Lecture 22 : Short and Sweet: How to Determine Orders of Reaction

In many kinetics problems, the first order of business (a pun) is to determine the order of a reaction. The order of a reaction is simply the sum of the exponents on the concentration terms for a rate law:

$$\text{Rate} = k[A]^x[B]^y \qquad \text{reaction order} = x + y$$

Example 1: $\text{Rate} = k\,[A]^1[B]^0 = k\,[A]$

is **1st order in [A]** and **0th order in [B]** and **1st order for the reaction**.

Example 2: $\text{Rate} = k\,[A]^3[B]^{0.5}$
is **3rd order in [A]**, **half order in [B]** and **3.5 order overall**.

What does the reaction order tell us: We need to know the **order of a reaction** because it **tells us the functional relationship between concentration and rate**. It determines how the amount of a compound speeds up or retards a reaction. For example, a reaction **order of three** means the **rate of reaction increases as the cube of the concentration**. A **reaction order of -1** means the compound actually **retards the rate of reaction**.

Determining Reaction Order:

Here are four ways to learn the order of reaction from easiest to hardest:
1. They tell you in the problem. "In the **first order reaction** of …."
2. You are given **units for the rate constant**. For example, if a reaction is **first order** the **units are reciprocal time**:
$$\text{Proof: rate} = k\,[A]^1 \text{ and rearranging, } k = \text{rate}/M = (M/sec)/M = 1/sec = sec^{-1}$$

In other words, the order of a reaction with $k = 1.24 \times 10^{-2}\,min^{-1}$ is first order.
Do the unit canceling yourself to find that

Zero order	1st order	2nd order
$k = Msec^{-1}$	$k = sec^{-1}$	$k = M^{-1}sec^{-1}$

Remember, this only tells you the total order for the reaction, not the individual orders.

3. **Method of initial rates.** The favorite of every kinetics exam in general chemistry, you will be given a series of varying concentrations and a rate and from this asked to determine the individual and reaction rates.

Trial	Example 1 [A]	[B]	rate		Example 2 [A]	[B]	rate		Example 3 [A]	[B]	rate
1	.1	.1	1×10^{-4}		.1	.1	2×10^{-3}		.1	.1	5×10^{-5}
2	.1	.2	1×10^{-4}		.1	.3	54×10^{-3}		.2	.1	5×10^{-5}
3	.3	.1	3×10^{-4}		.15	.1	4.5×10^{-3}		1.84	.2	2.5×10^{-5}
order	1	0	1 overall		2	3	5 overall		0	-1	-1 overall

In each case, you set up **a ratio of concentrations and rates** to fit the expression: $\text{rate} = k[A]^x$ or $\text{rate} = k[B]^y$ and ask, what does the order x or y have to be to make the equation true?

Example 1:
- hold [A] in trial 1 and 2 constant, then
  $\text{rate}_2 /\text{rate}_1 = k([B_2]/[B_1])^y$ so $1x10^{-4}/1x10^{-4} = k\,(.2/.1)^y$ and $y = 0$. This is a 0th order reaction in B.
- now hold [B] in trial 1 and 3 constant, then
  $\text{rate}_3 /\text{rate}_1 = k([A_3]/[A_1])^x$ so $3x10^{-4}/1x10^{-4} = k\,(.3/.1)^x$ and $x = 1$. This is a 1st order reaction in A.

Example 2:
- hold [A] in trial 1 and 2 constant, then
  $rate_2/rate_1 = k([B_2]/[B_1])^y$ so $54 \times 10^{-3}/2 \times 10^{-3} = k(.3/.1)^y$ and $y = 3$. This is a 3rd order reaction in B.
- now hold [B] in trial 1 and 3 constant, then
  $rate_3/rate_1 = k([A_3]/[A_1])^x$ so $4.5 \times 10^{-3}/2 \times 10^{-3} = k(.15/.1)^x$ and $x = 2$. This is a 2nd order reaction in A.

Example 3:
- hold [B] in trial 1 and 2 constant, then
  $rate_2/rate_1 = k([A_2]/[A_1])^x$ so $5 \times 10^{-5}/5 \times 10^{-5} = k(.1/.1)^x$ and $x = 0$. This is a 1st order reaction in A.
- It is not necessary to hold [A] constant because it is first order and the rate doesn't change with [A].
  $rate_3/rate_1 = k([B_3]/[B_1])^y$ so $2.5 \times 10^{-5}/5 \times 10^{-5} = k(.2/.1)^y$ and $y = -1$. This is a -1 order in reaction in B.

Do this yourself for each example above. The answers are in the rows at the bottom of the tables.

4. Determining **order** from **integrated rate equation**. The final method for determining orders is indirect and unlikely to be asked on a test, but it really shows whether you know your kinetics. Note that the integrated rate law solutions for zero, first and second order expressions are different functions but all can be written in the form of a straight line. This means that if I plot the concentration, [A], as a function of time for each expression below, the correct order should yield a straight line function. For thrills lets do it for the data in a first order reaction, but apply the functions for all three equations

Zero order	First order	Second order
$y = mx + b$	$y = mx + b$	$y = mx + b$
$[C] = -ck\ t + [C_0]$	$\ln[C] = -ck\ t + \ln[C_0]$	$1/[C] = ck\ t + 1/[C_0]$

300K concentration time data		2nd order	1st order	Zero order
time	[C]	1/[C]	ln [C]	[C]
0	?			
1	.12	8.33	**-2.1**	.12
2	.074	13.5	**-2.6**	.074
3	.044	22.7	**-3.1**	.044
4	.027	37.0	**-3.6**	.027
5	.016	62.5	**-4.1**	.016
6	.009	111	**-4.6**	.009
8	.0036	277	**-5.6**	.0036
10	.0013	769	**-6.6**	.0013

Isn't this exciting, notice that the only one that is a straight line is first order, hence the reaction is first order in [C]. Yet another way to find the order of a reaction!!