

19. *Define the problem:* Given the rate law of a reaction, determine what happens to the rate when the concentration is changed.

*Develop a plan:* Knowing the rate law, the rate increase can be determined by creating a ratio to provide a simple relationship between the rate changes and the concentration changes.

*Execute the plan:* The rate law is:  $\text{rate} = k[A]^2$ . Make a ratio of the rate law of the reaction under two different conditions: the initial condition (designated by a subscript "1",  $\text{rate}_1 = k[A]_1^2$ ) compared to the final condition (designated by subscript "2",  $\text{rate}_2 = k[A]_2^2$ )

$$\text{rate change factor} = \frac{\text{rate}_2}{\text{rate}_1} = \frac{k[A]_2^2}{k[A]_1^2} = \left(\frac{[A]_2}{[A]_1}\right)^2$$

- (a) When the concentration is tripled, the concentration ratio is  $\frac{[A]_2}{[A]_1} = 3$ ,

so the rate change factor  $= 3^2 = 9$ . The rate increases by a factor of nine.

- (b) When the concentration is halved, the concentration ratio is  $\frac{[A]_2}{[A]_1} = \frac{1}{2}$ ,

so the rate change factor  $= \left(\frac{1}{2}\right)^2 = \frac{1}{4}$ . The rate will be one-fourth as fast.

*Check your answers:* It makes sense that the rate is faster when the concentration is larger and vice versa. It also makes sense that the rate change is larger than the concentration change, because the reaction is second-order.

### **Effect of Concentration on Reaction Rates**

20. *Define the problem:* Given the rate law of a reaction, determine what happens to the rate when the concentrations are changed.

*Develop a plan:* Knowing the rate law, the rate increase can be determined by creating a ratio to provide a simple relationship between the rate changes and the concentration changes.

*Execute the plan:* The rate law is:  $\text{rate} = k[A]^2[B]$ . Make a ratio of the rate law of the reaction under two different conditions: the initial condition (designated by a subscript "1",  $\text{rate}_1 = k[A]_1^2[B]_1$ ) compared to the final condition (designated by subscript "2",  $\text{rate}_2 = k[A]_2^2[B]_2$ )

$$\text{rate change factor} = \frac{\text{rate}_2}{\text{rate}_1} = \frac{k[A]_2^2[B]_2}{k[A]_1^2[B]_1} = \left(\frac{[A]_2}{[A]_1}\right)^2 \times \left(\frac{[B]_2}{[B]_1}\right)$$

When the concentration of A is doubled, the concentration ratio is  $\frac{[A]_2}{[A]_1} = 2$ .

When the concentration of B is halved, the concentration ratio is  $\frac{[B]_2}{[B]_1} = \frac{1}{2}$ ,

so the rate change factor  $= 2^2\left(\frac{1}{2}\right) = 2$ . The rate increases by a factor of two.

*Check your answer:* The affect of doubling [A] on the rate is greater than the affect of halving [B]. The [B] decrease slows down the reaction, but not as much as the doubling of [A] speeds it up, since the reaction is second-order in A and only first-order in B. The net result is a modest increase in the rate of the reaction. This answer makes sense.

21. Use the methods described in the answer to **Question 19**.

- (a) The reaction is second-order in NO<sub>2</sub> and zeroth-order in CO, so the rate law has powers of 2 and zero on the concentrations of NO<sub>2</sub> and CO, respectively.

$$\text{rate} = k[\text{NO}_2]^2[\text{CO}]^0$$

Because any number raised to the zero power results in 1, that says the rate is unaffected by the concentration of CO.

$$\text{rate} = k[\text{NO}_2]^2$$

- (b) A ratio gives the rate change factor:

$$\text{rate change factor} = \frac{\text{rate}_2}{\text{rate}_1} = \frac{k[\text{NO}_2]_2^2}{k[\text{NO}_2]_1^2} = \left( \frac{[\text{NO}_2]_2}{[\text{NO}_2]_1} \right)^2$$

When the concentration of NO<sub>2</sub> is halved, the concentration ratio is  $\frac{[\text{NO}_2]_2}{[\text{NO}_2]_1} = \frac{1}{2}$ ,

so the rate change factor =  $\left(\frac{1}{2}\right)^2 = \frac{1}{4}$ . The rate will be one fourth as fast.

- (c) Because the rate law does not include concentration dependence for CO, the rate will be unchanged when the CO concentration is doubled.

24. *Define the problem:* Given the rate law of a reaction, the value of the rate constant, and initial concentrations, determine the initial rate of disappearance of the reactant and the appearance of one product at those concentrations.

*Develop a plan:* Plug the concentrations and the rate constant into the rate law.

*Execute the plan:*  $\text{rate} = k[\text{CH}_3\text{COOCH}_3][\text{OH}^-]$

- (a) Initial rate =  $(0.14 \text{ L mol}^{-1}\text{s}^{-1}) \times (0.025 \text{ M}) \times (0.025 \text{ M}) = 8.8 \times 10^{-5} \text{ M/s}$

- (b) The stoichiometric relationship between the reactant CH<sub>3</sub>COOCH<sub>3</sub> and the product CH<sub>3</sub>OH is 1:1, so the rate of appearance of CH<sub>3</sub>OH is the same as the rate of disappearance of CH<sub>3</sub>COOCH<sub>3</sub> =  $8.8 \times 10^{-5} \text{ M/s}$

*Check your answers:* The small concentration and the small rate constant make the initial rate quite small. These answers make sense.

26. *Define the problem:* Given the initial concentrations and initial rates of a reaction for several different experimental conditions for the same chemical reaction, determine the rate law and the rate constant for the reaction.

*Develop a plan:* In Section 13.2, the method of finding the rate law from initial rates is described for getting the orders. However, comparing pairs of experiments where only one of the concentrations is different and relating that to the changes in the rate does not give consistent results. So, here we will derive a linear equation relating the concentrations and the rates and graph the results. Once the orders are determined, plug the data into the rate law to determine the value of k.

*Execute the plan:* Because I and II are reactants and are both varied in the different experiments we will seek a rate law looks like this:  $\text{rate} = k[\text{I}]^i[\text{II}]^j$  where k, i, and j are currently unknown.

(a) Comparing experiments with [I] constant, the rate law can be simplified to:

$$\text{rate} = k'[\text{II}]^j \quad \text{where } k' = k[\text{I}]^i$$

If we take the log of both sides of the equation, we can derive a linear relationship:

$$\log(\text{rate}) = \log(k') + \log([\text{II}]^j)$$

$$\log(\text{rate}) = \log(k') + j \log[\text{II}]$$

$$\log(\text{rate}) = j \log[\text{II}] + \log(k')$$

Comparing to the equation of a line:  $y = mx + b$ , we see that if we plot  $\log(\text{rate})$  against  $\log[\text{II}]$ , the slope of the line will be the reaction order,  $j$ .

Similarly comparing experiments with [II] constant, the rate law can be simplified to:

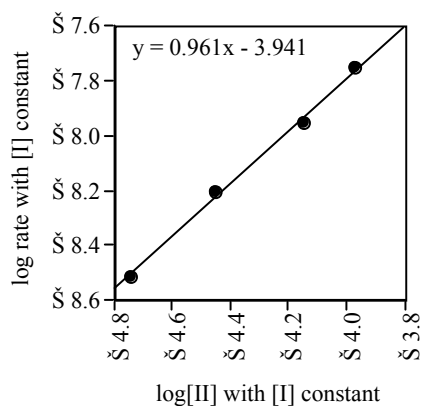
$$\text{rate} = k''[\text{I}]^i \quad \text{where } k'' = k[\text{II}]^j$$

This gives a similar linear relationship:  $\log(\text{rate}) = i \log[\text{I}] + \log(k'')$

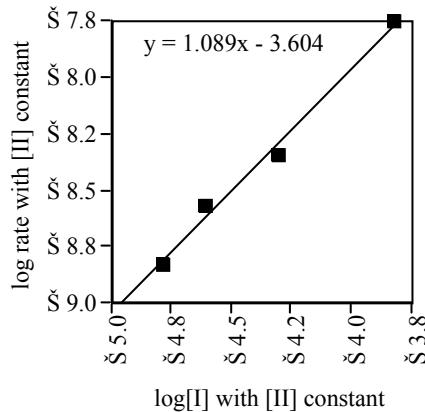
Comparing to the equation of a line:  $y = mx + b$ , we see that if we plot  $\log(\text{rate})$  against  $\log[\text{I}]$ , the slope of the line will be the reaction order,  $i$ .

Four data sets have constant [I] and four data sets have constant [II].

<b>log[II]</b> with constant [I]	<b>log rate</b> with constant [I]	<b>log[I]</b> with constant [II]	<b>log rate</b> with constant [II]
-4.745	-8.509	-4.783	-8.824
-4.453	-8.201	-4.606	-8.569
-4.149	-7.951	-4.304	-8.345
-3.975	-7.752	-3.827	-7.752



So, the reaction order of reactant II ( $j$ ) is one.



So, the reaction order of reactant I (i) is also one. So, rate =  $k[I][II]$

(b) Solve the rate law for k: 
$$k = \frac{\text{rate}}{[I][II]}$$

Plug in each experiment's data. Here is an example of the first experiment's calculation:

$$k_1 = \frac{1.50 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}}{(1.65 \times 10^{-5} \text{ mol/L})(10.6 \times 10^{-5} \text{ mol/L})} = 0.858 \text{ L mol}^{-1} \text{ s}^{-1}$$

$[I] \times 10^5$ (mol/L)	$[II] \times 10^5$ (mol/L)	Initial rate $\times 10^9$ (mol L <sup>-1</sup> s <sup>-1</sup> )	Rate constant (L mol <sup>-1</sup> s <sup>-1</sup> )
1.65	10.6	1.50	0.858
14.9	10.6	17.7	1.12
14.9	7.10	11.2	1.06
14.9	3.52	6.30	1.20
14.9	1.76	3.10	1.18
4.97	10.6	4.52	0.858
2.48	10.6	2.70	1.03

The average of these seven rate constants is  $1.04 \text{ L mol}^{-1} \text{ s}^{-1}$

*Check your answers:* The variations in the values of k and the deviation of the slopes from the exact integer values expected for the orders make these results unsatisfying. In addition, we can try to get the value of k from the y-intercepts of the graphs:

First Graph:  $b = \log(k^i) = \log(k[I]^i)$

$$k = \frac{10^b}{[I]^i} = \frac{10^{-3.941}}{(14.9 \times 10^{-5})^1} = 0.769 \text{ L mol}^{-1} \text{ s}^{-1}$$

Second Graph:  $b = \log(k^j) = \log(k[II]^j)$

$$k = \frac{10^b}{[II]^j} = \frac{10^{-3.604}}{(10.6 \times 10^{-5})^1} = 2.35 \text{ L mol}^{-1} \text{ s}^{-1}$$

These are not very close to each other either. These wide variations might suggest a systematic error in the collection of the data under various conditions.

28. *Define the problem:* Given the initial concentrations and initial rates of a reaction for several different experimental conditions for the same chemical reaction, determine the reaction orders, the rate law, the rate constant and the relative rates of the reaction given specific rate.

*Develop a plan:* In Section 3.2, the method of finding the rate law from initial rates is described for getting the orders. Then compare pairs of experiments where only one of the concentrations is different and relate that to the changes in the rate. Once the orders are determined, plug the data into the rate law to determine the value of k. Use stoichiometric relationships between reactants and products, as described in Section 3.1, to relate the rates of reactants and products.

*Execute the plan:* The reactants are A and B. Data are available for the changes in each of these reactants' concentrations, so the rate law looks like this:

$$\text{rate} = k[\text{A}]^i[\text{B}]^j \quad \text{where } k, i \text{ and } j \text{ are currently unknown.}$$

- (a) Looking at Experiments 1 and 2, the initial concentration of B doubles, the initial concentration of A stays constant, and the initial rate changes by a factor of two. The rate change is the same as the concentration change, which suggests that the rate is proportional to the concentration of B, and the order with respect to B is one.
- (b) Looking at Experiments 3 and 4, the initial concentration of A doubles, the initial concentration of B stays constant, and the initial rate changes by a factor of four. The rate change is the square of the concentration change, which suggests that the rate is proportional to the square of the concentration of A, and the order with respect to A is two.
- (c) The overall order is the sum of each reactant order. Here, the reaction is third-order.
- (d) The rate law now looks like this:  $\text{rate} = k[\text{A}]^2[\text{B}]^1$

(e) Solve the rate law for k: 
$$k = \frac{\text{rate}}{[\text{A}]^2[\text{B}]}$$

Plug in each experiment's data. Here is an example of the calculation for Experiment 1:

$$k_1 = \frac{0.012 \text{ mol L}^{-1}\text{s}^{-1}}{(6.0 \times 10^{-3} \text{ mol/L})^2 (1.0 \times 10^{-3} \text{ mol/L})} = 3.3 \times 10^5 \text{ L}^2 \text{ mol}^{-2}\text{s}^{-1}$$

[A] (mol/L)	[B] (mol/L)	Initial rate (mol L <sup>-1</sup> s <sup>-1</sup> )	Rate constant (L <sup>2</sup> mol <sup>-2</sup> s <sup>-1</sup> )
6.0 × 10 <sup>-3</sup>	1.0 × 10 <sup>-3</sup>	0.012	3.3 × 10 <sup>5</sup>
6.0 × 10 <sup>-3</sup>	2.0 × 10 <sup>-3</sup>	0.024	3.3 × 10 <sup>5</sup>
2.0 × 10 <sup>-3</sup>	1.5 × 10 <sup>-3</sup>	0.0020	3.3 × 10 <sup>5</sup>
4.0 × 10 <sup>-3</sup>	1.5 × 10 <sup>-3</sup>	0.0080	3.3 × 10 <sup>5</sup>

The average of these four rate constants is  $3.3 \times 10^5 \text{ L}^2 \text{ mol}^{-2}\text{s}^{-1}$

- (f) The relative rates depend on the stoichiometric coefficients (Equation 13.3). Here, the stoichiometric relationship is 2A : 1C : 3D

$$-\frac{1}{2} \left( \frac{\Delta[\text{A}]}{\Delta t} \right) = \frac{1}{1} \left( \frac{\Delta[\text{C}]}{\Delta t} \right) = \frac{1}{3} \left( \frac{\Delta[\text{D}]}{\Delta t} \right)$$

$$\frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{2} \left( -\frac{\Delta[\text{A}]}{\Delta t} \right) = \frac{1}{2} (0.034 \text{ mol L}^{-1}\text{s}^{-1}) = 0.017 \text{ mol L}^{-1}\text{s}^{-1}$$

$$\frac{\Delta[\text{D}]}{\Delta t} = \frac{3}{2} \left( -\frac{\Delta[\text{A}]}{\Delta t} \right) = \frac{3}{2} (0.034 \text{ mol L}^{-1}\text{s}^{-1}) = 0.051 \text{ mol L}^{-1}\text{s}^{-1}$$

*Check your answers:* The fact that every experiment gives the same rate constant makes it clear that the rate law determined properly describes the experimental data.