Method of Initial Rates

How can you use rate data to determine the order of a reaction?

Why?

In most cases, the rate law for a chemical reaction cannot be derived theoretically. If the reaction is a multi-step reaction, the rate law does not correspond to the balanced chemical equation. Finding the rate law would be simple if we could observe the reactions at the molecular level, but that is not possible. We must use indirect evidence. There are many experimental techniques that can be used to determine the rate law for a reaction. Determining the initial rate of a reaction and seeing how that initial rate changes when the concentrations of reactants are changed is one way of using experimental data to determine the rate law.

Model 1 – The Effect of Exponents

$$y = kx^n$$

where $k = 5$

x	If $n = 0$, then $y = ?$	If $n = 1$, then $y = ?$	If $n = 2$, then $y = ?$
1			
2			
3			
4			

1. Consider the mathematical equation in Model 1.
   a. What letter represents a constant in the equation?

   b. What is the value of the constant?

   c. What letter represents the exponent in the equation?

   d. Does *x* in the equation represent the independent variable, dependent variable or a constant?

2. Fill in the table in Model 1 using the mathematical equation provided. Divide the work among group members.

3. Refer to Model 1. Use complete sentences to describe the change in y as x increases when $n = 0$. Justify the pattern you see using your knowledge of mathematics.

4. Refer to the column in the Model 1 table where $n = 1$.

   a. When x doubles, what happens to y?

   b. When x triples, what happens to y?

5. Use a complete sentence to describe the change in y as x increases when $n = 1$. Justify the pattern you see using your knowledge of mathematics.

6. Refer to the column in the Model 1 table where $n = 2$.

   a. When x triples, what happens to y?

   b. When x quadruples, what happens to y?

7. Use a complete sentence to describe the change in y as x increases when $n = 2$. Justify the pattern you see using your knowledge of mathematics.

8. Consider the data below and determine the value of the exponent q. Justify your answer with an explanation or a mathematical equation.

   $\boldsymbol{r = st^q}$

t	r
5	15
10	30
15	45

9. Solve for the constant s in Question 8 above.

10. Consider the data below and determine the value of the exponent q. Justify your answer with an explanation or a mathematical equation.

$r = st^q$

t	r
10	3
20	3
30	3

11. Consider the data below and determine the value of the exponent q. Justify your answer with an explanation or a mathematical equation.

$r = st^q$

t	r
2	12
4	48
6	108

12. Solve for the constant s in Question 11 above.

Model 2 – Decolorization of a Dye

rate = k[dye]^n

where $k = 3.40 \times 10^3$

[dye]	If $n = 0$, then rate = ?	If $n = 1$, then rate = ?	If $n = 2$, then rate = ?
0.10 M			
0.20 M			
0.30 M			

13. Identify the reactant in the process being studied in Model 2.

14. Refer to Model 2.

    a. Circle the rate law for the decolorization of a dye in Model 2.

    b. What variable represents the constant in the rate law?

    c. What variable represents the order of the reaction?

15. Fill in the table in Model 2. Divide the work among group members. *Note:* The unit for rate should be "molarity per second" in all cases.

16. How does the initial rate of reaction change as the concentration of the reactant increases when the order of the reaction is zero?

17. How does the initial rate of reaction change as the concentration of the reactant increases when the order of the reaction is one?

18. How does the initial rate of the reaction change as the concentration of the reactant increases when the order of the reaction is two?

19. Consider the data below.

rate = $k[O_3]^n$

$[O_3]$	Initial Rate
0.44 atm	0.01848 atm/min
0.88 atm	0.03696 atm/min

a. Determine the order of the reaction with respect to ozone. Justify your answer with an explanation or a mathematical equation.

b. Use one set of data from the table to calculate the value and unit of *k*. *Hint:* What unit must *k* have in order for the rate to have the unit atm/min?

20. Consider the data below.

rate = $k[KI]^n$

[KI]	Initial Rate
0.10 M	8.4×10^{-6} M/s
0.30 M	7.6×10^{-5} M/s

a. Determine the order of the reaction with respect to potassium iodide. Justify your answer with an explanation or a mathematical equation.

b. Use one set of data from the table to calculate the value and unit of the rate constant *k*. *Hint:* The units of *k* in this question will not be the same units as the *k* in Question 19.

21. Consider the data below.

rate = $k[H_2O_2]^n$

$[H_2O_2]$	Initial Rate
0.20 M	382 M/s
0.56 M	382 M/s

a. Determine the order of the reaction with respect to hydrogen peroxide. Justify your answer with an explanation or a mathematical equation.

b. Use one set of data from the table to calculate the value and unit of the rate constant *k*.

Read This!

The rate of a reaction is obtained by determining the concentration of a reactant or product in the reaction over time. This could occur through spectrophotometry for colored solutions, pressure changes for gaseous components, temperature changes for highly endothermic or exothermic reactions or pH for acids or bases—just to name a few. When concentration data are graphed versus time the slope of the curve is the rate of the reaction at that moment. Because the rate may change as the concentrations of reactants change the initial rate is the most dependable data point to use when determining the order of a reaction.

Model 3 – Reaction with Two Reactants

	$[N_2]$	$[H_2]$	Initial Rate
Trial 1	4.3×10^{-3} M	2.2×10^{-4} M	9.60×10^{-6} M/s
Trial 2	4.3×10^{-3} M	4.4×10^{-4} M	9.60×10^{-6} M/s
Trial 3	8.6×10^{-3} M	4.4×10^{-4} M	1.92×10^{-5} M/s

22. What are the reactants of the process being studied in Model 3?

23. Consider the data in Model 3.

a. Compare the concentration of nitrogen in trials 1 and 2.

b. Compare the concentration of nitrogen in trials 1 and 3.

Read This!

When there are multiple reactants in a process, each reactant must be studied independently while the other reactant is held at constant concentration. This allows the experimenter to determine the effect of changing the concentration of a specific reactant on the initial rate.

24. Consider the data in Model 3.

    a. Which trials should be considered when determining the order of reaction with respect to nitrogen gas?

    b. Which trials should be considered when determining the order of reaction with respect to hydrogen gas?

25. Explain why no useful conclusion about the exponents of the rate law could be drawn by comparing the data in trials 1 and 3 of Model 3.

26. Determine the order of reaction with respect to nitrogen.

27. Determine the order of reaction with respect to hydrogen.

28. Write the full rate law for the process in Model 3.

29. Use data from Model 3 to determine the value and unit of the rate constant, k, in the rate law.

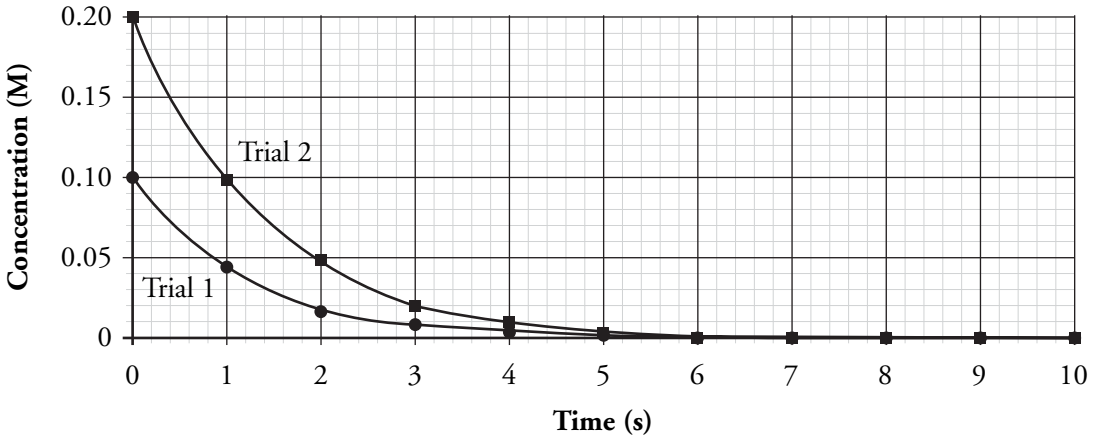
30. Use the data below to determine the rate law for the process shown. Include the value and units on the rate constant k in your answer.

$2NO(g) + O_2(g) \rightarrow NO_2(g)$

Experiment	**Initial [NO] (mole L^{-1})**	**Initial [O_2] (mole L^{-1})**	**Initial Rate of Formation of NO_2 (mole $L^{-1}s^{-1}$)**
1	0.10	0.10	2.5×10^{-4}
2	0.20	0.10	5.0×10^{-4}
3	0.20	0.40	8.0×10^{-3}

Extension Questions

32. Consider the graph below.



a. What were the initial concentrations of the reactant being studied in the two trials for this rate law experiment?

b. Estimate the initial rate for each trial using data from the graph.

c. Estimate the rate for each trial between 4 and 5 seconds into the reaction.

d. Why is the initial rate preferred to rates determined later in the process for determining the order of reaction with respect to a particular reactant?