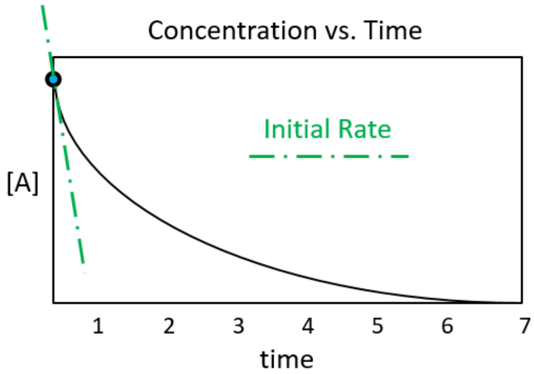
The Method of Initial Rates:



As its name says, the method of initial rates uses the rate at the beginning of a reaction to determine the order in the reactants. For instance, let's say we have the following hypothetical reaction:

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

Experiment	[A] (mol/L)	[B] (mol/L)	[C] (mol/L)	Rate (mol/L/s)
1	0.008	0.001	0.250	4.50×10^{-9}
2	0.016	0.001	0.250	1.80×10^{-8}
3	0.016	0.001	0.125	2.25×10^{-9}
4	0.016	0.002	0.250	1.80×10^{-8}

We use the initial rate to find the orders because right when the reaction starts, our concentrations of reagents should be exactly what we loaded into the container. If you think of a reaction as a factory with a slow step, what can happen with time is that some reagent gets stock piled (it slows down the reaction) if its involved in the slow step and this can produce inaccurate results later on. The reactions MUST also be at the same temperature (this way k is constant).

We can do the following:

$$\frac{\text{rate}_1}{\text{rate}_1} = \frac{k[A]^x[B]^y[C]^z}{k[A]^x[B]^y[C]^z}$$

And

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{4.50 \times 10^{-9}}{1.80 \times 10^{-8}} = \frac{k[0.008]^x[0.001]^y[0.250]^z}{k[0.016]^x[0.001]^y[0.250]^z}$$

*The items in red cancel because they have the same value.

$$\frac{4.50 \times 10^{-9}}{18.0 \times 10^{-9}} = \frac{[0.008]^x}{[0.016]^x}$$

I converted the rates to the same base 10 power – because then it becomes possible to do this question without a calculator. This is not necessary but using your math skills will lead to faster results in chemistry:

$$\frac{1}{4} = \left[\frac{1}{2}\right]^x$$

We then know $x = 2$. If we were unsure, we could take the log of both sides:

$$\log\left(\frac{1}{4}\right) = \log\left[\frac{1}{2}\right]^x \text{ and } \log\left(\frac{1}{4}\right) = x\log\left(\frac{1}{2}\right) \text{ and } \frac{\log\left(\frac{1}{4}\right)}{\log\left(\frac{1}{2}\right)} = x \text{ giving } x = 2$$

Using logs works regardless of the numbers… because math! (this course applies a LOT of Grade 12 math concepts). Then we can find the orders of the other reagents:

$$\frac{\text{rate}_2}{\text{rate}_3} = \frac{1.80 \times 10^{-8}}{2.25 \times 10^{-9}} = \frac{\color{red}{\text{k}[0.016]^2[0.001]^{\text{y}}}[0.250]^{\text{z}}}{\color{red}{\text{k}[0.016]^2[0.001]^{\text{y}}}[0.125]^{\text{z}}}$$

*Notice in the above reaction, I put in 2 for the order of A because we already know it. This is not important in this example but WILL be in the future.

$$\frac{1.80 \times 10^{-8}}{2.25 \times 10^{-9}} = \left[\frac{0.250}{0.125}\right]^{\text{z}} \text{ and } 8 = [2]^{\text{z}}, \qquad \text{giving z} = 3$$

Then we can do the last reagent:

$$\frac{\text{rate}_3}{\text{rate}_4} = \frac{1.80 \times 10^{-8}}{1.80 \times 10^{-8}} = \frac{\color{red}{\text{k}[0.016]^2}[0.001]^{\text{y}}\color{red}{[0.250]^3}}{\color{red}{\text{k}[0.016]^2}[0.002]^{\text{y}}\color{red}{[0.250]^3}}$$

And

$$1 = \left[\frac{1}{2}\right]^{y}, \qquad \text{giving y} = 0 \text{ (any number to the power of zero is 1)}$$

This means that x, y and z are 2, 0 and 3 respectively.

This gives rate $= \text{k}[\text{A}]^2[\text{B}]^0[\text{C}]^3$

Because the reactions were all performed at the same temperature, we could cancel k – it would be indentical for every experiment. This means we can use any experiment to find k:

$$\text{rate}_1 = \text{k}[\text{A}]^2[\text{C}]^3$$

$$4.50 \times 10^{-9}\frac{\text{M}}{\text{s}} = \text{k}[0.008 \text{ M}]^2[0.250 \text{ M}]^3$$

$$\frac{4.50 \times 10^{-9}\frac{\text{M}}{\text{s}}}{[0.008 \text{ M}]^2[0.250 \text{ M}]^3} = \text{k} \quad \text{and} \quad \text{k} = 0.0045\frac{1}{\text{sM}^4}$$

*B was excluded because any number to the zero means the reaction rate does not depend on its concentration. Interestingly, if we had no B, there would be no reaction – so it is a necessary reagent, it just doesn't affect the rate.

Notice that we get the units of k through simple unit analysis. k can also be written as $0.0045 \text{ M}^{-4}\text{s}^{-1}$ and as $0.0045 \text{ L}^4\text{mol}^{-4}\text{s}^{-1}$. We can do the same thing with any experiment, let's use experiment 3 demonstrate:

$$\text{rate}_3 = \text{k}[\text{A}]^2[\text{C}]^3$$

$$2.25 \times 10^{-9}\frac{\text{M}}{\text{s}} = \text{k}[0.016 \text{ M}]^2[0.125 \text{ M}]^3$$

$$\frac{2.25 \times 10^{-9}\frac{\text{M}}{\text{s}}}{[0.016 \text{ M}]^2[0.125 \text{ M}]^3} = \text{k} \quad \text{and} \quad \text{k} = 0.0045\frac{1}{\text{sM}^4}$$

There is a rapid way of finding the order in any reagent for a reaction as well:

Experiment	[A] (mol/L)	[B] (mol/L)	[C] (mol/L)	Rate (mol/L/s)
1	0.008	0.001	0.250	4.50×10^{-9}
2	0.016	0.001	0.250	1.80×10^{-8}
3	0.016	0.001	0.125	2.25×10^{-9}
4	0.016	0.002	0.250	1.80×10^{-8}

If A is doubled, rate goes up by 4, therefore $2^x = 4$, x=2 and the order in A is 2.

This works because, most of the time, instructors have 2 experiments where every concentration except for one is constant. Our procedure was as follows:

$\frac{0.016}{0.008} = 2$ and $\frac{18.0 \times 10^{-9}}{4.50 \times 10^{-9}} = 4$, therefore $2^2 = 4$ and the order must be two ($[2A]^2 = 4[A]^2$)

We can do this for the rest of the reagents and we find:

Experiment	[A] (mol/L)	[B] (mol/L)	[C] (mol/L)	Rate (mol/L/s)
1	0.008	0.001	0.250	4.50×10^{-9}
2	0.016	0.001	0.250	1.80×10^{-8}
3	0.016	0.001	0.125	2.25×10^{-9}
4	0.016	0.002	0.250	1.80×10^{-8}

A: $2^x = 4$ and $x = 2$

B: $2^y = 1$ and $y = 0$

C: $2^z = 8$ and $z = 3$

Giving us rate $= \mathrm{k}[\mathrm{A}]^2[\mathrm{B}]^0[\mathrm{C}]^3$

Note that if the concentration of A changes by 3, we would see something like $3^x = 9$ and $x = 2$.

This rapid methodology only works because professors tend to use simple numbers on exams. But what if the numbers aren't simple or what if there is no experiment where every reactant except for one cancels?

What if we can't do the easy method or there are no 2 experiments with the same concentration of a reagent, enabling its cancellation?

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

Given the following experiments, find the order in every reactant and the rate constant:

Experiment	$[NO_{2(g)}]$ (mol/L)	$[CO_{(g)}]$ (mol/L)	Rate (mol/L/s)
1	0.04	0.03	2.40×10^{-6}
2	0.08	0.06	9.60×10^{-6}
3	0.04	0.10	2.40×10^{-6}

We can already see

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{2.40 \times 10^{-6}}{2.40 \times 10^{-6}} = \frac{k[0.04]^m[0.03]^n}{k[0.04]^m[0.01]^n}$$

And

$$\frac{2.40 \times 10^{-6}}{2.40 \times 10^{-6}} = \frac{[0.03]^n}{[0.01]^n} \quad \text{giving } 1 = \left[\frac{3}{1}\right]^x$$

We know the other coefficients (the ones for CO) and can now use ANY two reactions where $[NO_{2(g)}]$ is different to find its order:

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{2.40 \times 10^{-6}}{9.60 \times 10^{-6}} = \frac{k[0.04]^m[0.03]^0}{k[0.08]^m[0.06]^0} \text{ and } \frac{1}{4} = \frac{[0.04]^m}{[0.08]^m}$$

Giving m=2

We can also use any other reactions where $[NO_{2(g)}]$ is different

$$\frac{\text{rate}_2}{\text{rate}_3} = \frac{9.60 \times 10^{-6}}{2.40 \times 10^{-6}} = \frac{k[0.08]^m[0.06]^0}{k[0.04]^m[0.10]^0} \text{ and } \frac{4}{1} = \frac{[0.08]^m}{[0.04]^m}$$

Giving m=2 again.

The overall rate law is rate $= k\left[NO_{2(g)}\right]^2\left[CO_{(g)}\right]^0$ and, using any experiment, we find the rate constant is $1.5 \times 10^{-3}\,\frac{1}{sM}$.

We can do a harder example using what we know:

Experiment	$[O_{3(g)}]$ (mol/L)	$[O_{2(g)}]$ (mol/L)	Rate (mol/L/s)
1	0.01	0.03	5.00×10^{-2}
2	0.02	0.04	1.50×10^{-1}
3	0.01	0.05	3.00×10^{-2}

The answer is given far below; you can try it out.

The order in O3 is 2, in O2 is -1 (it actually slows down reaction!) and the k value is 15.