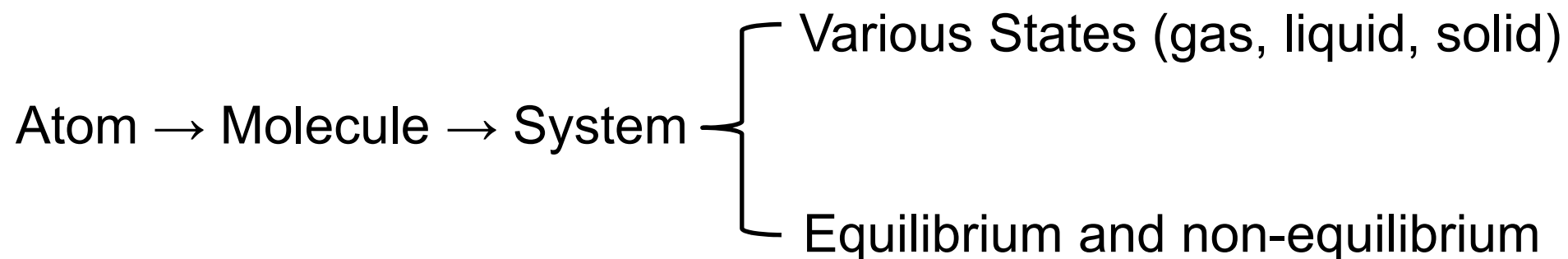
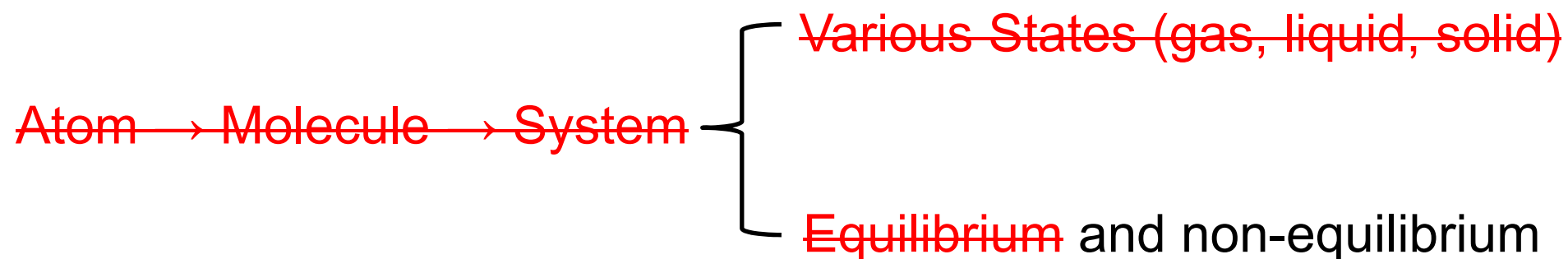


Bottom-up Approach of Understanding Chemical Principles



Bottom-up Approach of Understanding Chemical Principles



Focus 7

Kinetics

Thermodynamics versus Kinetics

Thermodynamics tells us **which way** a chemical reaction will go.

Kinetics tells us **how fast** a chemical reaction will go, as well as **how to control** the rate.



Figure 7A.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
Sergei Butorin/Shutterstock



Figure 7A.2
Atkins, *Chemical Principles: The Quest for Insight*, 7e
Emory Kristof/National Geographic Creative

Reactions proceed at different rates.

Reaction Rates, Deriving the Laws

Chemical rates are **changes in concentration** over a **time interval**.

Rates can be either an (1) **average** or (2) **instantaneous**.

The advantage of an (1) **average** rate is they are *easy to calculate*. The disadvantage is they tend to be very general and *not exact*.

The advantage of an (2) **instantaneous** rate is it gives very specific *exact information*. The disadvantage is the time it takes to *set up and make the calculation*.

Average Reaction Rates

Average rates change in molar concentration of **reactants**, **R**.

$\Delta[R] = [R]_{t_2} - [R]_{t_1}$ divided by the time interval $\Delta t = t_2 - t_1$

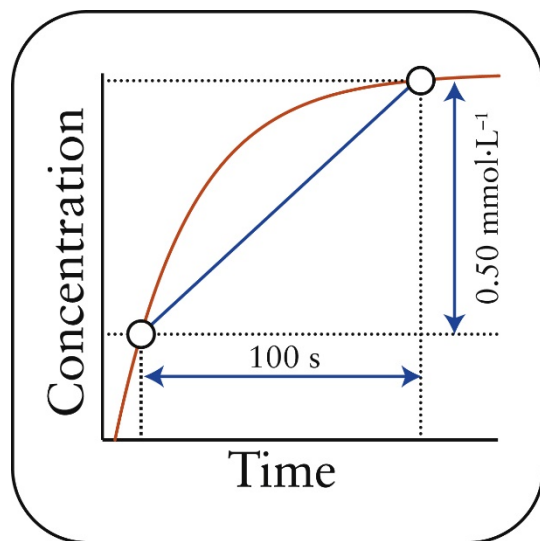
Average rate of **consumption** of **R** = $-\frac{\Delta[R]}{\Delta t}$

Note on the “-” meaning reactants disappear.

For **products P** = $\frac{\Delta[P]}{\Delta t}$

Remember that [] stands for concentration or mol·L⁻¹.

Example 7A.1 Suppose we are studying the reaction
 $2 \text{HI(g)} \rightarrow \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$ and find that, in an interval of 100. s, the
 concentration of HI decreases from $4.00 \text{ mmol}\cdot\text{L}^{-1}$ to $3.50 \text{ mmol}\cdot\text{L}^{-1}$.
 What is the average consumption rate of HI?



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Since we are watching reactants “go away,” we expect to see a negative slope.

$$\mathbf{R} = - \frac{\Delta[\mathbf{R}]}{\Delta t} = - \frac{[\mathbf{R}]_{t_2} - [\mathbf{R}]_{t_1}}{t_2 - t_1}, - \frac{(3.50 - 4.00) \text{ mmol}\cdot\text{L}^{-1}}{100. \text{ s}}$$

$$= 5.0 \times 10^{-3} \text{ mmol HI}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$$

We just calculated the blue line.

Note, $10^{-3} \text{ mmol} = \mu\text{mol}$, so in this example $-5.0 \times 10^{-3} \text{ mmol HI}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$
 $= -5.0 \mu\text{mol HI}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$

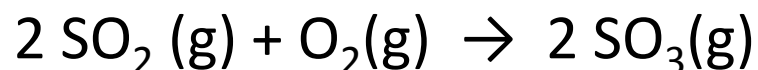
Unique Average Rate Based on Stoichiometry

To **avoid confusion** when reporting rates of a reaction, rates are always reported as the relationship of the *stoichiometric coefficients*. Thus, the rate is the same for the reaction, no matter for which species the rate is reported. For example,



$$R = -\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t}$$

Given the following balanced equation, determine the rate of reaction with respect to $[\text{SO}_2]$.



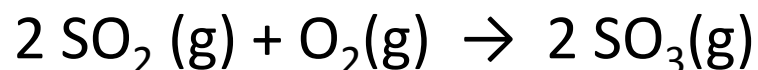
A. $\text{Rate} = - \frac{\Delta[\text{SO}_2]}{2\Delta t}$

B. $\text{Rate} = + \frac{\Delta[\text{SO}_2]}{2\Delta t}$

C. $\text{Rate} = - \frac{\Delta[\text{SO}_2]}{\Delta t}$

D. $\text{Rate} = + \frac{2\Delta[\text{SO}_2]}{\Delta t}$

Given the following balanced equation, determine the rate of reaction with respect to $[\text{SO}_2]$.



A. $\text{Rate} = - \frac{\Delta[\text{SO}_2]}{2\Delta t}$

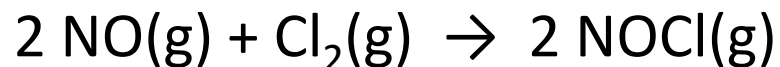
B. $\text{Rate} = + \frac{\Delta[\text{SO}_2]}{2\Delta t}$

C. $\text{Rate} = - \frac{\Delta[\text{SO}_2]}{\Delta t}$

D. $\text{Rate} = + \frac{2\Delta[\text{SO}_2]}{\Delta t}$

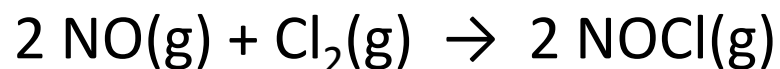
Clicker Answer: 1 of 10

Given the following balanced equation, if the rate of Cl_2 loss is $4.5 \times 10^{-2} \text{ M/s}$, then what is the rate of formation of NOCl ?



- A. $4.5 \times 10^{-2} \text{ M/s}$
- B. $2.25 \times 10^{-2} \text{ M/s}$
- C. $9.0 \times 10^{-2} \text{ M/s}$
- D. $4.5 \times 10^{-1} \text{ M/s}$

Given the following balanced equation, if the rate of Cl_2 loss is $4.5 \times 10^{-2} \text{ M/s}$, then what is the rate of formation of NOCl ?



- A. $4.5 \times 10^{-2} \text{ M/s}$
- B. $2.25 \times 10^{-2} \text{ M/s}$
- C. $9.0 \times 10^{-2} \text{ M/s}$
- D. $4.5 \times 10^{-1} \text{ M/s}$

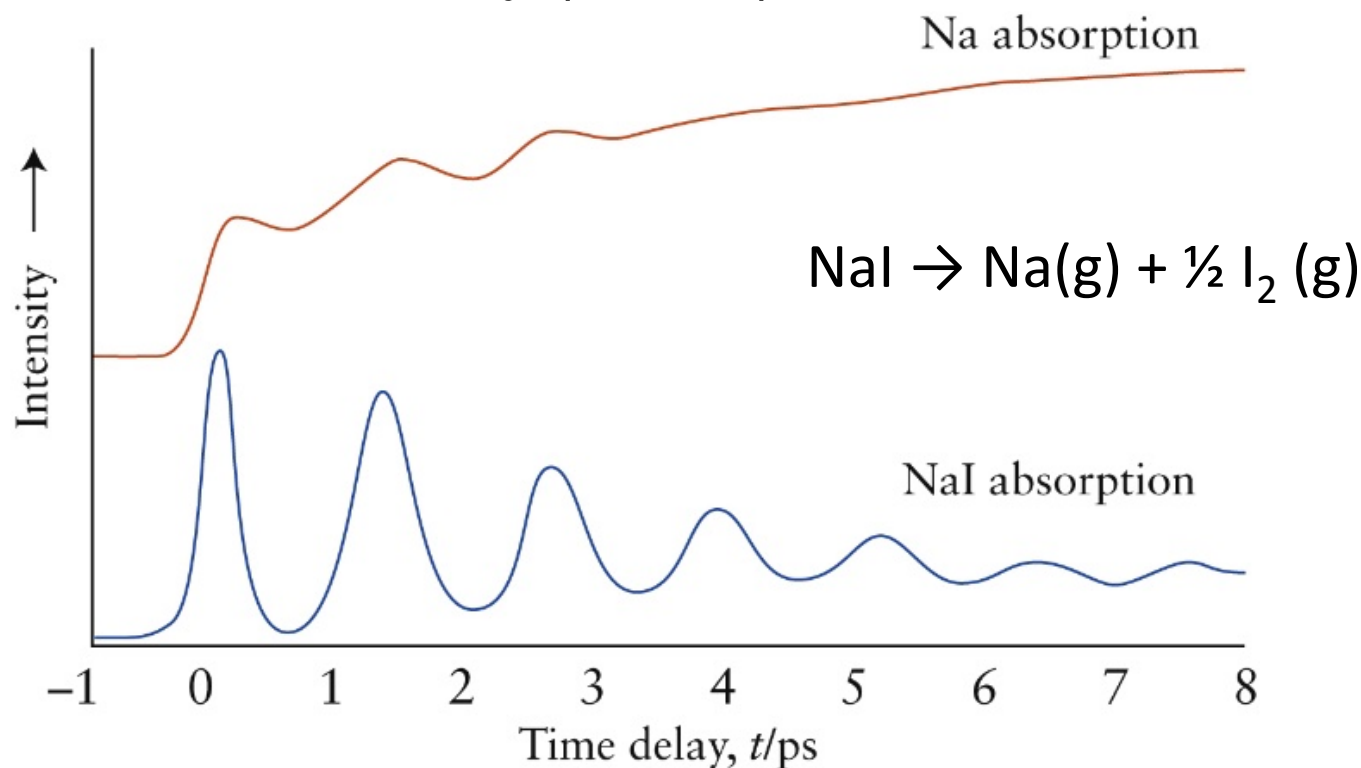
What happens to atoms during a reaction?

The time scale it takes for an atom to react is approximately 1 femtosecond ($1 \text{ fs} = 10^{-15} \text{ s}$). This is the time it takes for a bond to stretch, bend, and/or break.

Chemistry experiments now use lasers to analyze the structure of molecules. Femtosecond pulses of radiation are sent from a laser to the sample.

What happens to atoms during a reaction?

Femtochemistry (10^{-15} s)



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The laser's frequency is faster than the bond stretching of Na and I.

Instantaneous Rate of Reaction

Reactions slow down as reactants are used up.

An “instant” rate is found by measuring two concentrations, *as close together in time* as possible.

A better method is to find the **slope of the tangent** that provides the *instantaneous rate*.

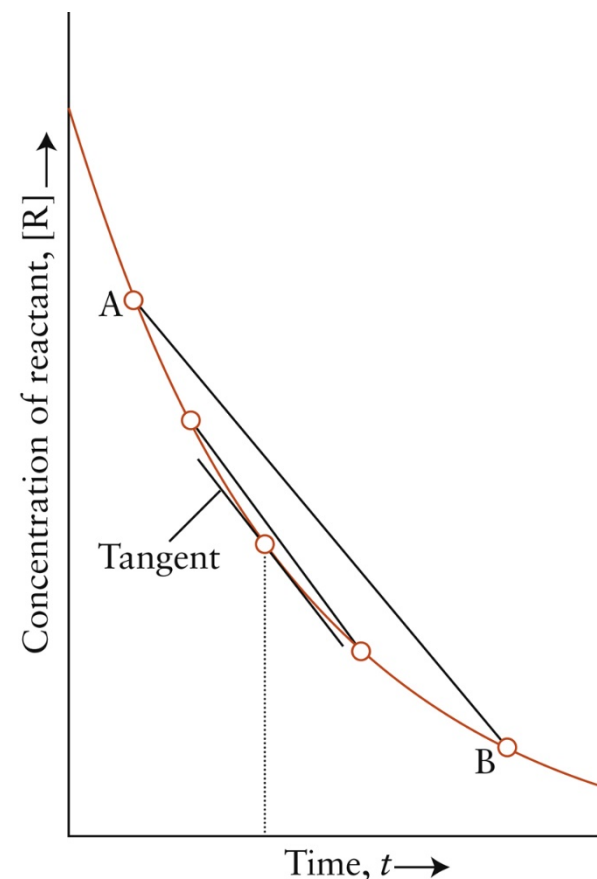


Figure 7A.4
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Instantaneous Rate of Reaction: Computers

Though a computer can calculate tangent lines, we need to devise methods to **determine the equations for these lines**, which are called **rate laws**.

Rate of penicillin deterioration

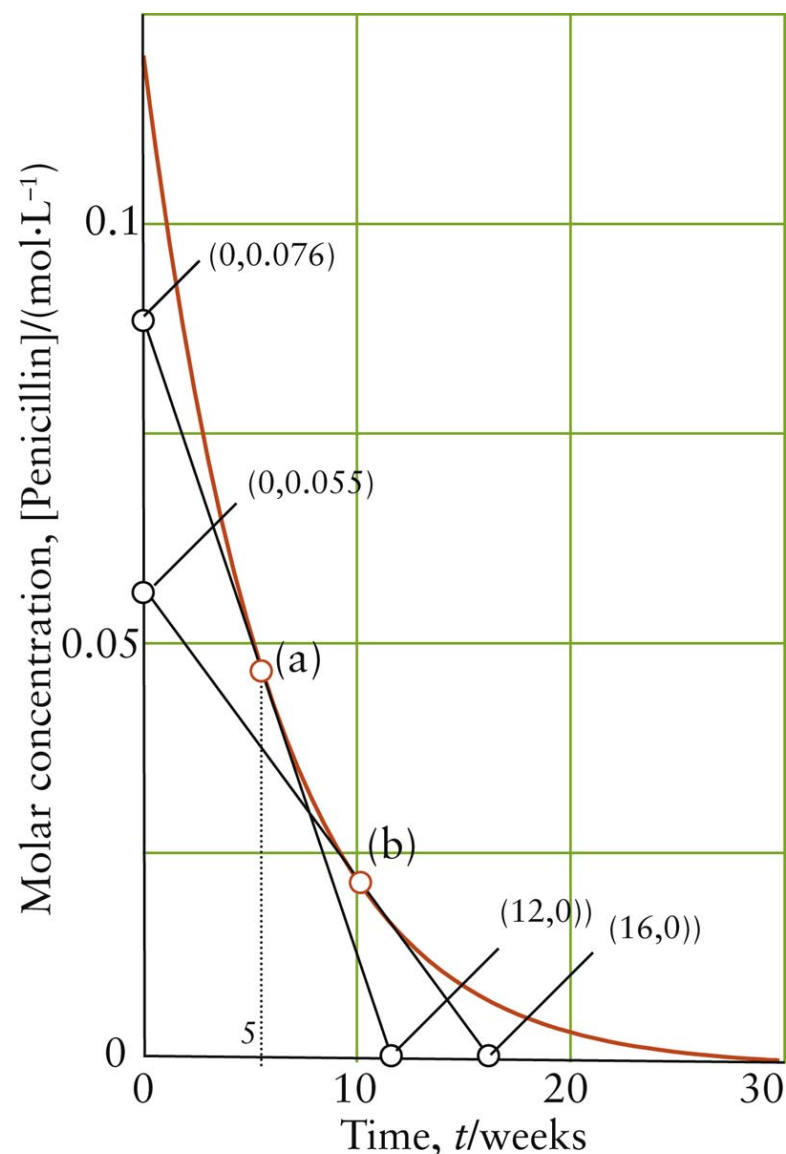


Figure 7A.5
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The Order of a Rate Law

There are two parts to every rate law: (1) how fast the line changes or speed (initial rate); and (2) the shape of the line called the rate law.

We will start by showing a typical experiment to find part 1, the speed.

To avoid complications, arising from products interfering with our measurements, observations are made in just the first few seconds of the beginning of the reaction.

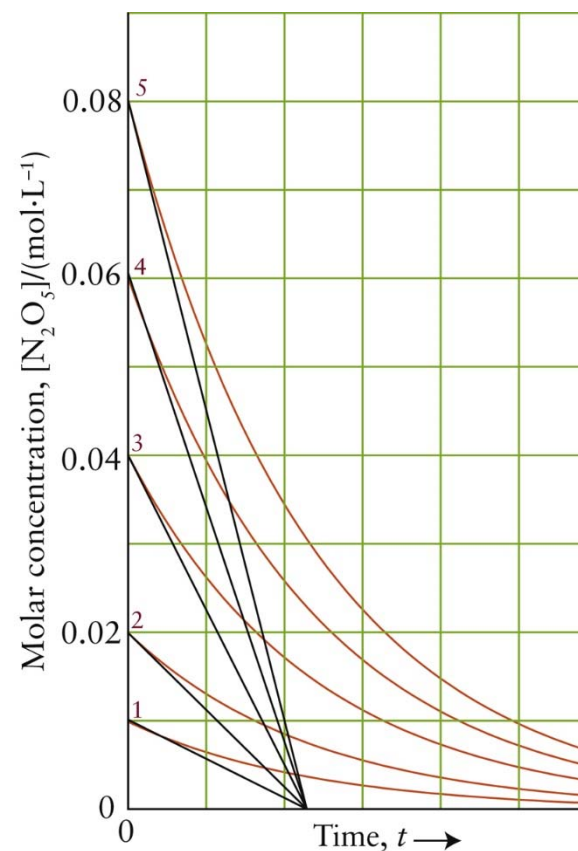


Figure 7A.6
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The Order of a Rate Law

Five separate reactions with different concentrations are plotted.



After the first few seconds we look to see how much of the **reactant** has converted to products.

Next, we plot $\frac{\text{initial rate}}{\text{concentration}}$.

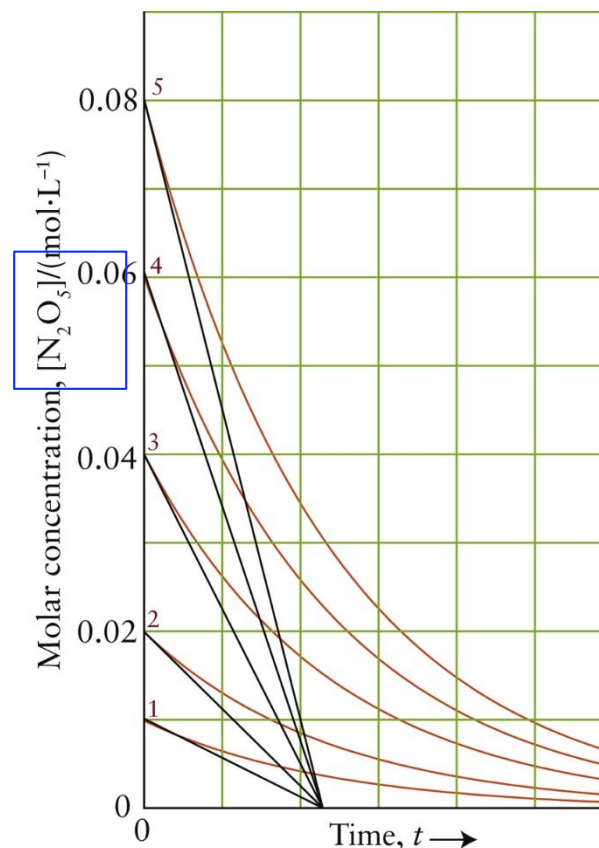


Figure 7A.6
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The Order of a Rate Law

Plotting $\frac{\text{initial rate}}{\text{concentration}}$ we get a straight line.

“m” is the rate constant for this reaction and is proportional to concentration at this temperature.

The slope of the line, k , is the speed (rate of change). Here it is $5.2 \times 10^{-3} \text{ s}^{-1}$.

$\text{rate} = k[\text{N}_2\text{O}_5]$ is called a rate law.

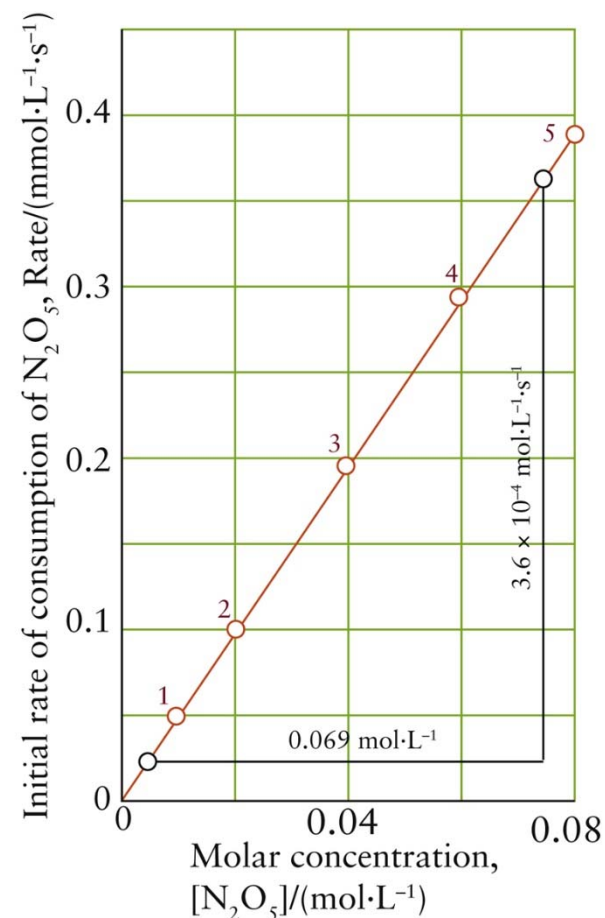


Figure 7A.7
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The Order of a Rate Law

Here is **a different** reaction: $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$.

However, when plotting our experimental data we **do not get a straight line**.

Therefore, we need to re-plot our data differently.

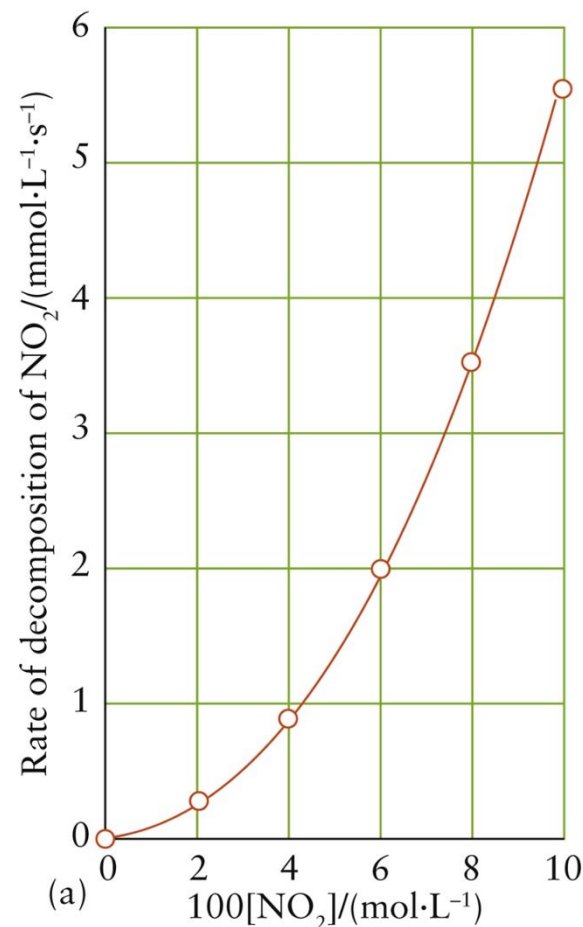


Figure 7A.8a
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The Order of a Rate Law

We re-plot $\frac{\text{initial rate}}{[\text{NO}_2]^2} = k$. Now, we do get straight line.

The rate law is now

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

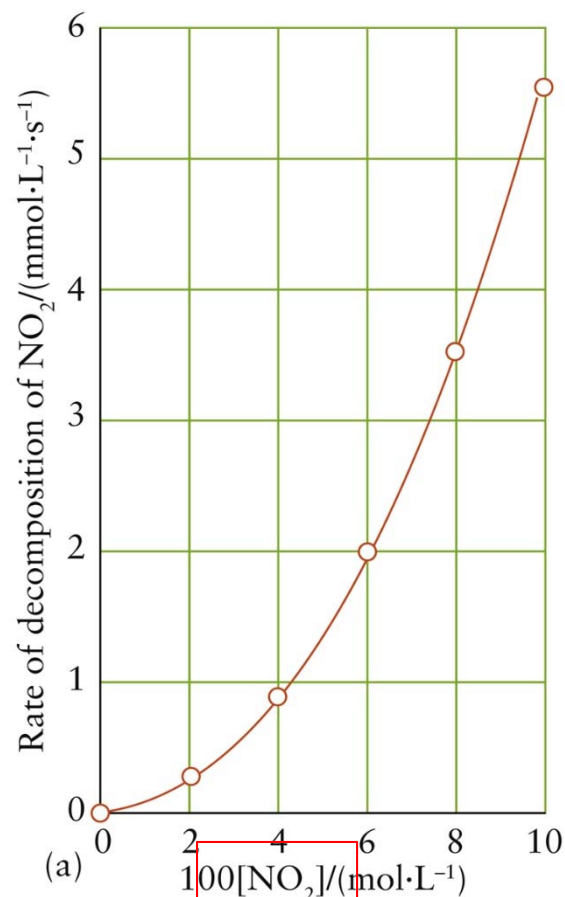


Figure 7A.8a
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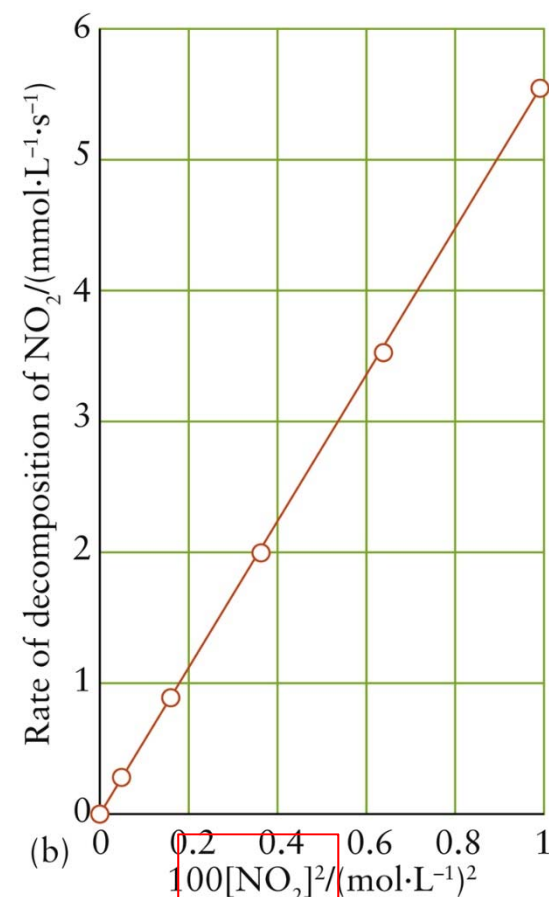
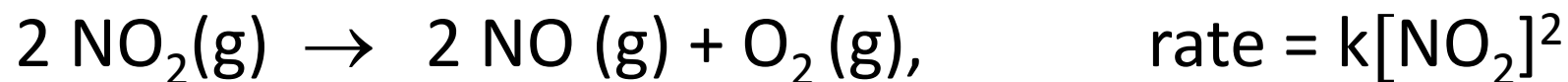
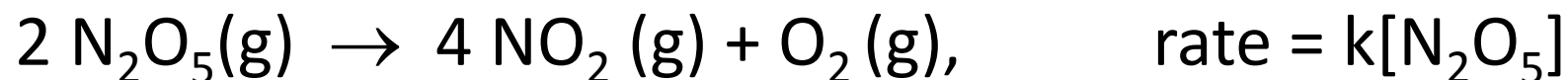


Figure 7A.8b
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The order of a rate law

We have two different rate laws for two different reactions.



In the first reaction, the rate changes directly to changes in reactant concentrations.

The second reaction, the rate changes by a factor of 2, or $2^2 = 4$.

The Order of a Rate Law

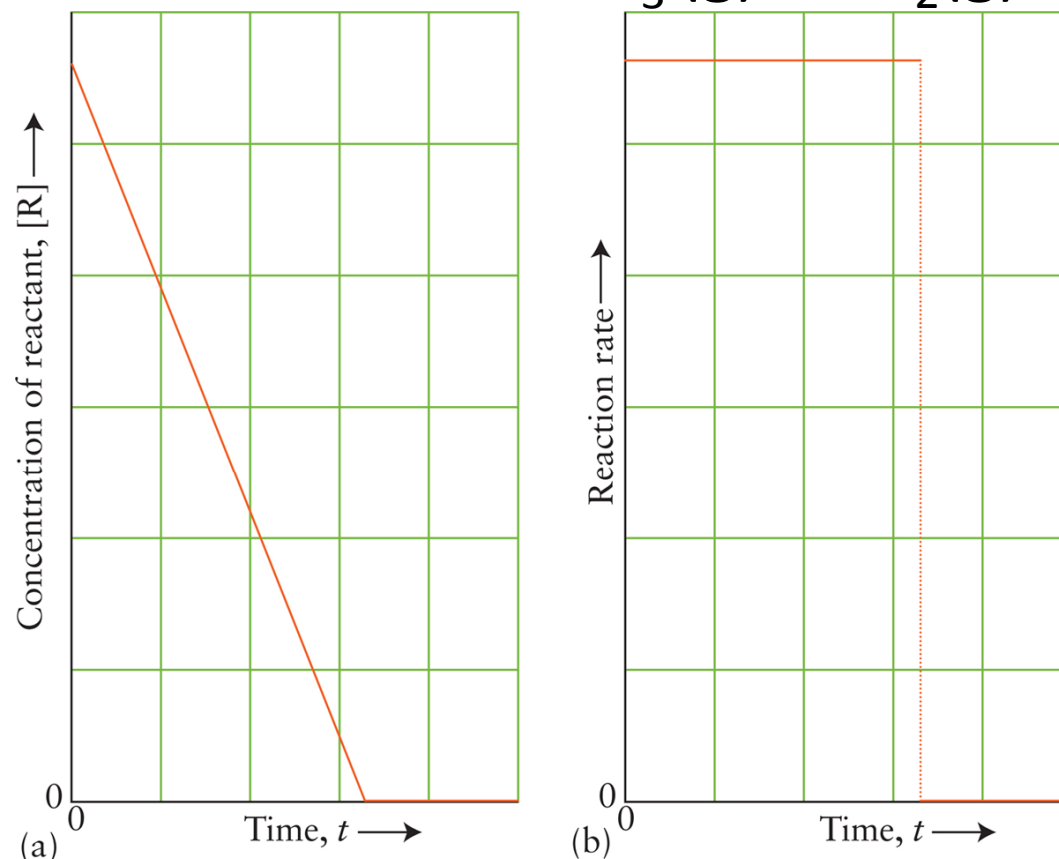
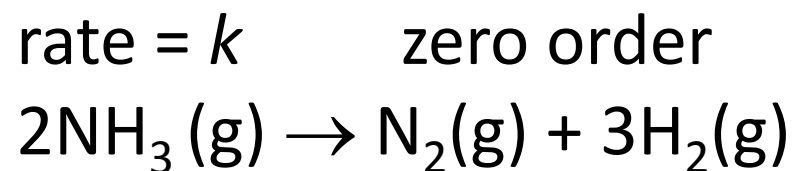


Figure 7A.9
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The concentration falls
at a constant rate until
reactants are exhausted.

Once exhausted, the rate
falls abruptly to zero.

The order of a rate law

Rate = constant \times [concentration]^a where **a** is called the **order**

rate = k	zero order
rate = k[N ₂ O ₅]	first order
rate = k[NO ₂] ²	second order

Orders gives us important insight as to **how** the reaction works. The overall order is 2 for a second order, and 1 or 0 for first and zero order, respectively.

Most reactions are either first or second order.

In zero order cases, only a catalyts can control the rate.

The Order of a Rate Law

In general, if $\text{rate} = k [\text{A}]^a [\text{B}]^b$ then the **overall order** is the sum of the powers $a + b + \dots$

Reaction	Rate law	Temp (K)	Rate constant $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
$2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2$	$k[\text{N}_2\text{O}]$	1000	0.76 s^{-1}
$\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$	$k[\text{H}_2][\text{I}_2]$	500	4.3×10^{-7} $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
		600	4.4×10^{-4}
		700	6.3×10^{-2}
$\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2 \text{H}_2\text{O}$	$k[\text{H}_3\text{O}^+][\text{OH}^-]$	298	1.5×10^{11} $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$

Self-test 7A.3A When the NO concentration is doubled, the rate of the reaction $2 \text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{NO}_2\text{(g)}$ increases by a factor of 4. When both the O_2 and the NO concentrations are doubled, the rate increases by a factor of 8. What are (a) the reactant orders, (b) the overall order of the reaction, and (c) the units of k if the rate is expressed in moles per liter per second ?

(a) To find the order of a reaction, we need to find the powers in our rate expression. For a generic expression, we know

$$\text{Rate} = k [\text{A}]^a [\text{B}]^b$$

We know that by doubling the $[\text{NO}]$ and holding the $[\text{O}_2]$ constant, the rate increased by 4, or $4 = 2^a$, so $a = 2$ to make this true.

$$\underbrace{\quad\quad\quad}_{\text{rate}} = [\text{A}]^a$$

In a second experiment, doubling both the $[\text{NO}]$ and $[\text{O}_2]$ the rate goes up 8 times faster, which means $8_{\text{rate}} = 2^a \times 2^b$. Since we know $a = 2$, then $8 = 4 \times 2^b$, and thus $b = 1$ because $8 = 4 \times 2^1$.

Self-test 7A.3A When the NO concentration is doubled, the rate of the reaction $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$ increases by a factor of 4. When both the O_2 and the NO concentrations are doubled, the rate increases by a factor of 8. What are (a) the reactant orders, (b) the overall order of the reaction, and (c) the units of k if the rate is expressed in moles per liter per second ?

(b) Overall order for the rate $= k [\text{A}]^a [\text{B}]^b$ is $a + b$. Here, $a = 2$, $b = 1$, or $2 + 1 = 3$, or third order.

(c) We know that we must **keep the rate as Ms^{-1}** , so the units of k must change. So far we have rate $= k [\text{NO}]^2 [\text{O}_2]^1$ with units on the right as $k(\text{M})^2(\text{M})$. To keep the units on both sides of the equation the same, k must be $\text{M}^{-2}\text{s}^{-1}$ or $\text{mol}^{-2}\text{L}^2\text{s}^{-1}$ or $\frac{\text{L}^2}{\text{mol}^2\text{s}}$.

Self-test 7A.3B When the concentration of 2-bromo-2-methylpropane, $\text{C}_4\text{H}_9\text{Br}$, is doubled, the rate of the reaction $\text{C}_4\text{H}_9\text{Br}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{C}_4\text{H}_9\text{OH}(\text{aq}) + \text{Br}^-(\text{aq})$ increases by a factor of 2. When both the $\text{C}_4\text{H}_9\text{Br}$ and the OH^- concentrations are doubled, the rate increase is the same, a factor of 2. What are (a) the reactant orders, (b) the overall order of the reaction, and (c) the units of k if the rate is expressed in moles per liter per second ?

(a) $\text{Rate} = k [\text{A}]^a [\text{B}]^b$

We know that by doubling the $[\text{C}_4\text{H}_9\text{Br}]$ and holding the $[\text{OH}^-]$ constant, the rate increased by 2, or $2 = 2^a$. In this case we know $a = 1$.

In a second experiment, doubling both the $[\text{C}_4\text{H}_9\text{Br}]$ and $[\text{OH}^-]$ we ended up with the same rate, which means $2 = 2^a \times 2^b$. Since we know $a = 1$, then $2 = 2 \times 2^b$, and therefore $b = 0$, that is, $2 = 2 \times 2^0$.

7A.3B continued: When the concentration of 2-bromo-2-methylpropane, $\text{C}_4\text{H}_9\text{Br}$, is doubled, the rate of the reaction $\text{C}_4\text{H}_9\text{Br}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{C}_4\text{H}_9\text{OH}(\text{aq}) + \text{Br}^-(\text{aq})$ increases by a factor of 2. When both the $\text{C}_4\text{H}_9\text{Br}$ and the OH^- concentrations are doubled, the rate increase is the same, a factor of 2. What are (a) the reactant orders, (b) the overall order of the reaction, and (c) the units of k if the rate is expressed in moles per liter per second ?

(b) The overall order for the rate $= k [\text{A}]^a [\text{B}]^b$ is $a + b$. Here, $a = 1$, $b = 0$, or $1 + 0 = 1$, or first order.

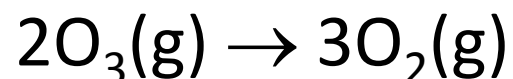
(c) We know that we must **keep rate as Ms^{-1}** , so the units of k must change. So far we have $\text{rate} = k [\text{C}_4\text{H}_9\text{Br}][\text{OH}^-]^0$ with units on the right as $k(\text{M})$. To keep the units on both sides of the equation the same, k must be s^{-1} or $\frac{1}{\text{s}}$.

Negative Orders

Orders can be negative: (concentration)⁻¹, $[A]^{-1} = \frac{1}{[A]}$.

This says that [A] *slows down* and *reverses* the reaction!

Decomposition of ozone is such an example.



The experimentally determined rate law is

$$\text{Rate} = k \frac{[\text{O}_3]^2}{[\text{O}_2]} = k[\text{O}_3]^2[\text{O}_2]^{-1}$$

Determining Orders and Rate Law from Experimental Data

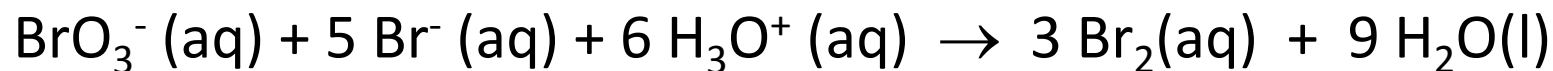
From this data, determine the (1) order, a and b; (2) rate constant, k ; and (3) the rate expression.

$$\text{Rate} = k [\text{A}]^a [\text{B}]^b$$

Rates are measured experimentally.

Exp.	Initial Conc. (mol·L ⁻¹)			Initial rate
	BrO ₃ ⁻	Br ⁻	H ₃ O ⁺	mmol BrO ₃ ⁻ · L ⁻¹ · s ⁻¹
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

Example 7A.2 Find (1) order, a and b; (2) rate constant, k ; and (3) the rate expression for the following reaction.



Exp.	Initial Conc. ($\text{mol}\cdot\text{L}^{-1}$)			Initial rate
	BrO_3^-	Br^-	H_3O^+	$\text{mmol BrO}_3^- \cdot \text{L}^{-1} \cdot \text{s}^{-1}$
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

In Self-test 15.3 A/B **we were told** how much the rate changed, and from that we found the order and rate expression.

So, in this problem **we need to find** that for ourselves. We are given enough information to find k .

The plan is to find a, b, c, and k from $\text{rate} = k[\text{BrO}_3^-]^a[\text{Br}^-]^b[\text{H}_3\text{O}^+]^c$.

Exp.	Initial Conc. (mol·L ⁻¹)			Initial rate
	BrO ₃ ⁻	Br ⁻	H ₃ O ⁺	mmol BrO ₃ ⁻ ·L ⁻¹ ·s ⁻¹
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

If we double [BrO₃⁻], how much does the rate increase?

Look at the difference between Experiment 1 and Experiment 2. The only thing changing is bromate. Bromide and hydronium are held constant. The change in rate and concentrations are

$$\frac{\text{rate Exp 2}}{\text{rate Exp 1}} = \frac{2.4}{1.2} = 2 \quad \text{and} \quad \frac{[\text{BrO}_3^-] \text{ Exp 2}}{[\text{BrO}_3^-] \text{ Exp 1}} = \frac{.20}{.10} = 2$$

(rate) 2 = 2^a, so in this case we know a = 1.

Exp.	Initial Conc. (mol·L ⁻¹)			Initial rate
	BrO ₃ ⁻	Br ⁻	H ₃ O ⁺	mmol BrO ₃ ⁻ · L ⁻¹ · s ⁻¹
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

Looking at Exp. 1 and 3, bromide triples. Bromate and hydronium are the same, while the rate increases by $3.5/1.2 = 2.9$. Thus, $2.9 = 3^b$, and so b is 1.

Looking at Exp. 2 and 4, hydronium increases by 1.5. Bromate and bromide are the same, while the rate increases by $5.5/2.4 = 2.29$. Thus, $2.29 = 1.5^c$, and so c is 2.

Note: For “ c ” we could have used $2.29 = 1.5^c$ or $c = \frac{\ln 2.29}{\ln 1.5} = 2$.

Our expression so far is $\text{rate} = k [\text{BrO}_3^-]^1 [\text{Br}^-]^1 [\text{H}_3\text{O}^+]^2$.

The overall order is $1 + 1 + 2 = 4$.

To find k , we turn to the table and choose any experiment and plug the data in to find k .

Experiment	Initial concentration ($\text{mol}\cdot\text{L}^{-1}$)			Initial rate ($(\text{mmol BrO}_3^-)\cdot\text{L}^{-1}\cdot\text{s}^{-1}$)
	BrO_3^-	Br^-	H_3O^+	
1	0.10	0.10	0.10	1.2

We can use the data from experiment 1, for instance.

$$1.2 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}\text{s}^{-1} = k [0.10 \text{ mol}\cdot\text{L}^{-1}]^1 [0.10 \text{ mol}\cdot\text{L}^{-1}]^1 [0.10 \text{ mol}\cdot\text{L}^{-1}]^2 ,$$

$$k = \frac{1.2 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}\text{s}^{-1}}{[0.10 \text{ mol}\cdot\text{L}^{-1}]^1 [0.10 \text{ mol}\cdot\text{L}^{-1}]^1 [0.10 \text{ mol}\cdot\text{L}^{-1}]^2} = 12 \frac{\text{L}^3}{\text{mol}^3\cdot\text{s}} = 12 \text{ mol}^{-3}\cdot\text{L}^3\cdot\text{s}^{-1}.$$

which we can use for our final rate expression: $\text{rate} = 12 \text{ mol}^{-3}\cdot\text{L}^3\cdot\text{s}^{-1} [\text{BrO}_3^-]^1 [\text{Br}^-]^1 [\text{H}_3\text{O}^+]^2$