

Unit 4, Lesson 05: The Rate Law

At the beginning of this unit, we said that increasing the concentration of the reactants usually increases the rate of a chemical reaction. Now that you understand about reaction mechanisms, you can understand why the “usually” is there.

Consider the reaction: $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$

The actual mechanism is:

Step 1: $2 \text{NO}_2 \rightarrow \text{NO} + \text{NO}_3$ (slow)

Step 2: $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$ (fast)

There are two reactants: NO_2 and CO

- if we increase the concentration of the NO_2 , the reaction rate increases, just as we would expect
- however, if we increase the concentration of CO , the reaction rate does not change

Why?

The slowest step in a reaction mechanism is the rate-determining step.

That is, the overall rate of a chemical reaction depends ONLY on the rate of the slowest step.

In the reaction mechanism above, the slowest step involves the bimolecular collision of two molecules of NO_2 . It makes sense that if the concentration of NO_2 is increased, the NO_2 molecules will be more crowded, so there will be more collisions and the reaction rate will increase.

Carbon monoxide (CO) is involved in the second, fast step of the reaction mechanism. This step has no impact on the overall reaction rate because it is not the rate-determining step. Adding more CO will not increase the rate of the rate-determining step, so it has no effect on the overall reaction rate.

The relationship between the concentration of the reactants and the overall rate of a chemical reaction is called the **Rate Law** for that reaction. The Rate Law depends on the rate-determining step of a reaction mechanism, so it must be determined experimentally.

The Rate Law for the above reaction is:

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

k is the rate constant

- its value depends on temperature
- as long as temperature is constant, k is constant

the rate law exponent for NO_2 is 2 because, in the RDS, 2 molecules of NO_2 collide

the rate law exponent for CO is 0 because, in the RDS, 0 molecules of CO collide

Using the rate law for the reaction, we can see that:

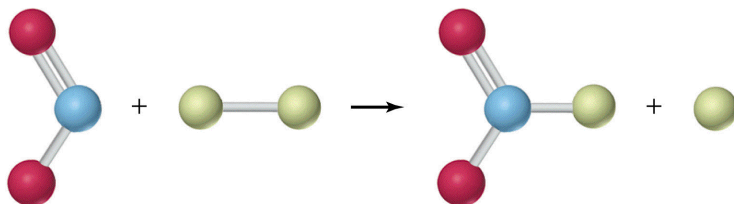
- the reaction rate is proportional to the molar concentration of NO_2 **squared**
- we say that the reaction is “second order” with respect to $[\text{NO}_2]$
- the reaction rate is not affected by changes in the concentration of CO
- we say that the reaction is “zero order” with respect to $[\text{CO}]$
- the reaction is $(2 + 0) =$ second order, overall

If the reaction mechanism is known, then the rate law can be written from the molecularity of the rate-determining step.

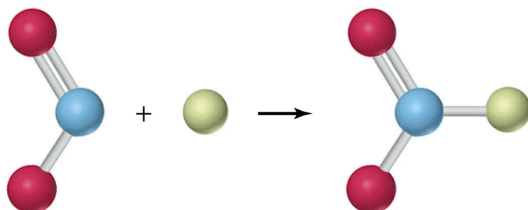
eg. for the reaction: $2 \text{NO}_2 (\text{g}) + \text{F}_2 (\text{g}) \rightarrow 2 \text{NO}_2\text{F} (\text{g})$

The reaction mechanism is:

Step 1: $\text{NO}_2 (\text{g}) + \text{F}_2 (\text{g}) \rightarrow \text{NO}_2\text{F} (\text{g}) + \text{F} (\text{g})$ (slow)



Step 2: $\text{NO}_2 (\text{g}) + \text{F} (\text{g}) \rightarrow \text{NO}_2\text{F} (\text{g})$ (fast)



From the rate determining step, the rate law for this reaction is:

$$\text{rate} = k[\text{NO}_2]^1[\text{F}_2]^1$$

- in the RDS, one molecule of NO_2 collides with one molecule of F_2
- the reaction is first order with respect to NO_2
- the reaction is first order with respect to F_2
- the reaction is $(1 + 1) = \text{second order overall}$

Note: there is **NO** relationship between the *overall* reaction and the rate law. The rate law depends only on the rate-determining step of the reaction mechanism and must be determined experimentally.

If the rate mechanism for a reaction is unknown, you can determine the rate law (the relationship between concentration of reactants and reaction rate) by performing a series of experiments. The concentration of one reactant is varied while the concentration of all other reactants is held constant:

eg. For the reaction: $A + B \rightarrow C$, the following experimental data was recorded:

Trial #	[A]	[B]	Initial Reaction Rate
1	0.10 mol/L	0.10 mol/L	0.20 mol/L·s
2	0.20 mol/L	0.10 mol/L	0.20 mol/L·s
3	0.30 mol/L	0.10 mol/L	0.20 mol/L·s
4	0.40 mol/L	0.10 mol/L	0.20 mol/L·s

In this example, [B] was held constant. Even though the concentration of reactant A was changed, there was no effect on the overall reaction rate. From this result, we know that:

- reactant A must not be involved in the rate determining step of the reaction mechanism
- the overall reaction rate is not affected by the [A], or the reaction is **zero order** with respect to [A]
- we can write the rate equation as: $\text{rate} = k[A]^0[B]^?$

Now, let's look at the same reaction and see if changing the concentration of B affects the reaction rate. To do this, we must hold the concentration of A constant, but change the concentration of B:

Trial #	[A]	[B]	Initial Reaction Rate
1	0.10 mol/L	0.10 mol/L	0.20 mol/L·s
2	0.10 mol/L	0.20 mol/L	0.40 mol/L·s
3	0.10 mol/L	0.40 mol/L	0.80 mol/L·s
4	0.10 mol/L	0.80 mol/L	1.60 mol/L·s

In this example, changing [B] did affect the reaction rate:

- reactant B must be involved in the rate determining step of the reaction mechanism
- when [B] doubled, the reaction rate doubled
- if we graphed the reaction rate versus [B], we would get a straight-line relationship. That is, there is a linear (one to one) relationship between the [B] and the reaction rate
- because there is a one to one relationship between [B] and rate, we say that the reaction rate is **first order** with respect to [B]
- we can write the rate equation as: $\text{rate} = k[A]^0[B]^1$

So, for the reaction $A + B \rightarrow C$ we have determined experimentally that:

- the rate of the reaction is not affected by [A], so it is zero order with respect to [A]
- the rate of the reaction increases in a one to one fashion with [B], so the reaction rate is first order with respect to [B]
- the **overall** order of the reaction is equal to the sum of the orders of the reactants, so the overall order of the reaction is (0 + 1) or 1 overall

For some reactions, as the concentration of a reactant doubles, the rate quadruples (increases by 4). That is, the rate increases with $[X]^2$. This is called a second-order reaction. Reactions can also be third order, or even a fractional order, but we will deal with only zero, first and second order reactions in this course.

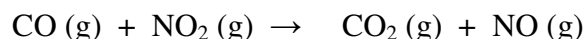
In general, the rate law can be written:

$$\text{rate} = k [\text{A}]^m [\text{B}]^n [\text{C}]^p$$

where k is the rate constant at a specified temperature
 m is the order of the reaction in terms of $[\text{A}]$
 n is the order of the reaction in terms of $[\text{B}]$
 p is the order of the reaction in terms of $[\text{C}]$

the overall order of the reaction is $(m + n + p)$

eg. The following experimental data was recorded for the reaction:



Write the rate law for the reaction and calculate the value of the rate constant, k

Trial #	[CO]	[NO ₂]	Initial Reaction Rate
1	0.10 mol/L	0.10 mol/L	5.0×10^{-3} mol/L·s
2	0.10 mol/L	0.20 mol/L	20.0×10^{-3} mol/L·s
3	0.20 mol/L	0.10 mol/L	5.0×10^{-3} mol/L·s

The rate law will have the general equation: $\text{rate} = k [\text{CO}]^m [\text{NO}_2]^n$

1. To find the value of “m” :

- You need to find experimental data in which $[\text{CO}]$ is changed but $[\text{NO}_2]$ is held constant. Trials 1 and 3 meet these requirements
- as $[\text{CO}]$ doubles (0.10 mol/L to 0.20 mol/L), the reaction rate stays constant. This means that the reaction rate is unaffected by $[\text{CO}]$ and that CO must not be involved in the rate determining step of the reaction mechanism
- the reaction is zero order with regard to $[\text{CO}]$; so far, the rate law is $\text{rate} = k [\text{CO}]^0 [\text{NO}_2]^n$

2. To find the value of “n” :

- You need to find experimental data in which $[\text{NO}_2]$ is changed but $[\text{CO}]$ is held constant. Trials 1 and 2 meet these requirements
- as $[\text{NO}_2]$ doubles (0.10 mol/L to 0.20 mol/L), the reaction rate quadruples (is multiplied by 4). That is, rate is proportional to $[\text{NO}_2]^2$. NO_2 must be involved in the rate determining step of the reaction mechanism
- the reaction is second order with regard to $[\text{NO}_2]$; the rate law, so far, is $\text{rate} = k [\text{CO}]^0 [\text{NO}_2]^2$

3. To calculate the value of “k”:

- the value of k is constant for a given temperature, so we can substitute in the values for concentration and rate from any single trial and solve for k
- if $\text{rate} = k [\text{CO}]^0 [\text{NO}_2]^2$, we can rearrange the equation to solve for k

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

Substitute in the values from any one trial, let's use trial #1

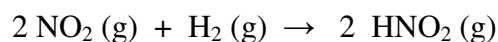
$$= \frac{5.0 \times 10^{-3} \text{ mol/L}\cdot\text{s}}{[0.10 \text{ mol/L}\cdot\text{s}]^0 [0.10 \text{ mol/L}\cdot\text{s}]^2}$$

Remember, $[0.10 \text{ mol/L}\cdot\text{s}]^0 = 1$

$$= 0.50 \text{ L/mol}\cdot\text{s} \quad (\text{the units for a second order reaction are L/mol}\cdot\text{s})$$

therefore, the overall rate law is: **rate = 0.50 L/mol·s $[\text{CO}]^0 [\text{NO}_2]^2$**

eg. The following experimental data was recorded at 800 °C for the reaction:



Write the rate law for the reaction and calculate the value of the rate constant, k

Trial #	[NO ₂]	[H ₂]	Initial Reaction Rate
1	0.001 mol/L	0.004 mol/L	0.002 mol/L·s
2	0.002 mol/L	0.004 mol/L	0.008 mol/L·s
3	0.003 mol/L	0.004 mol/L	0.018 mol/L·s
4	0.004 mol/L	0.001 mol/L	0.008 mol/L·s
5	0.004 mol/L	0.002 mol/L	0.016 mol/L·s
6	0.004 mol/L	0.003 mol/L	0.024 mol/L·s

The rate law will have the general equation: $\text{rate} = k [\text{NO}_2]^m [\text{H}_2]^n$

1. To find the value of “m” :

- find experimental data in which [NO₂] is changed but [H₂] is held constant. Trials 1 and 2 meet these requirements
- using trials 1 and 2, when concentration doubles from 0.001 to 0.002 moles/L, the reaction rate quadruples from 0.002 to 0.008 moles/L seconds
- the exponential value for 'm' for the [NO₂] is the mathematical relationship between these two values. i.e. $2^m = 4$ therefore $m = 2$ because $2^2 = 4$
- to confirm this, compare trials 1 and 3. The concentration of the NO₂ gas triples. The rate jumps by a factor of nine. Therefore $3^m = 9$, so $m = 2$ because $3^2 = 9$
- so far, the rate law expression is: $\text{rate} = k[\text{NO}]^2[\text{H}_2]^n$

2. To find the value of “n”:

- use trials in which the [NO₂] is kept constant and the [H₂] changes. Look at trials 4 and 5
- the H₂ concentration doubles and the rate doubles. $2^n = 2$ therefore $n = 1$ since $2^1 = 2$
- to confirm this, look at trials 4 and 6. The H₂ concentration triples from 0.001 to 0.003 mol/L. The rate also triples from 0.008 to 0.024 mol/L s
- $3^n = 3$ therefore $n = 1$ since $3^1 = 3$
- the rate law expression can be rewritten as $\text{rate} = k [\text{NO}]^2 [\text{H}_2]^1$

3. Determine the value of 'k'.

- 'k' is a constant. It's value should not change unless temperature changes. Choose any one of the experiments. It should not matter which one. We will use experiment 1.
- Using the rate law, above fill in the values from the data table.

$$0.002 \text{ mol/L sec} = k (0.001 \text{ mol/L})^2 \cdot (0.004 \text{ mol/L})$$

$$0.002 \text{ mol/L sec} = k \cdot (0.000001 \text{ mol}^2/\text{L}^2) \cdot (0.004 \text{ mol/L})$$

$$0.002 \text{ mol/L sec} = k \cdot 0.000\ 000\ 009 \text{ mol}^3/\text{L}^3$$

$$k = \frac{0.002 \text{ mol/L sec}}{0.000\ 000\ 009 \text{ mol}^3/\text{L}^3}$$

$$= 500,000 \text{ L}^2 / (\text{sec} \cdot \text{mol}^2) \text{ or } 500,000 \text{ L}^2 \cdot \text{sec}^{-1} \cdot \text{mol}^{-2} \text{ (the units for a third order reaction)}$$

$$= 500,000 \text{ L}^2 / (\text{sec} \cdot \text{mol}^2) \text{ or } 500,000 \text{ L}^2 \cdot \text{sec}^{-1} \cdot \text{mol}^{-2} \text{ (the units for a third order reaction)}$$

the rate law equation for this reaction is $\text{rate} = 500,000 \text{ L}^2 / (\text{sec} \cdot \text{mol}^2) [\text{NO mole/L}]^2 [\text{H}_2 \text{ mol/L}]$
and, overall it is a third order reaction

Summary:

Rate- Determining Step	Molecularity	Rate Law	Overall Rxn Order	Units for k
$A \rightarrow \text{products}$	unimolecular	$\text{rate} = k [A]^1$	first order	$1/s$ or s^{-1}
$A + A \rightarrow \text{products}$	bimolecular	$\text{rate} = k [A]^2$	second order	$L / (\text{mol} \cdot s)$ or $L (\text{mol} \cdot s)^{-1}$
$A + B \rightarrow \text{products}$	bimolecular	$\text{rate} = k [A]^1 [B]^1$	second order	$L / (\text{mol} \cdot s)$ or $L (\text{mol} \cdot s)^{-1}$
$A + A + B \rightarrow \text{products}$	termolecular	$\text{rate} = k [A]^2 [B]^1$	third order	$L^2 / (\text{mol}^2 \cdot s)$ or $L^2 \cdot \text{mol}^{-2} \cdot s^{-1}$
$A + A + B + B \rightarrow \text{products}$	name?	$\text{rate} = k [A]^2 [B]^2$	fourth order	$L^3 / (\text{mol}^3 \cdot s)$ or $L^3 \cdot \text{mol}^{-3} \cdot s^{-1}$

Homework:

1. Read pages 278 to 283 in McGraw-Hill
2. Answer questions 5 to 8 on page 284
3. Answer questions 2 – 5 on page 288
4. Read pages 298 to 300
5. Answer questions 17 to 20 on page 301