Teacher's Tools® Chemistry

Kinetics: Rate Laws: Student Review Notes

Rate Laws: Determining rate laws from **concentration vs. rate data**. These problems are pretty easy if you understand the basic algebra of the rate laws (remember, [ ] means molar concentration)

Zero order: r = k ←————————— rate won't change with concentration changes.

First order in A: r = k[A] ←——————— rate will change linearly with the concentration of A, i.e., if you double [A] the rate should double.

Second order in A: $r = k[A]^2$ ←———— rate will change as the square of a change in [A], i.e., if you double [A] the rate will increase by a factor of 4.

So when you are given a table of concentration vs. rate data look at the factor by which concentration changes and back out the factor by which rate changes.

For example: **A + B <====> products**

[A]	[B]	rate(mol/L·s)
.1	.1	4.6×10^{-4}
.2	.1	9.1×10^{-4}
.3	.1	1.3×10^{-3}
.1	.2	1.8×10^{-3}

We know the general form of the rate law

$$r = k[A]^m[B]^n$$

use two data points and divide rate expressions (gets rid of k, the rate constant)

$$\frac{r_2}{r_1} = \left(\frac{[A]_2}{[A]_1}\right)^m \left(\frac{[B]_2}{[B]_1}\right)^n$$

pick points where one concentration is constant

$[A]_2 = [A]_1$ (gets n)
$[B]_2 = [B]_1$ (gets m)

* A lot of this is just eyeballing, like:

$$\frac{r_2}{r_1} = 2 = [2]^n$$

$$n = 1 \quad \text{etc,}$$

(Or this one, which is a little tougher than the one on the left)

[A]	[B]	rate(mol/L·s)
.2	.4	1
.4	.6	4.5
.8	.2	1

Again, you know the general form of the rate law:

$$r = k[A]^m[B]^n$$

and you can take ratios to eliminate k, the rate constant. **BUT**, there are no pairs of data points where the concentration of one of the reactants is constant. Therefore, you have to use logarithms and two equations and two unknowns to find m and n in the rate law.

Here we go:

A: $\dfrac{r_1}{r_2} = \dfrac{1}{4.5} = \left(\dfrac{.2}{.4}\right)^m \cdot \left(\dfrac{.4}{.6}\right)^n = .5^m \, .67^n$

B: $\dfrac{r_2}{r_3} = \dfrac{4.5}{1} = \left(\dfrac{.4}{.8}\right)^m \cdot \left(\dfrac{.6}{.2}\right)^n = .5^m \, .3^n$
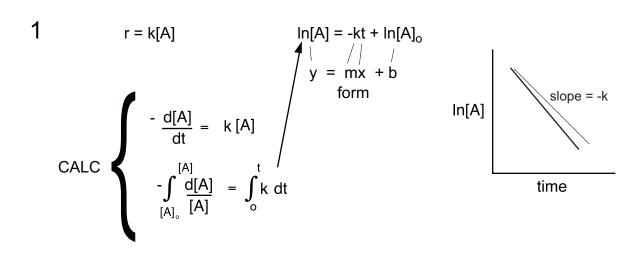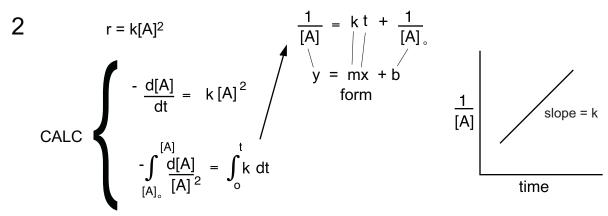
A: $\ln(.22) = m\ln(.5) + n\ln(.67)$
     $-1.5 = -.69m - .4n$ ←——┐
B: $\ln(4.5) = m\ln(.5) + n\ln(3)$ Solve by
     $1.5 = -.69m + 1.1n$ ←——┘ addition for m and n

$$n = 2 \quad \text{and} \quad m = 1$$

    0104SN02.pdf

Kinetics: Rate Laws: Student Review Notes

Rate Laws: You can determine rate laws from **concentration vs. time** data. These problems are a little tougher than [A] vs. rate problems because you have to look at the behavior of the entire data set to determine the rate relationship. You don't have to know calculus to do these problems just algebra. But if you do know some basic integral calculus it's easy to see where the relationships come from. **The whole name of the game here is what form of the concentration of reactant A, [A], do you need to plot against time,t, in order to get a linear relationship.**

Order	Rate Law	Integrated Concentration-time Relationship	Plot to Determine the Rate Law

0

$r = k$

$$[A] = -kt + [A]_o$$

$$y = mx + b$$
form

CALC
$$-\frac{d[A]}{dt} = k$$

$$-\int_{[A]_o}^{[A]} d[A] = \int_o^t k\, dt$$

[A] vs. time, slope = -k

1

$r = k[A]$

$$\ln[A] = -kt + \ln[A]_o$$

$$y = mx + b$$
form

CALC
$$-\frac{d[A]}{dt} = k[A]$$

$$-\int_{[A]_o}^{[A]} \frac{d[A]}{[A]} = \int_o^t k\, dt$$

ln[A] vs. time, slope = -k

2

$r = k[A]^2$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_o}$$

$$y = mx + b$$
form

CALC
$$-\frac{d[A]}{dt} = k[A]^2$$

$$-\int_{[A]_o}^{[A]} \frac{d[A]}{[A]^2} = \int_o^t k\, dt$$

$\frac{1}{[A]}$ vs. time, slope = k

Kinetics: Rate Laws: Student Review Notes

Half-life <-- these are just little chemistry/math problems. Each rate order has a specific half-life form. Often you'll be asked to find k, the rate constant, or, if you are given the rate constant and the initial concentration, to find the half-life.

* What you want to do is look at the linear-forms of the concentration time expressions for each rate order.

* Always remember that in half-life problems you don't have to be given numbers for concentrations. What you know is that at the half-life time the concentration of the reacting species is equal to half of its initial concentration ($[A] = 1/2[A]_o$).

Here's a summary for zero, first, and second order reactions:

Again, you are applying the condition $[A] = [A]_o/2$
to the integrated rate law and solving for the half-life time.

Order	Integrated Rate Law	1/2-life expression	Dependence upon concentration
0	$[A] - [A]_o = -kt$	$t_{1/2} = \dfrac{[A]_o}{2k}$	yes
1	$\ln[A] - \ln[A]_o = -kt$	$t_{1/2} = \dfrac{.69}{k}$	no
2	$\dfrac{1}{[A]} - \dfrac{1}{[A]_o} = kt$	$t_{1/2} = \dfrac{1}{[A]_o k}$	yes

Units of the Rate Constant

If you are given a rate constant and asked to identify the order of the rate law, you simply have to look at the **units of the rate constant** to figure it out.

Rate always has the units of M/s or mol/L·s

Zero order: r = k ⟵——————— Rate constant k, has the units of M/s or mol/L·s

First order in A: r = k[A] ⟵——————— Rate constant k, has the units inverse seconds or s^{-1}

Second order in A: r = k[A]^2 ⟵——— Rate constant k, has the units of $M^{-1}s^{-1}$ or L/mol·s