



KINETICS

RATE LAWS FROM CONCENTRATIONS

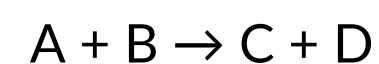
CHEMISTRY 165 // SPRING 2020

RATE LAWS

What do rate laws tell us?

A rate law gives us the quantitative relationship between the rate of a reaction and the concentration(s) of the reactant(s).

For example, for the general chemical reaction



the rate law can be expressed as

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

In the rate law:

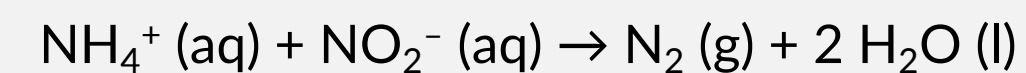
- k is the rate constant, which is constant for a specific chemical reaction under a specific temperature.
- $[A]$ and $[B]$ are the concentrations of the two reactants.
- a and b are the orders of the reaction with respect to either of the reactants. This value tells us *how much* the rate is affected by the reactant's concentration, where larger orders equate to greater effects.

Q: *Are the orders just the stoichiometric coefficients in the balanced equation?*

A: *No, you must determine the orders experimentally!*

GUIDED EXAMPLE

Consider the following chemical reaction:



Determine the rate law for this reaction given the following experimental data.

Expt.	$[\text{NH}_4^+]_0$ (M)	$[\text{NO}_2^-]_0$ (M)	Initial Rate (M/s)
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2	0.100	0.010	2.70×10^{-7}
3	0.200	0.010	5.40×10^{-7}

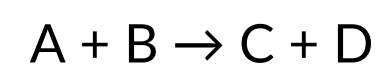
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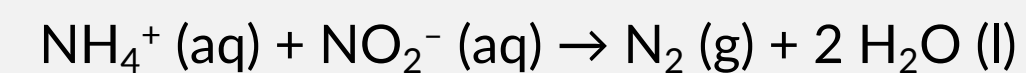
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Always begin by constructing the general rate law expression: $\text{Rate} = k[\text{NH}_4^+]^a[\text{NO}_2^-]^b$

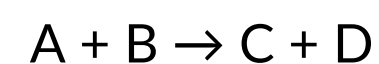
We use the “**isolation method**” to determine the order (a and b) of the reaction with respects to reactants A and B. The values of a and b tell us how sensitive the rate is to the concentrations of the reactants. **To do this, we compare two experiments in which only one reactant's concentration is changing while the other reactant's concentrations stays constant.**

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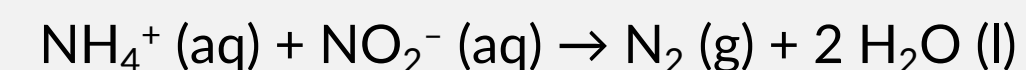
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In experiments 1 and 2, $[\text{NH}_4^+] = 0.100 \text{ M}$ for both experiments but $[\text{NO}_2^-]$ is different. Comparing the two experiments we find the value of $b = 1$.

Set up a ratio between the two experiments. I like to put the larger rate value on the top (in the numerator) so that I get integers instead of fractions. I use subscripts to indicate the experiment.

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[\text{NH}_4^+]_2^a[\text{NO}_2^-]_2^b}{k[\text{NH}_4^+]_1^a[\text{NO}_2^-]_1^b}$$

We can cancel out k and $[\text{NH}_4^+]^a$ since both are constants now!

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{NO}_2^-]_2^b}{[\text{NO}_2^-]_1^b}$$

We are left with an expression relating the rate and $[\text{NO}_2^-]^b$, which allows us to determine the order b .

$$\frac{2.70 \times 10^{-7} \text{ M/s}}{1.35 \times 10^{-7} \text{ M/s}} = \left(\frac{0.010 \text{ M}}{0.0050 \text{ M}} \right)^b$$
$$2 = 2^b$$

In the vast majority of examples, it is quite easy to determine the value of the order without math. But, the math is not bad either:

$$b = 1$$

$$2 = 2^b$$
$$\log(2) = \log(2^b)$$
$$\log(2) = b \cdot \log(2)$$
$$b = 1$$

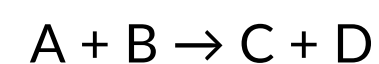
Some of you may find it straightforward to determine the order by inspection, which is fine. In such a case, you will still want to compare experiments 1 and 2. In experiments 1 and 2, $[\text{NO}_2^-]$ is doubled and the rate doubles as well. This indicates a first-order reaction because the concentration and rate are increasing by the same factor.

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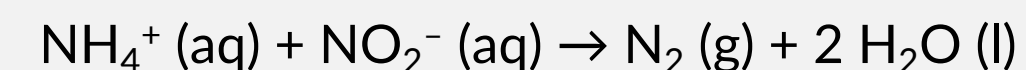
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In experiments 2 and 3, $[\text{NO}_2^-] = 0.010 \text{ M}$ for both experiments but $[\text{NH}_4^+]$ is different. Comparing the two experiments we find the value of $a = 1$.

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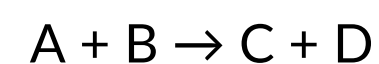
$$\begin{aligned} \frac{\text{Rate}_3}{\text{Rate}_2} &= \frac{k[\text{NH}_4^+]_3^a[\text{NO}_2^-]_3^b}{k[\text{NH}_4^+]_2^a[\text{NO}_2^-]_2^b} \\ \frac{\text{Rate}_3}{\text{Rate}_2} &= \frac{[\text{NH}_4^+]_3^a}{[\text{NH}_4^+]_2^a} \\ \frac{5.40 \times 10^{-7} \text{ M/s}}{2.70 \times 10^{-7} \text{ M/s}} &= \left(\frac{0.200 \text{ M}}{0.100 \text{ M}}\right)^a \\ 2 &= 2^a \\ a &= 1 \end{aligned}$$

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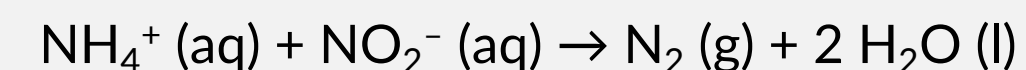
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In experiments 1 and 2, $[\text{NH}_4^+] = 0.100 \text{ M}$ for both experiments but $[\text{NO}_2^-]$ is different. Comparing the two experiments we find the value of $b = 1$.

In experiments 2 and 3, $[\text{NO}_2^-] = 0.010 \text{ M}$ for both experiments but $[\text{NH}_4^+]$ is different. Comparing the two experiments we find the value of $a = 1$.

And what about the rate constant, k ? We can just pick an experiment and plug in the associated concentrations and rate value into the rate law we just derived. I will pick experiment 1, though it does not matter which you pick, to determine that $k = 2.7 \times 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$.

$$\begin{aligned}\text{Rate}_1 &= k[\text{NH}_4^+]_1^1[\text{NO}_2^-]_1^1 \\ 1.35 \times 10^{-7} \frac{\text{M}}{\text{s}} &= k(0.100 \text{ M})^1(0.0050 \text{ M})^1 \\ k &= \frac{1.35 \times 10^{-7} \text{ M/s}}{(0.100 \text{ M})^1(0.0050 \text{ M})^1} \\ k &= 2.7 \times 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}\end{aligned}$$

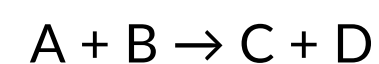
The units of k differ for different orders. If you use units in the calculation, then you don't have to memorize which units of k correspond to which orders.

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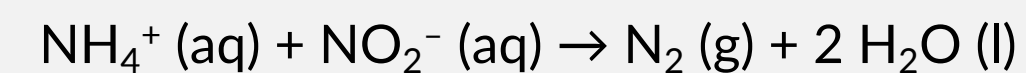
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In experiments 2 and 3, $[\text{NO}_2^-] = 0.010$ M for both experiments but $[\text{NH}_4^+]$ is different. Comparing the two experiments we find the value of $a = 1$.

And what about the rate constant, k ? We can just pick an experiment and plug in the associated concentrations and rate value into the rate law we just derived. I will pick experiment 1, though it does not matter which you pick, to determine that $k = 2.7 \times 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$.

So, the final rate law expression is:

$$\text{Rate} = k[\text{NH}_4^+]^1[\text{NO}_2^-]^1$$

$$k = 2.7 \times 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$$

We say this reaction is 2nd order overall, but 1st order in $[\text{NH}_4^+]$ and 1st order in $[\text{NO}_2^-]$.

PRACTICE PROBLEM 1

The following data were obtained for the reaction



Determine the rate law for this reaction and the value of the rate constant.

— *answer* —

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Compare experiments 1 and 2:

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Let's solve for b , which is the order of the reaction with respect to $[\text{OH}^-]$.

Compare experiments 2 and 3:

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This means that our rate law is:

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Let's solve for b , which is the order of the reaction with respect to $[\text{OH}^-]$.

Compare experiments 2 and 3:

$$\begin{aligned} \frac{\text{Rate}_2}{\text{Rate}_3} &= \frac{k[\text{ClO}_2]_2^a[\text{OH}^-]_2^b}{k[\text{ClO}_2]_3^a[\text{OH}^-]_3^b} \\ \frac{\text{Rate}_2}{\text{Rate}_3} &= \frac{[\text{OH}^-]_2^b}{[\text{OH}^-]_3^b} \\ \frac{2.30 \times 10^{-1} \text{ M/s}}{1.15 \times 10^{-1} \text{ M/s}} &= \left(\frac{0.100 \text{ M}}{0.0500 \text{ M}} \right)^b \\ 2 &= 2^b \\ b &= 1 \end{aligned}$$

PRACTICE PROBLEM 1

The following data were obtained for the reaction



Determine the rate law for this reaction and the value of the rate constant.

— answer —

Begin by constructing the generic rate law:

$$\text{Rate} = k[\text{ClO}_2]^a[\text{OH}^-]^b$$

Understand that we will need to solve for the orders a and b using the isolation method.

Let's solve for a , which is the order of the reaction with respect to $[\text{ClO}_2]$.

Compare experiments 1 and 2:

$$\begin{aligned} \frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{k[\text{ClO}_2]_2^a[\text{OH}^-]_2^b}{k[\text{ClO}_2]_1^a[\text{OH}^-]_1^b} \\ \frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{[\text{ClO}_2]_2^a}{[\text{ClO}_2]_1^a} \\ \frac{2.30 \times 10^{-1} \text{ M/s}}{5.75 \times 10^{-2} \text{ M/s}} &= \left(\frac{0.100 \text{ M}}{0.0500 \text{ M}} \right)^a \\ 4 &= 2^a \\ a &= 2 \end{aligned}$$

This means that our rate law is:

$$\text{Rate} = k[\text{ClO}_2]^2[\text{OH}^-]^1$$

Now that we have our rate law we can solve for the rate constant, k , by plugging in the values from a particular experiment. Again, I'll use experiment 1:

$$\begin{aligned} \text{Rate}_1 &= k[\text{ClO}_2]_1^2[\text{OH}^-]_1^1 \\ 5.75 \times 10^{-2} \frac{\text{M}}{\text{s}} &= k(0.0500 \text{ M})^2(0.100 \text{ M})^1 \\ k &= 230. \text{M}^{-2} \cdot \text{s}^{-1} \end{aligned}$$

Expt.	$[\text{ClO}_2]_0$ (M)	$[\text{OH}^-]_0$ (M)	Initial Rate (M/s)
1	0.0500	0.100	5.75×10^{-2}
2	0.100	0.100	2.30×10^{-1}
3	0.100	0.0500	1.15×10^{-1}

Let's solve for b , which is the order of the reaction with respect to $[\text{OH}^-]$.

Compare experiments 2 and 3:

$$\begin{aligned} \frac{\text{Rate}_2}{\text{Rate}_3} &= \frac{k[\text{ClO}_2]_2^a[\text{OH}^-]_2^b}{k[\text{ClO}_2]_3^a[\text{OH}^-]_3^b} \\ \frac{\text{Rate}_2}{\text{Rate}_3} &= \frac{[\text{OH}^-]_2^b}{[\text{OH}^-]_3^b} \\ \frac{2.30 \times 10^{-1} \text{ M/s}}{1.15 \times 10^{-1} \text{ M/s}} &= \left(\frac{0.100 \text{ M}}{0.0500 \text{ M}} \right)^b \\ 2 &= 2^b \\ b &= 1 \end{aligned}$$

PRACTICE PROBLEM 1

The following data were obtained for the reaction



Determine the rate law for this reaction and the value of the rate constant.

— answer —

Begin by constructing the generic rate law:

$$\text{Rate} = k[\text{ClO}_2]^a[\text{OH}^-]^b$$

Understand that we will need to solve for the orders a and b using the isolation method.

Let's solve for a , which is the order of the reaction with respect to $[\text{ClO}_2]$.

Compare experiments 1 and 2:

$$\begin{aligned} \frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{k[\text{ClO}_2]_2^a[\text{OH}^-]_2^b}{k[\text{ClO}_2]_1^a[\text{OH}^-]_1^b} \\ \frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{[\text{ClO}_2]_2^a}{[\text{ClO}_2]_1^a} \\ \frac{2.30 \times 10^{-1} \text{ M/s}}{5.75 \times 10^{-2} \text{ M/s}} &= \left(\frac{0.100 \text{ M}}{0.0500 \text{ M}} \right)^a \\ 4 &= 2^a \\ a &= 2 \end{aligned}$$

This means that our rate law is:

$$\text{Rate} = k[\text{ClO}_2]^2[\text{OH}^-]^1$$

Now that we have our rate law we can solve for the rate constant, k , by plugging in the values from a particular experiment. Again, I'll use experiment 1:

$$\begin{aligned} \text{Rate}_1 &= k[\text{ClO}_2]_1^2[\text{OH}^-]_1^1 \\ 5.75 \times 10^{-2} \frac{\text{M}}{\text{s}} &= k(0.0500 \text{ M})^2(0.100 \text{ M})^1 \\ k &= 230. \text{M}^{-2} \cdot \text{s}^{-1} \end{aligned}$$

Expt.	$[\text{ClO}_2]_0$ (M)	$[\text{OH}^-]_0$ (M)	Initial Rate (M/s)
1	0.0500	0.100	5.75×10^{-2}
2	0.100	0.100	2.30×10^{-1}
3	0.100	0.0500	1.15×10^{-1}

Let's solve for b , which is the order of the reaction with respect to $[\text{OH}^-]$.

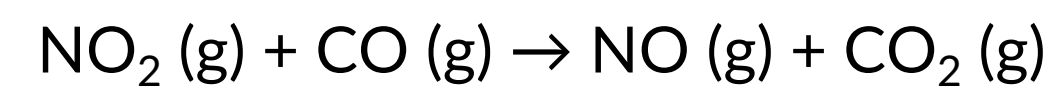
Compare experiments 2 and 3:

$$\begin{aligned} \frac{\text{Rate}_2}{\text{Rate}_3} &= \frac{k[\text{ClO}_2]_2^a[\text{OH}^-]_2^b}{k[\text{ClO}_2]_3^a[\text{OH}^-]_3^b} \\ \frac{\text{Rate}_2}{\text{Rate}_3} &= \frac{[\text{OH}^-]_2^b}{[\text{OH}^-]_3^b} \\ \frac{2.30 \times 10^{-1} \text{ M/s}}{1.15 \times 10^{-1} \text{ M/s}} &= \left(\frac{0.100 \text{ M}}{0.0500 \text{ M}} \right)^b \\ 2 &= 2^b \\ b &= 1 \end{aligned}$$

We say this reaction is 3rd order overall, but 2nd order with respect to $[\text{ClO}_2]$ and 1st order with respect to $[\text{OH}^-]$.

PRACTICE PROBLEM 2

The following data were obtained for the reaction



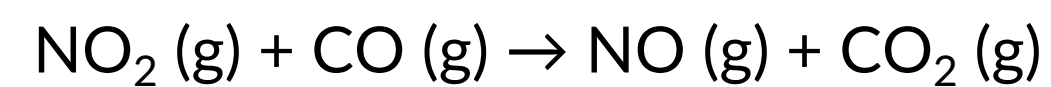
Determine the rate law for this reaction and the value of the rate constant.

— *answer* —

Expt.	$[\text{NO}_2]_0$ (M)	$[\text{CO}]_0$ (M)	Initial Rate (M/s)
1	0.263	0.826	1.44×10^{-5}
2	0.263	0.413	1.44×10^{-5}
3	0.526	0.413	5.76×10^{-5}

PRACTICE PROBLEM 2

The following data were obtained for the reaction



Determine the rate law for this reaction and the value of the rate constant.

— *answer* —

Begin by constructing the generic rate law:

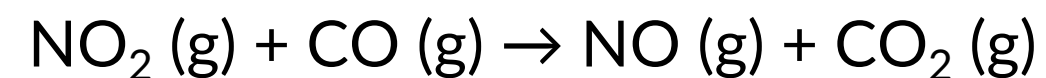
$$\text{Rate} = k[\text{NO}_2]^a[\text{CO}]^b$$

Understand that we will need to solve for the orders a and b using the isolation method.

Expt.	$[\text{NO}_2]_0$ (M)	$[\text{CO}]_0$ (M)	Initial Rate (M/s)
1	0.263	0.826	1.44×10^{-5}
2	0.263	0.413	1.44×10^{-5}
3	0.526	0.413	5.76×10^{-5}

PRACTICE PROBLEM 2

The following data were obtained for the reaction



Determine the rate law for this reaction and the value of the rate constant.

— *answer* —

Begin by constructing the generic rate law:

$$\text{Rate} = k[\text{NO}_2]^a[\text{CO}]^b$$

Understand that we will need to solve for the orders a and b using the isolation method.

Let's solve for a , which is the order of the reaction with respect to $[\text{NO}_2]$.

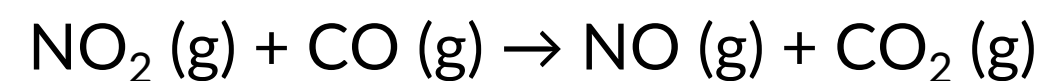
Compare experiments 2 and 3:

$$\begin{aligned}\frac{\text{Rate}_3}{\text{Rate}_2} &= \frac{\cancel{k}[\text{NO}_2]_3^a[\cancel{\text{CO}}]_3^b}{\cancel{k}[\text{NO}_2]_2^a[\cancel{\text{CO}}]_2^b} \\ \frac{\text{Rate}_3}{\text{Rate}_2} &= \frac{[\text{NO}_2]_3^a}{[\text{NO}_2]_2^a} \\ \frac{5.76 \times 10^{-5} \text{ M/s}}{1.44 \times 10^{-5} \text{ M/s}} &= \left(\frac{0.526 \text{ M}}{0.263 \text{ M}}\right)^a \\ 4 &= 2^a \\ a &= 2\end{aligned}$$

Expt.	$[\text{NO}_2]_0$ (M)	$[\text{CO}]_0$ (M)	Initial Rate (M/s)
1	0.263	0.826	1.44×10^{-5}
2	0.263	0.413	1.44×10^{-5}
3	0.526	0.413	5.76×10^{-5}

PRACTICE PROBLEM 2

The following data were obtained for the reaction



Determine the rate law for this reaction and the value of the rate constant.

— answer —

Begin by constructing the generic rate law:

$$\text{Rate} = k[\text{NO}_2]^a[\text{CO}]^b$$

Understand that we will need to solve for the orders a and b using the isolation method.

Let's solve for a , which is the order of the reaction with respect to $[\text{NO}_2]$.

Compare experiments 2 and 3:

$$\begin{aligned}\frac{\text{Rate}_3}{\text{Rate}_2} &= \frac{k[\text{NO}_2]_3^a[\text{CO}]_3^b}{k[\text{NO}_2]_2^a[\text{CO}]_2^b} \\ \frac{\text{Rate}_3}{\text{Rate}_2} &= \frac{[\text{NO}_2]_3^a}{[\text{NO}_2]_2^a} \\ \frac{5.76 \times 10^{-5} \text{ M/s}}{1.44 \times 10^{-5} \text{ M/s}} &= \left(\frac{0.526 \text{ M}}{0.263 \text{ M}}\right)^a \\ 4 &= 2^a \\ a &= 2\end{aligned}$$

Expt.	$[\text{NO}_2]_0$ (M)	$[\text{CO}]_0$ (M)	Initial Rate (M/s)
1	0.263	0.826	1.44×10^{-5}
2	0.263	0.413	1.44×10^{-5}
3	0.526	0.413	5.76×10^{-5}

Let's solve for b , which is the order of the reaction with respect to $[\text{CO}]$.

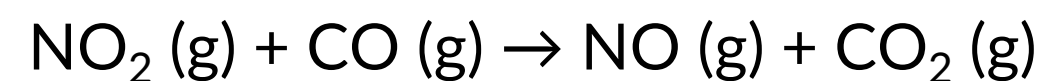
Compare experiments 1 and 2:

$$\begin{aligned}\frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{k[\text{NO}_2]_2^a[\text{CO}]_2^b}{k[\text{NO}_2]_1^a[\text{CO}]_1^b} \\ \frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{[\text{CO}]_2^b}{[\text{CO}]_1^b} \\ \frac{1.44 \times 10^{-5} \text{ M/s}}{1.44 \times 10^{-5} \text{ M/s}} &= \left(\frac{0.413 \text{ M}}{0.826 \text{ M}}\right)^b \\ 1 &= 0.5^b \\ b &= 0\end{aligned}$$

Remember that any number raised to the zero power is equal to 1.
 $1 = n^0$

PRACTICE PROBLEM 2

The following data were obtained for the reaction



Determine the rate law for this reaction and the value of the rate constant.

— *answer* —

Begin by constructing the generic rate law:

$$\text{Rate} = k[\text{NO}_2]^a[\text{CO}]^b$$

Understand that we will need to solve for the orders a and b using the isolation method.

Let's solve for a , which is the order of the reaction with respect to $[\text{NO}_2]$.

Compare experiments 2 and 3:

$$\begin{aligned}\frac{\text{Rate}_3}{\text{Rate}_2} &= \frac{k[\text{NO}_2]_3^a[\text{CO}]_3^b}{k[\text{NO}_2]_2^a[\text{CO}]_2^b} \\ \frac{\text{Rate}_3}{\text{Rate}_2} &= \frac{[\text{NO}_2]_3^a}{[\text{NO}_2]_2^a} \\ \frac{5.76 \times 10^{-5} \text{ M/s}}{1.44 \times 10^{-5} \text{ M/s}} &= \left(\frac{0.526 \text{ M}}{0.263 \text{ M}}\right)^a \\ 4 &= 2^a \\ a &= 2\end{aligned}$$

This means that our rate law is:

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

Expt.	$[\text{NO}_2]_0$ (M)	$[\text{CO}]_0$ (M)	Initial Rate (M/s)
1	0.263	0.826	1.44×10^{-5}
2	0.263	0.413	1.44×10^{-5}
3	0.526	0.413	5.76×10^{-5}

Let's solve for b , which is the order of the reaction with respect to $[\text{CO}]$.

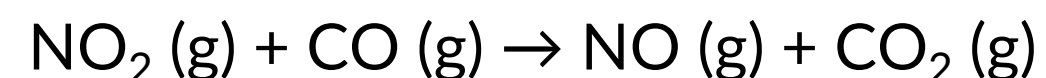
Compare experiments 1 and 2:

$$\begin{aligned}\frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{k[\text{NO}_2]_2^a[\text{CO}]_2^b}{k[\text{NO}_2]_1^a[\text{CO}]_1^b} \\ \frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{[\text{CO}]_2^b}{[\text{CO}]_1^b} \\ \frac{1.44 \times 10^{-5} \text{ M/s}}{1.44 \times 10^{-5} \text{ M/s}} &= \left(\frac{0.413 \text{ M}}{0.826 \text{ M}}\right)^b \\ 1 &= 0.5^b \\ b &= 0\end{aligned}$$

Remember that any number raised to the zero power is equal to 1.
 $1 = n^0$

PRACTICE PROBLEM 2

The following data were obtained for the reaction



Determine the rate law for this reaction and the value of the rate constant.

— answer —

Begin by constructing the generic rate law:

$$\text{Rate} = k[\text{NO}_2]^a[\text{CO}]^b$$

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Let's solve for a , which is the order of the reaction with respect to $[\text{NO}_2]$.

Compare experiments 2 and 3:

$$\begin{aligned}\frac{\text{Rate}_3}{\text{Rate}_2} &= \frac{k[\text{NO}_2]_3^a[\text{CO}]_3^b}{k[\text{NO}_2]_2^a[\text{CO}]_2^b} \\ \frac{\text{Rate}_3}{\text{Rate}_2} &= \frac{[\text{NO}_2]_3^a}{[\text{NO}_2]_2^a} \\ \frac{5.76 \times 10^{-5} \text{ M/s}}{1.44 \times 10^{-5} \text{ M/s}} &= \left(\frac{0.526 \text{ M}}{0.263 \text{ M}}\right)^a \\ 4 &= 2^a \\ a &= 2\end{aligned}$$

This means that our rate law is:

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

Now that we have our rate law we can solve for the rate constant, k , by plugging in the values from a particular experiment. Again, I'll use experiment 1:

$$\begin{aligned}\text{Rate}_1 &= k[\text{NO}_2]_1^2 \\ 1.44 \times 10^{-5} \frac{\text{M}}{\text{s}} &= k(0.263 \text{ M})^2 \\ k &= 2.08 \times 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}\end{aligned}$$

Expt.	$[\text{NO}_2]_0$ (M)	$[\text{CO}]_0$ (M)	Initial Rate (M/s)
1	0.263	0.826	1.44×10^{-5}
2	0.263	0.413	1.44×10^{-5}
3	0.526	0.413	5.76×10^{-5}

Let's solve for b , which is the order of the reaction with respect to $[\text{CO}]$.

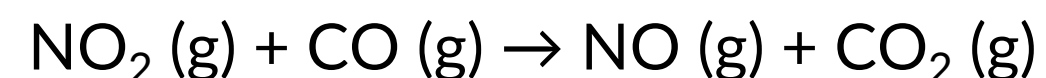
Compare experiments 1 and 2:

$$\begin{aligned}\frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{k[\text{NO}_2]_2^a[\text{CO}]_2^b}{k[\text{NO}_2]_1^a[\text{CO}]_1^b} \\ \frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{[\text{CO}]_2^b}{[\text{CO}]_1^b} \\ \frac{1.44 \times 10^{-5} \text{ M/s}}{1.44 \times 10^{-5} \text{ M/s}} &= \left(\frac{0.413 \text{ M}}{0.826 \text{ M}}\right)^b \\ 1 &= 0.5^b \\ b &= 0\end{aligned}$$

Remember that any number raised to the zero power is equal to 1.
 $1 = n^0$

PRACTICE PROBLEM 2

The following data were obtained for the reaction



Determine the rate law for this reaction and the value of the rate constant.

— *answer* —

Begin by constructing the generic rate law:

$$\text{Rate} = k[\text{NO}_2]^a[\text{CO}]^b$$

Understand that we will need to solve for the orders a and b using the isolation method.

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Compare experiments 2 and 3:

$$\begin{aligned}\frac{\text{Rate}_3}{\text{Rate}_2} &= \frac{k[\text{NO}_2]_3^a[\text{CO}]_3^b}{k[\text{NO}_2]_2^a[\text{CO}]_2^b} \\ \frac{\text{Rate}_3}{\text{Rate}_2} &= \frac{[\text{NO}_2]_3^a}{[\text{NO}_2]_2^a} \\ \frac{5.76 \times 10^{-5} \text{ M/s}}{1.44 \times 10^{-5} \text{ M/s}} &= \left(\frac{0.526 \text{ M}}{0.263 \text{ M}}\right)^a \\ 4 &= 2^a \\ a &= 2\end{aligned}$$

This means that our rate law is:

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

Now that we have our rate law we can solve for the rate constant, k , by plugging in the values from a particular experiment. Again, I'll use experiment 1:

$$\begin{aligned}\text{Rate}_1 &= k[\text{NO}_2]_1^2 \\ 1.44 \times 10^{-5} \frac{\text{M}}{\text{s}} &= k(0.263 \text{ M})^2 \\ k &= 2.08 \times 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}\end{aligned}$$

Expt.	$[\text{NO}_2]_0$ (M)	$[\text{CO}]_0$ (M)	Initial Rate (M/s)
1	0.263	0.826	1.44×10^{-5}
2	0.263	0.413	1.44×10^{-5}
3	0.526	0.413	5.76×10^{-5}

Let's solve for b , which is the order of the reaction with respect to $[\text{CO}]$.

Compare experiments 1 and 2:

$$\begin{aligned}\frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{k[\text{NO}_2]_2^a[\text{CO}]_2^b}{k[\text{NO}_2]_1^a[\text{CO}]_1^b} \\ \frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{[\text{CO}]_2^b}{[\text{CO}]_1^b} \\ \frac{1.44 \times 10^{-5} \text{ M/s}}{1.44 \times 10^{-5} \text{ M/s}} &= \left(\frac{0.413 \text{ M}}{0.826 \text{ M}}\right)^b \\ 1 &= 0.5^b \\ b &= 0\end{aligned}$$

Remember that any number raised to the zero power is equal to 1.
 $1 = n^0$

We say this reaction is 2nd order overall, but 2nd order with respect to $[\text{NO}_2]$ and 0th order with respect to $[\text{CO}]$. In other words $[\text{CO}]$ has no effect on the rate of the reaction!