KINETICS

RATE LAWS FROM CONCENTRATIONS

CHEMISTRY 165 // SPRING 2020

DR. MIOY T. HUYNH | 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

$$A + B \rightarrow C + D$$

the rate law can be expressed as

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

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:

$$NH_4^+ \text{ (aq)} + NO_2^- \text{ (aq)} \rightarrow N_2 \text{ (g)} + 2\ H_2O \text{ (l)}$$

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

Expt.	$[NH_4^+]_0$ (M)	$[NO_2^-]_0$ (M)	Initial Rate (M/s)
1	0.100	0.0050	1.35×10^{-7}
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Always begin by constructing the general rate law expression: $\text{Rate} = k[NH_4^+]^a[NO_2^-]^b$

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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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.

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

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.

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

$$2 = 2^b$$

$$b = 1$$

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:

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

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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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.

In experiments 2 and 3, $[\text{NH}_4^+]$ 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.

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{\cancel{k}[\text{NH}_4^+]_3^a\cancel{[\text{NO}_2^-]_3^b}}{\cancel{k}[\text{NH}_4^+]_2^a\cancel{[\text{NO}_2^-]_2^b}}$$

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{[\text{NH}_4^+]_3^a}{[\text{NH}_4^+]_2^a}$$

$$\frac{5.40 \times 10^{-7}\ \text{M/s}}{2.70 \times 10^{-7}\text{M/s}} = \left(\frac{0.200\ \text{M}}{0.100\ \text{M}}\right)^a$$

$$2 = 2^a$$

$$a = 1$$

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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.

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

$$\text{Rate}_1 = k[\text{NH}_4^+]_1^1[\text{NO}_2^-]_1^1$$

$$1.35 \times 10^{-7}\frac{\text{M}}{\text{s}} = k(0.100\ \text{M})^1(0.0050\ \text{M})^1$$

$$k = \frac{1.35 \times 10^{-7}\ \text{M/s}}{(0.100\ \text{M})^1(0.0050\ \text{M})^1}$$

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

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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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 $[\text{NO}_2^-]$.

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The following data were obtained for the reaction

$$2\ ClO_2\ (aq) + 2\ OH^-\ (aq) \rightarrow ClO_3^-\ (aq) + ClO_2^-\ (aq) + H_2O\ (l)$$

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

Compare experiments 1 and 2:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[\text{ClO}_2]_2^a[\text{OH}^-]_2^b}{k[\text{ClO}_2]_1^a[\text{OH}^-]_1^b}$$

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$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{ClO}_2]_2^a}{[\text{ClO}_2]_1^a}$$

$$\frac{2.30 \times 10^{-1}\ \text{M/s}}{5.75 \times 10^{-2}\ \text{M/s}} = \left(\frac{0.100\ \text{M}}{0.0500\ \text{M}}\right)^a$$

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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:

$$\frac{\text{Rate}_2}{\text{Rate}_3} = \frac{\cancel{k}\cancel{[\text{ClO}_2]_2^a}[\text{OH}^-]_2^b}{\cancel{k}\cancel{[\text{ClO}_2]_3^a}[\text{OH}^-]_3^b}$$

$$\frac{\text{Rate}_2}{\text{Rate}_3} = \frac{[\text{OH}^-]_2^b}{[\text{OH}^-]_3^b}$$

$$\frac{2.30 \times 10^{-1}\ \text{M/s}}{1.15 \times 10^{-1}\ \text{M/s}} = \left(\frac{0.100\ \text{M}}{0.0500\ \text{M}}\right)^b$$

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

Compare experiments 1 and 2:

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This means that our rate law is: $\text{Rate} = k[\text{ClO}_2]^2[\text{OH}^-]^1$

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$$2\ ClO_2\ (aq) + 2\ OH^-\ (aq) \rightarrow ClO_3^-\ (aq) + ClO_2^-\ (aq) + H_2O\ (l)$$

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

Expt.	$[ClO_2]_0$ (M)	$[OH^-]_0$ (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}

— 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:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{\cancel{k}[\text{ClO}_2]_2^a\cancel{[\text{OH}^-]_2^b}}{\cancel{k}[\text{ClO}_2]_1^a\cancel{[\text{OH}^-]_1^b}}$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{ClO}_2]_2^a}{[\text{ClO}_2]_1^a}$$

$$\frac{2.30 \times 10^{-1}\ \text{M/s}}{5.75 \times 10^{-2}\ \text{M/s}} = \left(\frac{0.100\ \text{M}}{0.0500\ \text{M}}\right)^a$$

$$4 = 2^a$$

$$a = 2$$

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

Compare experiments 2 and 3:

$$\frac{\text{Rate}_2}{\text{Rate}_3} = \frac{\cancel{k}\cancel{[\text{ClO}_2]_2^a}[\text{OH}^-]_2^b}{\cancel{k}\cancel{[\text{ClO}_2]_3^a}[\text{OH}^-]_3^b}$$

$$\frac{\text{Rate}_2}{\text{Rate}_3} = \frac{[\text{OH}^-]_2^b}{[\text{OH}^-]_3^b}$$

$$\frac{2.30 \times 10^{-1}\ \text{M/s}}{1.15 \times 10^{-1}\ \text{M/s}} = \left(\frac{0.100\ \text{M}}{0.0500\ \text{M}}\right)^b$$

$$2 = 2^b$$

$$b = 1$$

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:

$$\text{Rate}_1 = k[\text{ClO}_2]_1^2[\text{OH}^-]_1^1$$

$$5.75 \times 10^{-2}\ \frac{\text{M}}{\text{s}} = k(0.0500\ \text{M})^2(0.100\ \text{M})^1$$

$$k = 230.\ \text{M}^{-2} \cdot \text{s}^{-1}$$

PRACTICE PROBLEM 1

The following data were obtained for the reaction

$$2\ ClO_2\ (aq) + 2\ OH^-\ (aq) \rightarrow ClO_3^-\ (aq) + ClO_2^-\ (aq) + H_2O\ (l)$$

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

Expt.	$[ClO_2]_0$ (M)	$[OH^-]_0$ (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}

— 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:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{\cancel{k}[\text{ClO}_2]_2^a\cancel{[\text{OH}^-]_2^b}}{\cancel{k}[\text{ClO}_2]_1^a\cancel{[\text{OH}^-]_1^b}}$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{ClO}_2]_2^a}{[\text{ClO}_2]_1^a}$$

$$\frac{2.30 \times 10^{-1}\ \text{M/s}}{5.75 \times 10^{-2}\ \text{M/s}} = \left(\frac{0.100\ \text{M}}{0.0500\ \text{M}}\right)^a$$

$$4 = 2^a$$

$$a = 2$$

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

Compare experiments 2 and 3:

$$\frac{\text{Rate}_2}{\text{Rate}_3} = \frac{\cancel{k}\cancel{[\text{ClO}_2]_2^a}[\text{OH}^-]_2^b}{\cancel{k}\cancel{[\text{ClO}_2]_3^a}[\text{OH}^-]_3^b}$$

$$\frac{\text{Rate}_2}{\text{Rate}_3} = \frac{[\text{OH}^-]_2^b}{[\text{OH}^-]_3^b}$$

$$\frac{2.30 \times 10^{-1}\ \text{M/s}}{1.15 \times 10^{-1}\ \text{M/s}} = \left(\frac{0.100\ \text{M}}{0.0500\ \text{M}}\right)^b$$

$$2 = 2^b$$

$$b = 1$$

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:

$$\text{Rate}_1 = k[\text{ClO}_2]_1^2[\text{OH}^-]_1^1$$

$$5.75 \times 10^{-2}\ \frac{\text{M}}{\text{s}} = k(0.0500\ \text{M})^2(0.100\ \text{M})^1$$

$$k = 230.\ \text{M}^{-2} \cdot \text{s}^{-1}$$

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

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$

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

Expt.	$[NO_2]_0$ (M)	$[CO]_0$ (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}

— answer —

PRACTICE PROBLEM 2

The following data were obtained for the reaction

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$

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

Expt.	$[NO_2]_0$ (M)	$[CO]_0$ (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}

— 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.

PRACTICE PROBLEM 2

The following data were obtained for the reaction

$$NO_2\ (g) + CO\ (g) \rightarrow NO\ (g) + CO_2\ (g)$$

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

Expt.	$[NO_2]_0$ (M)	$[CO]_0$ (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}

— 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:

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{\cancel{k}[\text{NO}_2]_3^a\cancel{[\text{CO}]_3^b}}{\cancel{k}[\text{NO}_2]_2^a\cancel{[\text{CO}]_2^b}}$$

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{[\text{NO}_2]_3^a}{[\text{NO}_2]_2^a}$$

$$\frac{5.76 \times 10^{-5}\ \text{M/s}}{1.44 \times 10^{-5}\ \text{M/s}} = \left(\frac{0.526\ \text{M}}{0.263\ \text{M}}\right)^a$$

$$4 = 2^a$$

$$a = 2$$

PRACTICE PROBLEM 2

The following data were obtained for the reaction

$$NO_2\ (g) + CO\ (g) \rightarrow NO\ (g) + CO_2\ (g)$$

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

Expt.	$[NO_2]_0$ (M)	$[CO]_0$ (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}

— 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:

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{\cancel{k}[\text{NO}_2]_3^a\cancel{[\text{CO}]_3^b}}{\cancel{k}[\text{NO}_2]_2^a\cancel{[\text{CO}]_2^b}}$$

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{[\text{NO}_2]_3^a}{[\text{NO}_2]_2^a}$$

$$\frac{5.76 \times 10^{-5}\ \text{M/s}}{1.44 \times 10^{-5}\ \text{M/s}} = \left(\frac{0.526\ \text{M}}{0.263\ \text{M}}\right)^a$$

$$4 = 2^a$$

$$a = 2$$

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

Compare experiments 1 and 2:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{\cancel{k}\cancel{[\text{NO}_2]_2^a}[\text{CO}]_2^b}{\cancel{k}\cancel{[\text{NO}_2]_1^a}[\text{CO}]_1^b}$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{CO}]_2^b}{[\text{CO}]_1^b}$$

$$\frac{1.44 \times 10^{-5}\ \text{M/s}}{1.44 \times 10^{-5}\ \text{M/s}} = \left(\frac{0.413\ \text{M}}{0.826\ \text{M}}\right)^b$$

$$1 = 0.5^b$$

$$b = 0$$

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

$$NO_2\ (g) + CO\ (g) \rightarrow NO\ (g) + CO_2\ (g)$$

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

Expt.	$[NO_2]_0$ (M)	$[CO]_0$ (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}

— 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:

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{\cancel{k}[\text{NO}_2]_3^a\cancel{[\text{CO}]_3^b}}{\cancel{k}[\text{NO}_2]_2^a\cancel{[\text{CO}]_2^b}}$$

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{[\text{NO}_2]_3^a}{[\text{NO}_2]_2^a}$$

$$\frac{5.76 \times 10^{-5}\ \text{M/s}}{1.44 \times 10^{-5}\ \text{M/s}} = \left(\frac{0.526\ \text{M}}{0.263\ \text{M}}\right)^a$$

$$4 = 2^a$$

$$a = 2$$

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

Compare experiments 1 and 2:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{\cancel{k}\cancel{[\text{NO}_2]_2^a}[\text{CO}]_2^b}{\cancel{k}\cancel{[\text{NO}_2]_1^a}[\text{CO}]_1^b}$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{CO}]_2^b}{[\text{CO}]_1^b}$$

$$\frac{1.44 \times 10^{-5}\ \text{M/s}}{1.44 \times 10^{-5}\ \text{M/s}} = \left(\frac{0.413\ \text{M}}{0.826\ \text{M}}\right)^b$$

$$1 = 0.5^b$$

$$b = 0$$

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

This means that our rate law is: $\text{Rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2$

PRACTICE PROBLEM 2

The following data were obtained for the reaction

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$

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

Expt.	$[NO_2]_0$ (M)	$[CO]_0$ (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}

— 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:

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{\cancel{k}[\text{NO}_2]_3^a\cancel{[\text{CO}]_3^b}}{\cancel{k}[\text{NO}_2]_2^a\cancel{[\text{CO}]_2^b}}$$

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{[\text{NO}_2]_3^a}{[\text{NO}_2]_2^a}$$

$$\frac{5.76 \times 10^{-5}\ \text{M/s}}{1.44 \times 10^{-5}\ \text{M/s}} = \left(\frac{0.526\ \text{M}}{0.263\ \text{M}}\right)^a$$

$$4 = 2^a$$

$$a = 2$$

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

Compare experiments 1 and 2:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{\cancel{k}\cancel{[\text{NO}_2]_2^a}[\text{CO}]_2^b}{\cancel{k}\cancel{[\text{NO}_2]_1^a}[\text{CO}]_1^b}$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{CO}]_2^b}{[\text{CO}]_1^b}$$

$$\frac{1.44 \times 10^{-5}\ \text{M/s}}{1.44 \times 10^{-5}\ \text{M/s}} = \left(\frac{0.413\ \text{M}}{0.826\ \text{M}}\right)^b$$

$$1 = 0.5^b$$

$$b = 0$$

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

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:

$$\text{Rate}_1 = k[\text{NO}_2]_1^2$$

$$1.44 \times 10^{-5}\ \frac{\text{M}}{\text{s}} = k(0.263\ \text{M})^2$$

$$k = 2.08 \times 10^{-4}\ \text{M}^{-1} \cdot \text{s}^{-1}$$

PRACTICE PROBLEM 2

The following data were obtained for the reaction

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$

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

Expt.	$[NO_2]_0$ (M)	$[CO]_0$ (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}

— 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:

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{\cancel{k}[\text{NO}_2]_3^a\cancel{[\text{CO}]_3^b}}{\cancel{k}[\text{NO}_2]_2^a\cancel{[\text{CO}]_2^b}}$$

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{[\text{NO}_2]_3^a}{[\text{NO}_2]_2^a}$$

$$\frac{5.76 \times 10^{-5}\ \text{M/s}}{1.44 \times 10^{-5}\ \text{M/s}} = \left(\frac{0.526\ \text{M}}{0.263\ \text{M}}\right)^a$$

$$4 = 2^a$$

$$a = 2$$

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

Compare experiments 1 and 2:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{\cancel{k}\cancel{[\text{NO}_2]_2^a}[\text{CO}]_2^b}{\cancel{k}\cancel{[\text{NO}_2]_1^a}[\text{CO}]_1^b}$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{CO}]_2^b}{[\text{CO}]_1^b}$$

$$\frac{1.44 \times 10^{-5}\ \text{M/s}}{1.44 \times 10^{-5}\ \text{M/s}} = \left(\frac{0.413\ \text{M}}{0.826\ \text{M}}\right)^b$$

$$1 = 0.5^b$$

$$b = 0$$

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

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:

$$\text{Rate}_1 = k[\text{NO}_2]_1^2$$

$$1.44 \times 10^{-5}\ \frac{\text{M}}{\text{s}} = k(0.263\ \text{M})^2$$

$$k = 2.08 \times 10^{-4}\ \text{M}^{-1} \cdot \text{s}^{-1}$$

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!