12.3 - Determining the form of the Rate Law

Reaction	Rate Law
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	$\text{Rate} = k[NO]^2[O_2]$
$2NO(g) + 2H_2(g) \rightarrow 2N_2(g) + 2H_2O(g)$	$\text{Rate} = k[NO]^2[H_2]$
$2ICl(g) + H_2(g) \rightarrow 2HCl(g) + I_2(g)$	$\text{Rate} = k[ICl][H_2]$
$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$	$\text{Rate} = k[N_2O_5]$
$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$	$\text{Rate} = k[NO_2][F_2]$
$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$	$\text{Rate} = k[H_2O_2]$
$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$	$\text{Rate} = k[H_2][Br_2]^{\frac{1}{2}}$
$O_3(g) + Cl(g) \rightarrow O_2(g) + ClO(g)$	$\text{Rate} = k[O_3][Cl]$

Baby Steps

Every chemical reaction has its own unique parameters that govern its reaction rate.

The general form of a rate law is:

$$Rate = k[A]^n[B]^m[C]^p[etc...]^{etc...}$$

The first step in determining a rate law is figuring out what the order (n, m, p, . . .) of each reactant is: zero, fractional, first, second, etc.

The reaction's <u>overall order</u> is the sum of all the reactant's individual orders:

Overall = $n + m + p + etc. . .$

More Baby Steps

$$Rate = k[A]^n[B]^m[C]^p[etc...]^{etc...}$$

Once the rate law is determined, it can be used to find the rate constant *k*.

When *k* is known, the rate law can be used to figure out the rate at any point in the reaction, using additional concentration data provided.

Exponential Manipulation

It is worth noting that we'll be using exponential expressions a lot.

Some things:

A. Dividing exponents:

$$\frac{[Concentration\ 1]^n}{[Concentration\ 2]^n} = \left[\frac{Concentration\ 1}{Concentration\ 2}\right]^n$$

B. If the exponent is not obvious, you will have to use logarithms to isolate it.

Example: $1.38^n = 2.62$

$$n \bullet \ln 1.38 = \ln 2.62$$

$$n = \frac{\ln 2.62}{\ln 1.38} = \frac{0.9662}{0.3221} = 3$$

Initial Rates Method

One approach to determining the rate law for a reaction is the Initial Rates Method, which relies on data from various experiments (with different concentrations of reactants used).

The process must be used for EACH reactant to determine that reactant's order.

General form to use:

$$\boxed{\frac{Rate1}{Rate2} = \frac{k[A]^n[B]^m[C]^p[etc...]^{etc...}}{k[A]^n[B]^m[C]^p[etc...]^{etc...}}}$$

Note 1: a zero subscript outside brackets indicates initial concentrations: $[A]_0$.
Note 2: when possible, it is useful to use reactions where an obvious ratio is obtained (like 1 : 2).

Guided Rate Example

Consider the reaction:

$$2\ N_2O_{5(soln)} \longrightarrow 4\ NO_{2(soln)} + O_{2(g)}$$

Here, oxygen leaves the reaction solution and is not available to reverse the reaction.

In two experiments involving different initial amounts of N_2O_5, two initial rates are established for the reaction:

Trial	$[N_2O_5]$	Rate (mol/L s)
1	0.90 M	5.4 E -4
2	0.45 M	2.7 E -4

1. Determine the rate law using these data, then
2. find the value of k.

Guided Rate Example

1. To find the rate law, we must first establish the order of the reaction (we must find *n*).

$$\frac{Rate1}{Rate2} = \frac{k[N_2O_5]^n}{k[N_2O_5]^n}$$

$$\frac{5.4E-4\,mol/L\bullet s}{2.7E-4\,mol/L\bullet s} = \frac{k[0.90M]^n}{k[0.45M]^n}$$

$$2 = \frac{\cancel{k}[0.90M]^n}{\cancel{k}[0.45M]^n} = \left[\frac{0.90M}{0.45M}\right]^n = 2^n$$

$$\boxed{n = 1}$$

This is a first-order reaction, and the rate law is:

$$\boxed{Rate = k[N_2O_5]^1}$$

Guided Rate Example

2. To find *k*, we select either of the two trials, plug in values, and solve for it:

$$Rate = k[N_2O_5]^1$$

$$k = \frac{Rate}{[N_2O_5]} = \frac{5.4E-4\,mol/L\bullet s}{0.90\,mol/L} = \boxed{6.0E-4\,s^{-1}}$$

Use trial 2 to check for agreement with *k*.

A Note on *k* Units

Depending on the order, the units of *k* will differ wildly.

3. What units will *k* have for a second-order reaction?

$$Rate = k[A]^2$$

$$k = \frac{Rate}{[A]^2} = \frac{\frac{mol}{L\bullet s}}{\left(\frac{mol}{L}\right)^2} = \frac{\frac{mol}{L\bullet s}}{\frac{mol^2}{L^2}} = \frac{mol}{L\bullet s}\bullet\frac{L^2}{mol^2} = \boxed{\frac{L}{mol\bullet s}}$$

Two Component Reaction

Consider the reaction:

$$NH_4^+{}_{(aq)} + NO_2^-{}_{(aq)} \longrightarrow N_{2(g)} + 2\,H_2O_{(l)}$$

Using the following data set:

Trial	$[NH_4^+]$	$[NO_2^-]$	Initial Rate (mol/L s)
1	0.100	0.005	1.35 E -7
2	0.100	0.010	2.70 E -7
3	0.200	0.010	5.40 E -7

4. Determine the rate law for this reaction, and
5. the value of the rate constant *k*.

4. Two Component Rate Law

We must find the order of each reactant separately. Focusing on the ammonium ion, using trials 2 and 3 will allow for easy elimination of the nitrite ion:

$$\frac{Rate\,2}{Rate\,3} = \frac{k[NH_4^+]^n[NO_2^-]^m}{k[NH_4^+]^n[NO_2^-]^m}$$

$$\frac{2.70\,E-7\,mol/L\bullet s}{5.40\,E-7\,mol/L\bullet s} = \frac{\cancel{k}[0.100M]^n\cancel{[0.010M]^m}}{\cancel{k}[0.200M]^n\cancel{[0.010M]^m}}$$

$$0.5 = \left[\frac{0.100M}{0.200M}\right]^n = 0.5^n$$

$$\boxed{n=1}$$

NH_4^+ is a first-order reactant.

4. Two Component Rate Law

Nitrite ion, using trials 1 and 2 will allow for easy elimination of ammonium ion:

$$\frac{Rate1}{Rate2} = \frac{k[NH_4^+]^1[NO_2^-]^m}{k[NH_4^+]^1[NO_2^-]^m}$$

$$\frac{1.35E-7\,mol/L\bullet s}{2.70E-7\,mol/L\bullet s} = \frac{\cancel{k[0.100M]^1}[0.005M]^m}{\cancel{k[0.100M]^1}[0.010M]^m}$$

$$0.5 = \left[\frac{0.005M}{0.010M}\right]^m = 0.5^m$$

$$\boxed{m=1}$$

NO_2^- is a first-order reactant as well.

4. Putting it Together

Both of the reactants are first-order, so the rate law becomes:

$$\boxed{Rate = k[NH_4^+][NO_2^-]}$$

This results in a second-order reaction overall:

Overall Order = $n + m = 1 + 1 = 2$

5. Solving for *k*

We can use our rate law to solve for *k*, using any of the three trials (and then checking with the rest).

Using Trial 1, we get:

$$Rate1 = k[NH_4^+][NO_2^-]$$

$$k = \frac{Rate1}{[NH_4^+][NO_2]} = \frac{1.35E-7\frac{mol}{L\bullet s}}{0.100\frac{mol}{L}\bullet 0.005\frac{mol}{L}} = \frac{1.35E-7\frac{mol}{L\bullet s}}{0.0005\frac{mol^2}{L^2}}$$

$$= \boxed{2.7E-4\frac{L}{mol\bullet s}}$$

Homework

Read 12.4 in your Book

12.3 Problems
Due - Next Class