# Rate Laws

**Unit:** Kinetics

### Knowledge/Understanding:

* how the rate law and rate constant relate to experimental data
* what the rate constant means

### Skills:

* calculate rate law & rate constant from initial concentration experiment data
* calculate activation energy from the Arrhenius equation

initial rate: the rate at which reactants are converted to products at the instant when the reaction begins.

rate law: an equation that relates the rate of a chemical reaction to the concentrations of (zero or more of) the reactants.

Initial rate experiments can be used to determine which reactants affect the rate of a reaction, and to what extent.

The effect of a particular reactant is determined by comparing the rate of the reaction at two different concentrations of that reactant.

Consider the reaction:

2 NO (g) + O2 (g) → 2 NO2 (g)

The following initial rate data were collected:

|  |  |  |
| --- | --- | --- |
| [NO] | [O2] | rate |
| 0.010 | 0.010 | 2.5 × 10−3 |
| 0.010 | 0.020 | 5.0 × 10−3 |
| 0.030 | 0.020 | 4.5 × 10−2 |

Comparing the first *vs.* second experiments, we see that [NO] stays the same, but [O2] doubles. When [O2] doubles, the rate also doubles. Therefore, the rate is proportional to [O2]1 or just [O2].

Comparing the second *vs.* third experiments, we see that [O2] stays the same, but [NO] goes up by a factor of 3. When [NO] goes up by a factor of 3, the rate goes up by a factor of 9, which equals 32. Therefore, the rate is proportional to [NO]2.

The rate law is therefore:

rate = *k* [NO]2 [O2]

To determine the value of *k*, plug in the data from any of the three experiments. Arbitrarily selecting the second one:

5.0 × 10−3 = *k* [0.010]2 [0.020]

5.0 × 10−3 = *k* (2 × 10−6)



Note that the units for *k* are whatever is necessary to make the rate come out in . In this case, *k* is multiplied by concentration to the 3rd power, or by . In order to end up with the rate in , we need to cancel two of the moles from the numerator (hence the mol2 in the denominator), cancel two of the liters from the denominator (hence the ℓ2 in the numerator), and also get seconds into the denominator.

\*the power on the units of mol and liter should be 1 less than the order of the reaction. (ie: 3rd order = mol2/ ℓ 2s)

As a second example, consider the following reaction and initial rate data:

(CH3)3CBr (aq) + OH− (aq) → (CH3)3COH (aq) + Br−­­ (aq)

|  |  |  |  |
| --- | --- | --- | --- |
|  | [(CH3)3CBr] | [OH−] | rate |
| 1.) | 0.50 | 0.050 | 0.005 |
| 2.) | 1.0 | 0.050 | 0.010 |
| 3.) | 1.5 | 0.050 | 0.015 |
| 4.) | 1.0 | 0.10 | 0.010 |
| 5.) | 1.0 | 0.20 | 0.010 |

Looking at experiments #1 *vs.* #2, and #3, [OH−] is constant, [(CH3)3CBr] is increasing by a factor of 2, and the rate is also increasing by a factor of 2. Looking at #1 *vs.* #3, [OH−] is constant, [(CH3)3CBr] is increasing by a factor of 3, and the rate is also increasing by a factor of 3. These show that the rate is proportional to [(CH3)3CBr].

Looking at experiments #2, #4, and #5, [(CH3)3CBr] is constant, [OH−] is increasing, and the rate is constant. This means the rate is not related to [OH−], which means [OH−] will not appear in the rate law.

The rate law is therefore:

rate = *k* [(CH3)3CBr]

Now, plugging in to find the value of k, let’s choose experiment #2.

0.010 = k (1.0)



This time, because k is multiplied by only one concentration, we already have the units of . This means *k* only needs to put seconds in the denominator to get the desired rate units of .

## Reaction Mechanism

mechanism: a description of a chemical reaction that shows which atoms of a molecule participate in a chemical reaction and how the reaction proceeds.

Because the rate law shows which molecules contribute to the rate of the reaction, it therefore shows which molecules are involved in the rate-determining step. This means we can often make conclusions about the mechanism based on which molecules do and do not appear in the rate law.

For example, in the reaction:

(CH3)3CBr (aq) + OH− → (CH3)3COH (aq) + Br−

We found that the rate law was:

rate = *k* [(CH3)3CBr]

Because OH− was not included in the rate law, *this means OH− is not involved in the rate-determining step*.

In fact, the reaction is a two-step reaction, and the slow step is:



The equilibrium for formation of the (CH3)3C+ ion lies strongly to the left, which means molecules of (CH3)3C+ form only occasionally. However, once an ion does form, it finds an OH− ion to combine with it very quickly, and forms (CH3)3COH.

Multi-Step Reactions

Because the rate of a chemical reaction is determined by its slowest step, the rate law for a multi-step reaction will be the rate law for the slowest step.

If the first step of a two-step reaction is slow, and the second step is fast, the rate law is easy to calculate.

For example, the overall reaction:

NO2 (g) + CO (g) → NO (g) + CO2 (g)

Is really a two-step reaction:

          2 NO2 (g) → NO3 (g) + NO (g)     (slow)

NO3 (g) + CO (g) → NO (g) + CO2 (g)      (fast)

As expected, the rate law for this reaction is:

rate = *k1* [NO2]2

where *k1* is the rate constant for the first reaction.

If, however, the first step is fast and the second step is slow, the problem becomes a little more involved. Consider the reaction:

2 NO (g) + Br2 (g) → 2 NOBr (g)

This reaction happens in two steps:

        NO (g) + Br2 (g) → NOBr2 (g)       (fast)

NOBr2 (g) + NO (g) → 2 NOBr (g)     (slow)

In this reaction, the rate is:

rate = *k2* [NOBr2] [NO]

However, because NOBr2 does not appear in the overall reaction, we cannot use it in the rate law.

Therefore, this problem becomes more involved as we will need to substitute the [NOBr2] value in order to write a proper rate law for the entire reaction. Since the first step (fast) utilizes the reactants we need to express in the rate law, we can use it to substitute.

To get rid of the [NOBr2] term, we assume that the first reaction reaches equilibrium because it occurs quickly:

NO (g) + Br2 (g)  NOBr2 (g)

We’ll pause here to talk about what equilibrium represents quickly (kinetics & equilibrium notes)

If we use the equilibrium constant (Keq) for the fast reaction and solve it for [NOBr2], we can get a substitution value that utilizes the reactants we need to express in the rate law of the overall reaction:

\_\_[C]c\_\_\_

[A]a + [B]b



(In the above equations, *k1* is the rate constant for the first reaction, and *k−1* is the rate constant for the reverse of the first reaction.)

Now we substitute  for [NOBr2] in the original equation:



Because *k1*, *k−1*, and *k2* are all constants, we can combine them into a single constant *k*, which gives us the rate law:

rate = *k* [NO]2 [Br2]

Steps to take to determine the rate law when 2nd step is the slow step

1. Treat the fast step as having reached equilibrium and write out a Keq equation to represent it.
2. Rearrange the Keq equation to solve for the reactant you are substituting.
3. Plug the substituted value into the slow step rate law
4. Simplify by combining rate constants into one k-value and combine [ ] factors if necessary

Ie: k2(k1/k-1) = k and [A][B][A] = [A]2[B]