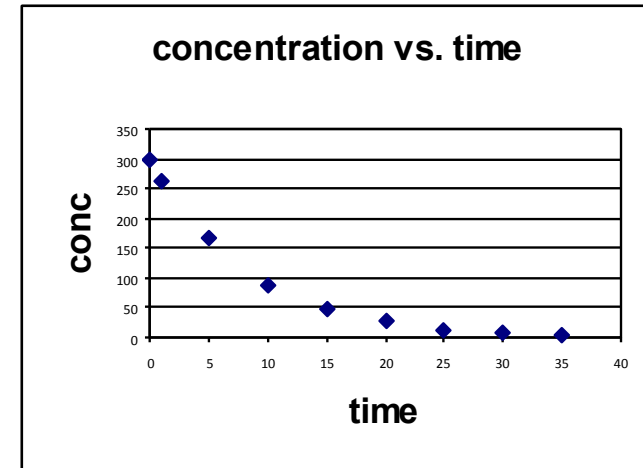
1<sup>st</sup> order –  $f(C) = \ln(C/C_0)$

2<sup>nd</sup> order –  $f(C) = 1/C - 1/C_0$

3<sup>rd</sup> order –  $f(C) = 1/C^2 - 1/C_0^2$

etc.

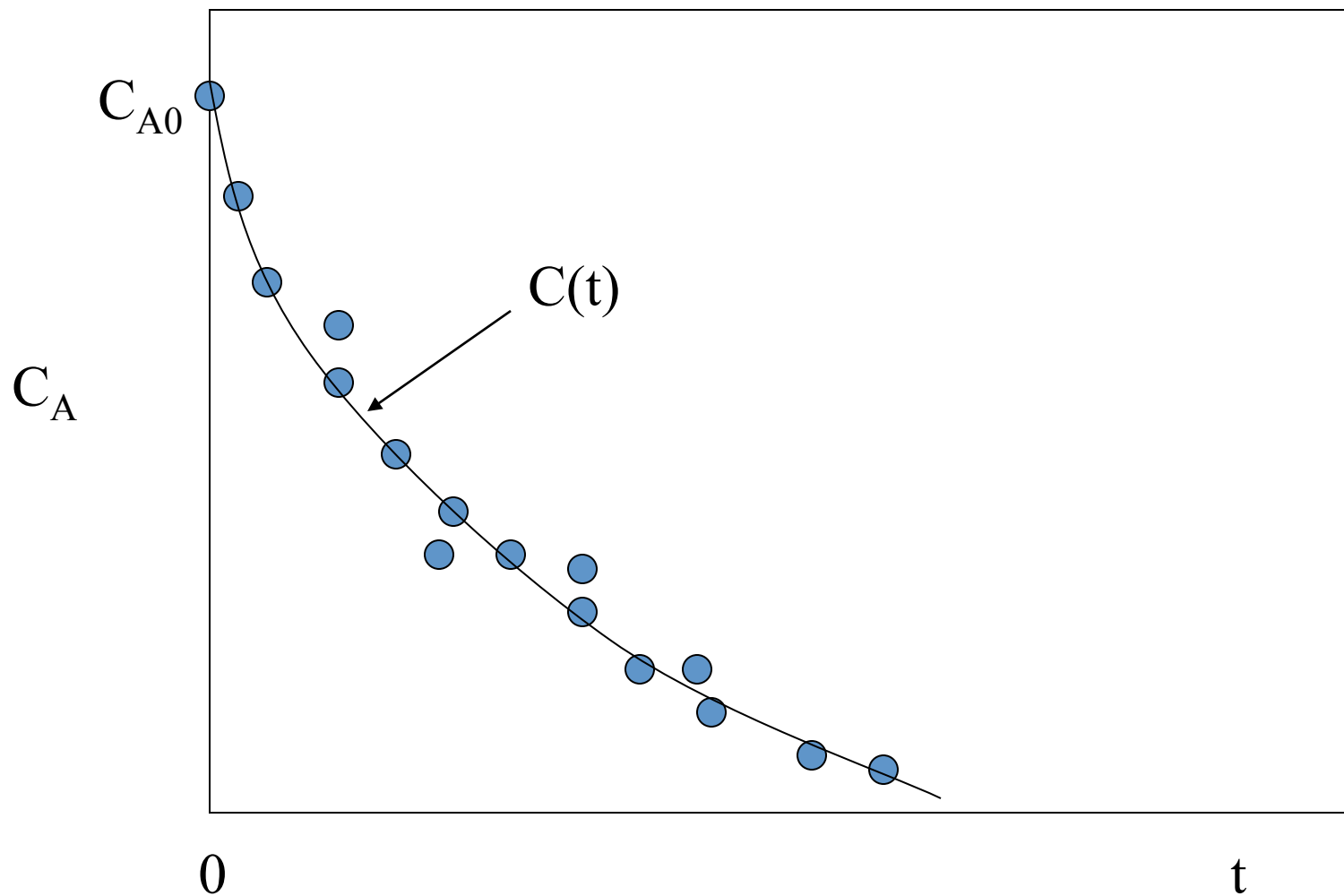
Note: Can also directly fit  $f(C)$  vs  $C$  models and do best fit model regression



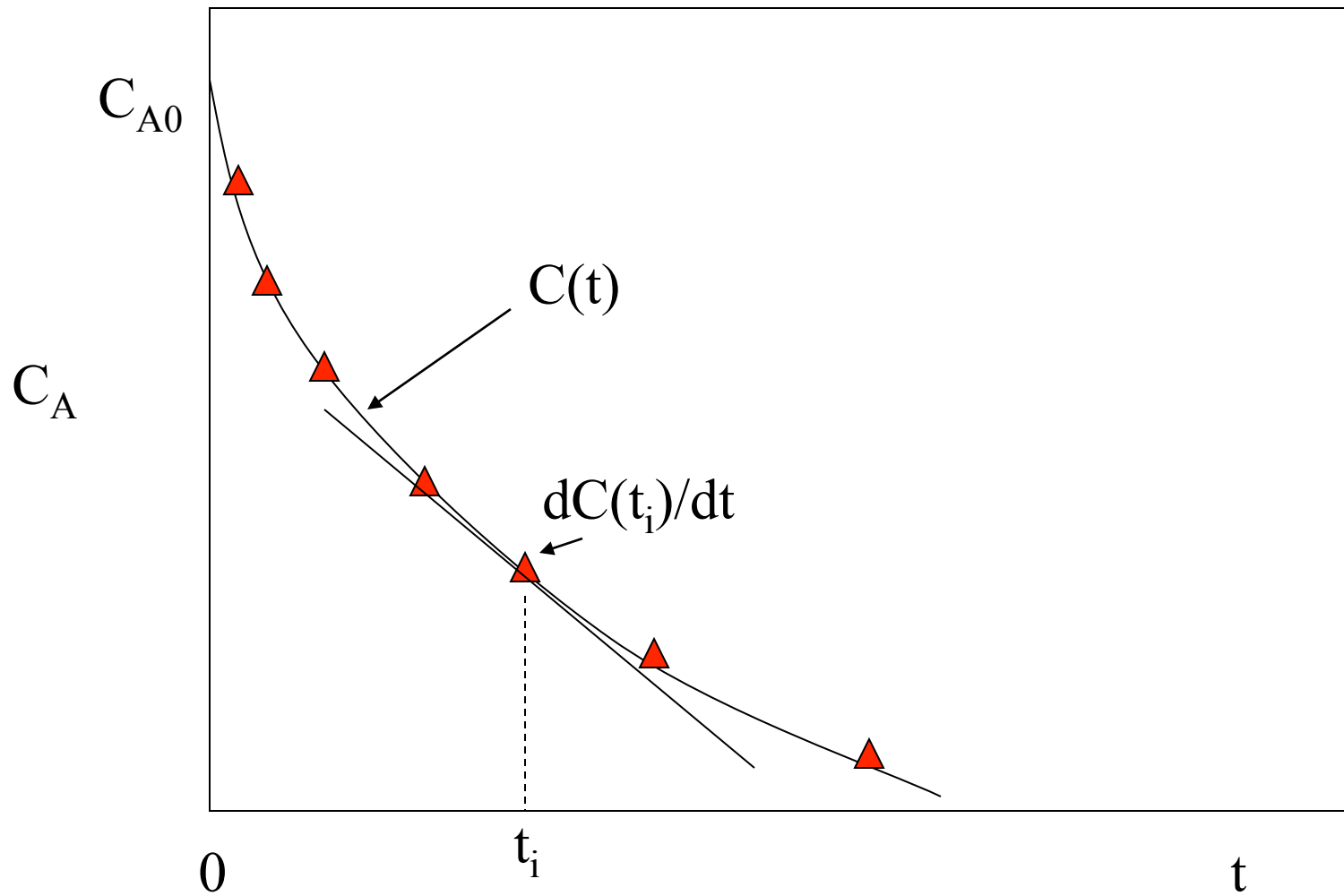
Differential reaction data analysis  
(Fit data, use to develop model  
see example 3.2 in text)

This method uses curve fitting or graphical plotting of the concentration vs. time data to obtain a  $C(t)$  function.  $dC(t)$ , the differential of  $C(t)$ , is calculated/estimated at various times and plotted vs. a hypothesized reaction rate model and compared for linearity.

First, carefully fit a smooth curve through the concentration vs. time data

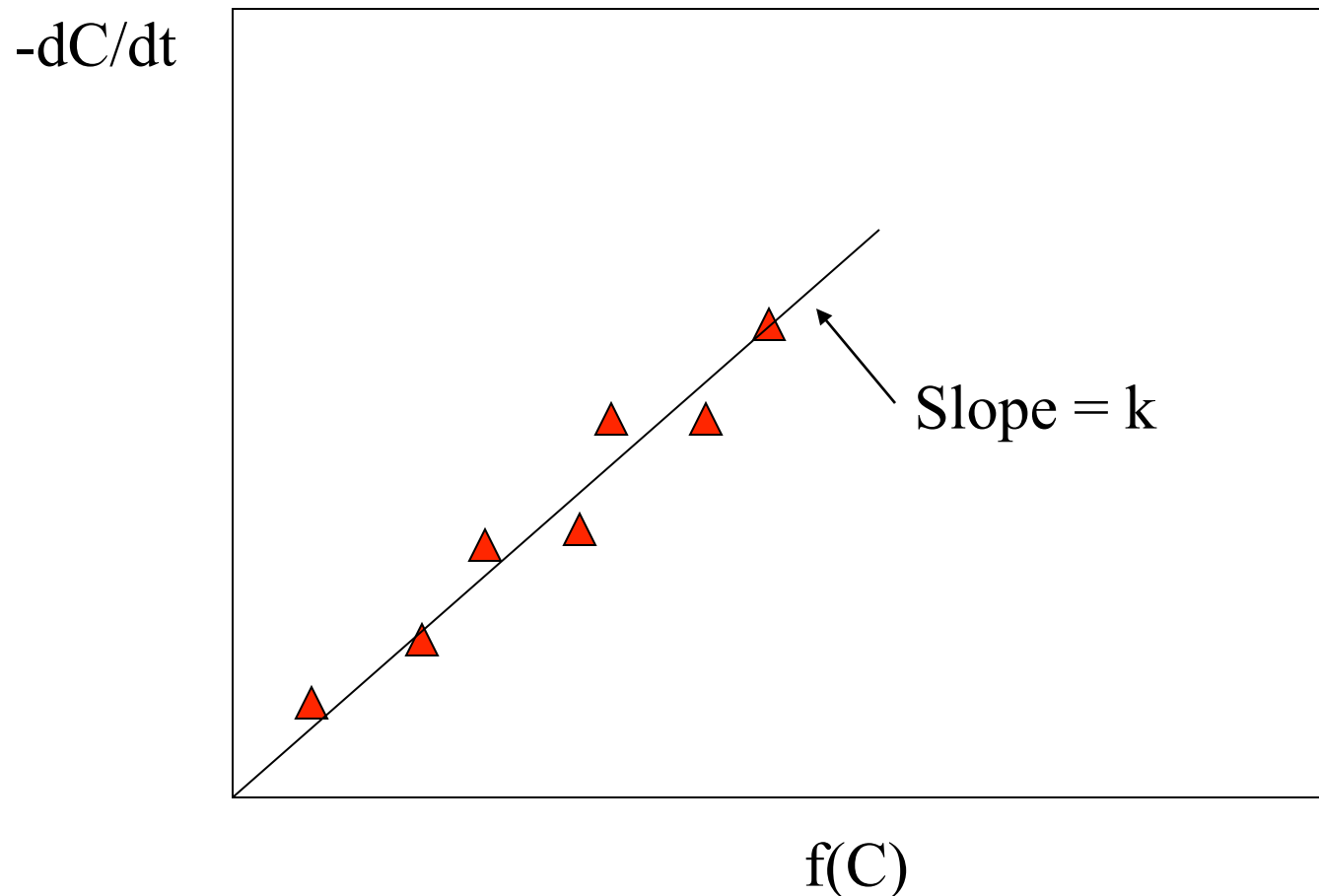


Calculate  $dC/dt$  at various values of  $t$



Select a rate equation,  $f(C)$ , plot  $dC/dt$  data vs.  $f(C)$  and evaluate for goodness of fit

$$-r_i = -dC_i/dt = k \cdot f(C_i)$$



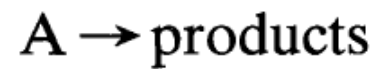
# For nth order rate models

- Fit data to curve,  $C(t)$
- Take derivatives,  $dC/dt$
- Plot log of  $-dC/dt$  vs.  $\log C(t)$  and fit to line
$$\ln(-dC/dt) = \ln k + n \cdot \ln C$$
- slope =  $n$ ,  $\exp(\text{intercept})=k$

e.g. 1<sup>st</sup> order,  $-dC(t)/dt = k \cdot C$ , 2<sup>nd</sup> order  $-dC(t)/dt = k \cdot C^2$

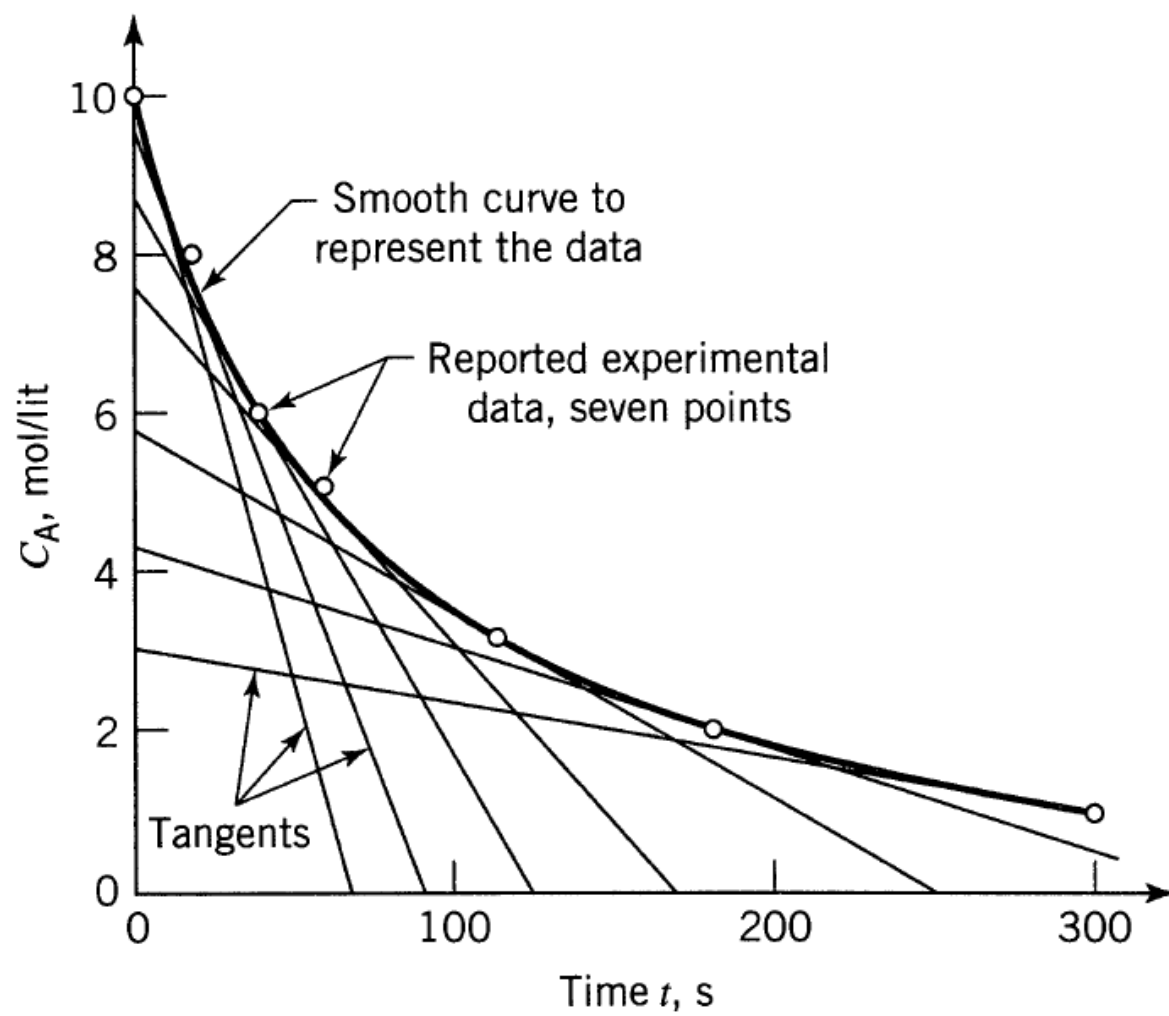
### Example 3.2

Reactant A decomposes in a batch reactor



Column 1	Column 2
Time $t, \text{ s}$	Concentration $C_A, \text{ mol/liter}$
0	$C_{A0} = 10$
20	8
40	6
60	5
120	3
180	2
300	1





**Figure E3.2a**

Column 1	Column 2	Column 3	Column 4	Column 5
Time $t, s$	Concentration $C_A, \text{mol/liter}$	Slope, from Fig. E3.2a $(dC_A/dt)$	$\log_{10} (-dC_A/dt)$	$\log_{10} C_A$
0	10	$(10 - 0)/(0 - 75) = -0.1333$	-0.875	1.000
20	8	$(10 - 0)/(-3 - 94) = -0.1031$	-0.987	0.903
40	6	$(10 - 0)/(-21 - 131) = -0.0658$	-1.182	0.778
60	5	$(8 - 0)/(-15 - 180) = -0.0410$	-1.387	0.699
120	3	$(6 - 0)/(-10 - 252) = -0.0238$	-1.623	0.477
180	2	$(4 - 1)/(24 - 255) = -0.0108$	-1.967	0.301
300	1	$(3 - 1)/(-10 - 300) = -0.0065$	-2.187	0.000

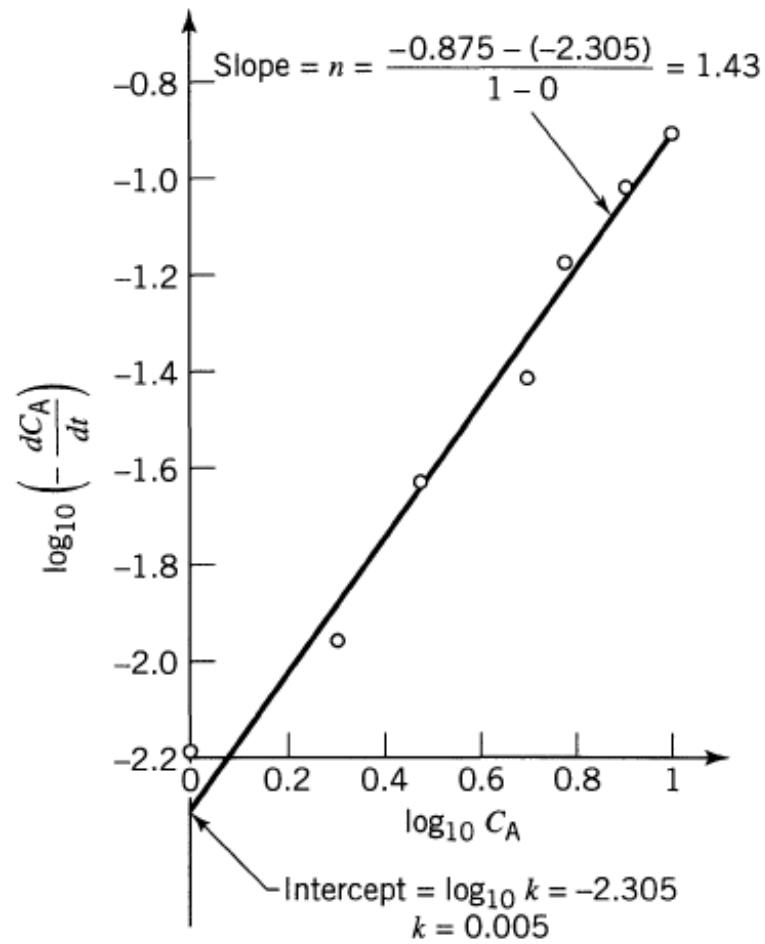
Next, to fit an  $n$ th-order rate equation to this data, or

$$-r_A = -\frac{dC_A}{dt} = kC_A^n$$

take logarithms of both sides (see columns 3 and 4), or

$$\log_{10}\left(-\frac{dC_A}{dt}\right) = \log_{10}k + n\log_{10}C_A$$

$\underbrace{\hspace{10em}}_{\text{y}} \quad \underbrace{\hspace{10em}}_{\text{x}}$   
intercept slope



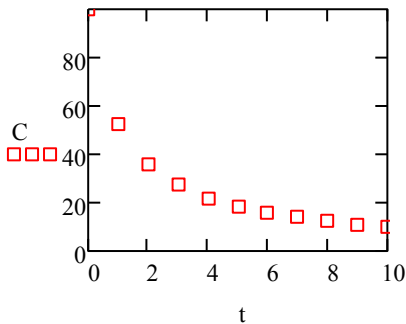
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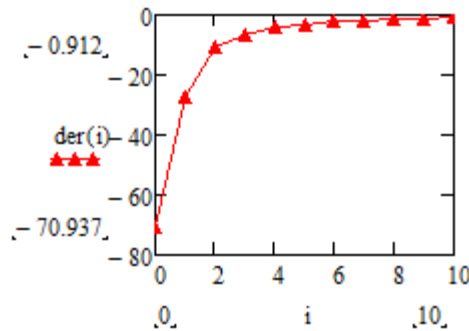
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$$-r_A = -\frac{dC_A}{dt} = \left(0.005 \frac{\text{liter}^{0.43}}{\text{mol}^{0.43} \cdot \text{s}}\right) C_A^{1.43}, \frac{\text{mol}}{\text{liter} \cdot \text{s}}$$

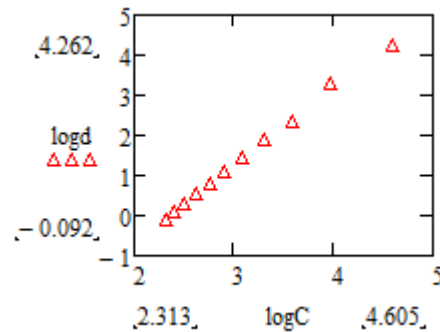
# Differential reaction data analysis (nth order rate model, see example 3.2 in text)



Concentration vs. time



Rate vs. time



Log (rate) vs. log (concentration)

Slope =  $n$ ,  $e^{\text{intercept}} = k$

## Notes:

1. The key issue here is the fitting of the curve  $C(t)$  to the data. This must be as accurate as possible, in order to get an adequate model representation.
2. Depending on the rate model hypothesized, there may be alternative plots for more effective evaluation (see course text p. 66)
3. Note that in evaluating the goodness of fit, an objective statistical analysis is needed (e.g. least squares, etc.)

Please be clear on the types of graphs presented in Chapt. 3

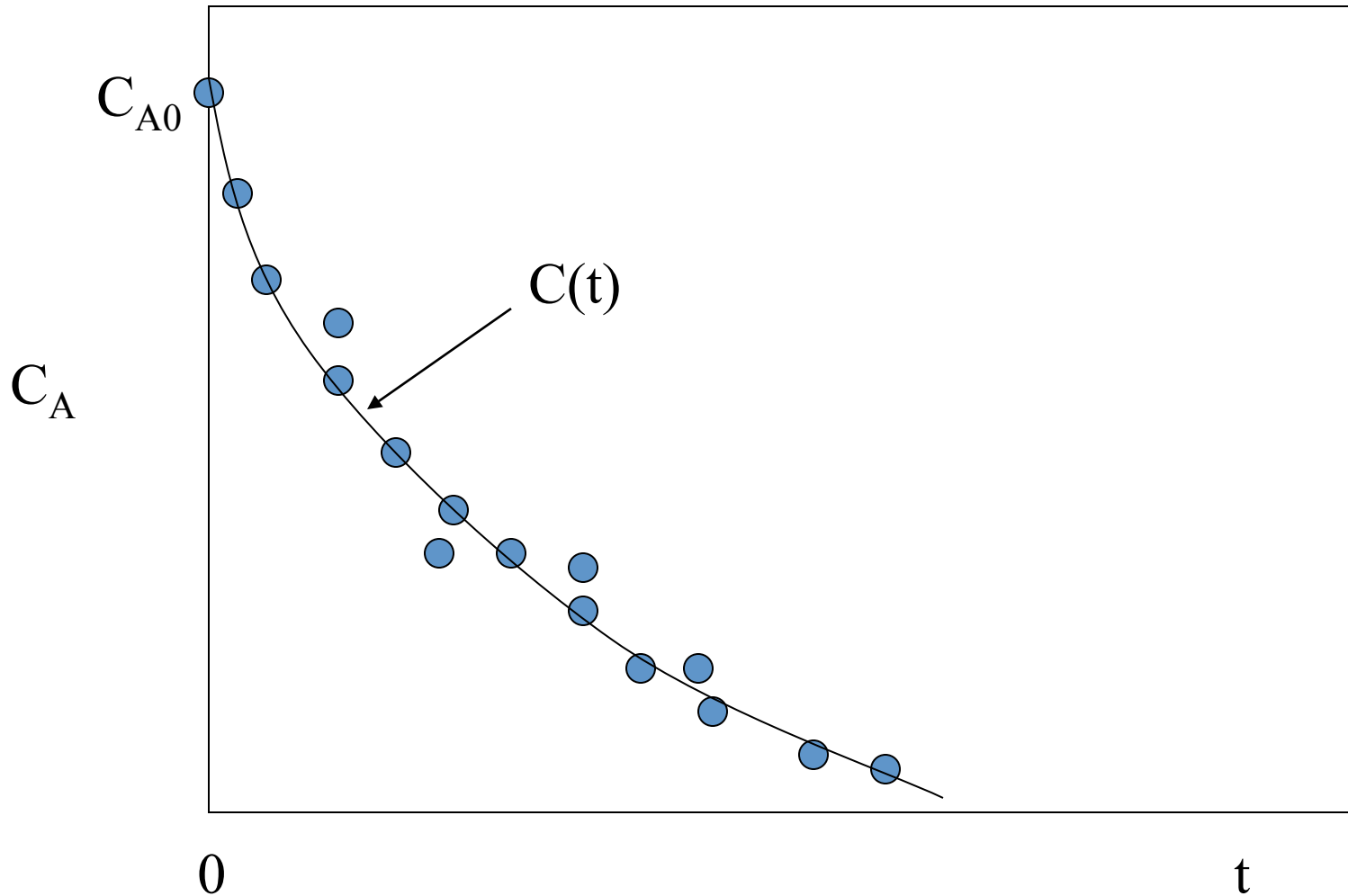
1. Concentration (C) vs. time (t) - how the concentration changes with time
2. Rate ( $dC/dt$ ) vs. concentration (C) - rate models, ie.  $r = dC/dt = f(C)$

Generally, we obtain C vs. t in the lab and compare it to different models to determine which model is best, i.e. integral method.

The model graphs presented in Chapter 3 plot the  $\int dC/f(C)$  vs. t which gives a linearized form of the rate model which can be analyzed using simple linear regression statistics.

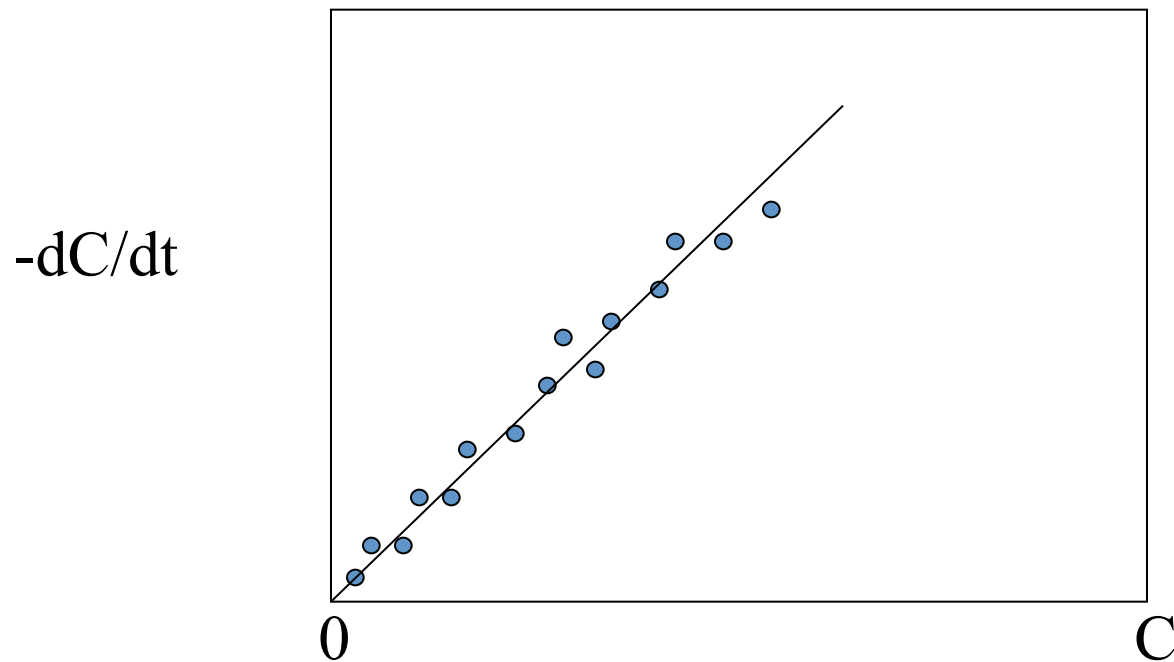
For the purposes of determining a model, you may also be provided with rate vs. concentration data. In these cases, the differential method of analysis would be used to determine the best rate model. This is particularly useful with reactions that do not follow a simple rate model, such as enzymatic reactions.

All  $C$  vs.  $t$  models generally look the same, like the plot below.  
It is generally difficult to see what kind of rate model would fit  
best simply by inspection.



Alternatively, consider the plot below of rate vs.  $C$ .  
What rate model would fit this data?

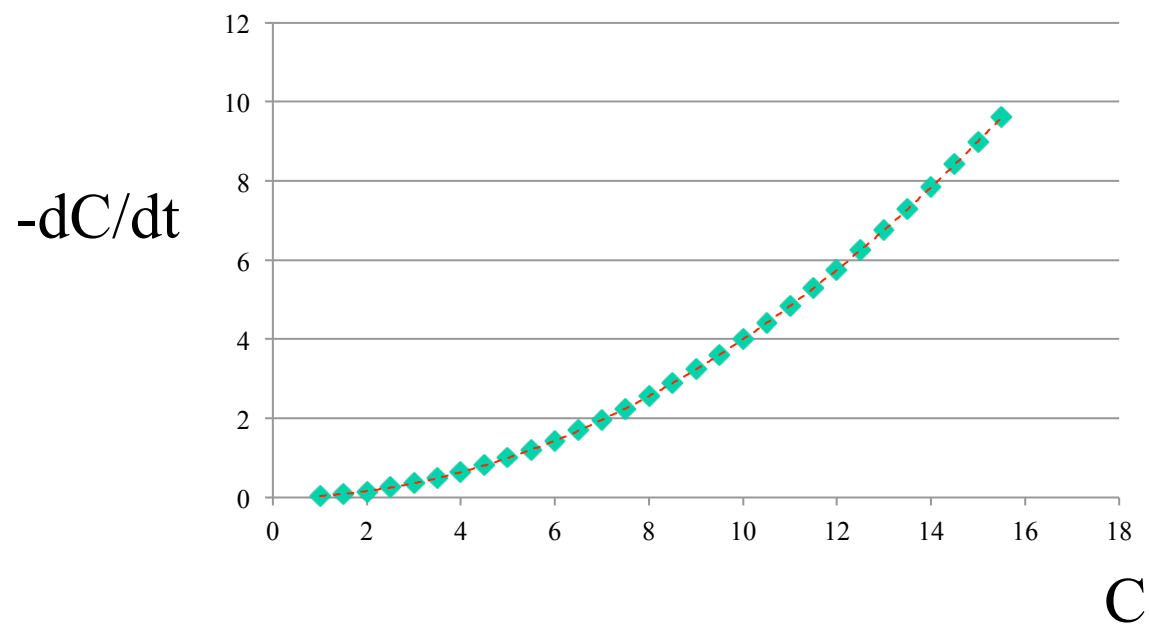
Clearly, this is a 1<sup>st</sup> order model, since  $dC/dt$  is proportional to  $C$ , i.e.  $-dC/dt = k C$



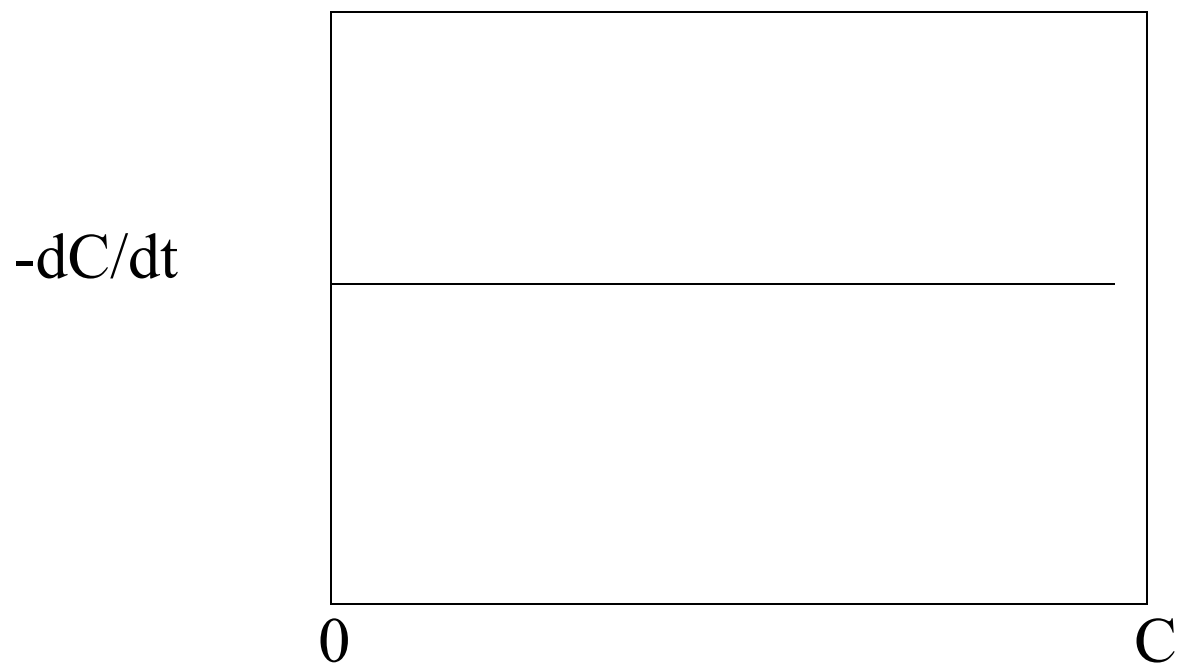


Consider the graph below which plots rate vs. C.

What rate model would fit this data?



What kind of rate order model would correspond to the plot below?



Now consider the plot below. In all our  $n^{\text{th}}$  order rate models, the rate increased with concentration. This was due to the concept that the rate of reaction is based on molecular collisions and collisions increase with increasing reactant concentration.

