

Factors That Affect the Rate of Reaction

A. Contact/interfacial area. The greater degree to which reactants are exposed to each other, the faster the reaction will proceed. An example is starting a fire (combustion of wood) with kindling instead of logs. In chemistry people try to make chemical reactors that maximize the amount of contact the reactants will have--you know they put a stirrer in the cup or something creative like that. Actually there is this one cool thing called a fluidized bed where you blow a gas up through a bunch of little beads, the beads all become airborne and the whole system looks like its flowing. It's a way of getting as much gas exposed to the beads as possible.

B. Temperature. Generally, increasing temperature will increase the rate of reaction because of two reasons:

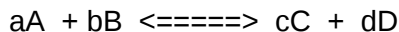
1. At higher temperatures, bonds within the reacting molecules are vibrating with more energy and are closer to the breaking point than at lower temperatures. So the molecules themselves are less stable.
2. At higher temperatures the average velocity of molecules goes up, and therefore when potentially reactive molecules collide there is a greater probability that they will react. Getting over the activation barrier has a lot to do with how hard molecules can slam into each other.

C. Presence of a catalyst. Catalysts increase the rate of reaction by placing one or more of the reactants in an environment in which they are more susceptible to chemical reaction. Catalysts lower the activation energy. Lots of times catalysts are metal surfaces in the reaction vessel. Reactants get close to the metal surface and interact with it. Basically the metal surface and the reactant pull on each other weakening the reactant. Now when another reactant comes along and bumps into the one being pulled on the reaction will occur more easily than if the two reactants just ran into each other in free space.

D. Presence of an inhibitor. Opposite of a catalyst. It does what it says it will do. It inhibits the reaction.

E. Concentration of reactants. This is usually the most important factor. A lot of kinetics is about determining a Rate Law for a specific reaction <-- the rate law is how the reaction rate depends upon concentration of reactants:

For example:



Zero order: $r = k$

First order in A: $r = k[A]$

First order in B: $r = k[B]$

Second order in A: $r = k[A]^2$

Second order in B: $r = k[B]^2$

First order in A, first order in B, second order overall: $r = k[A][B]$

You have to know how a rate law can be determined from different types of experimental data

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:

$$\frac{r_2}{r_1} = 4 = [2]^n$$

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

B: $\frac{r_2}{r_3} = \frac{4.5}{1} = \left(\frac{.4}{.8} \right)^m \cdot \left(\frac{.6}{.2} \right)^n = .5^m \cdot .3^n$

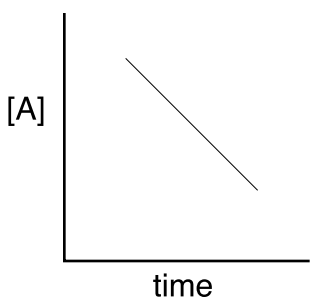
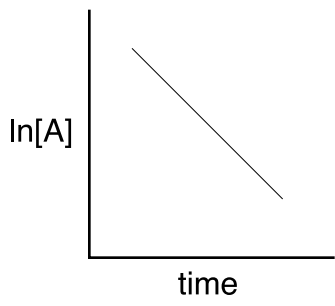
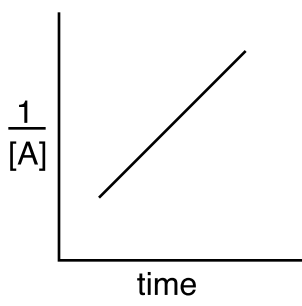
A: $\ln(.22) = m \ln(.5) + n \ln(.67)$
 $-1.5 = -.69m - .4n$

B: $\ln(4.5) = m \ln(.5) + n \ln(3)$
 $1.5 = -.69m + 1.1n$

Solve by addition for m and n

n = 2 and m = 1

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	Linear Concentration-time Relationship	Plot to Determine the Rate Law
0	$r = k$ $\left\{ \begin{array}{l} \text{CALC} \left\{ \begin{array}{l} -\frac{d[A]}{dt} = k \\ -\int_{[A]_0}^{[A]} d[A] = \int_{t_0}^t k dt \end{array} \right. \end{array} \right.$	$[A] = -kt + [A]_0$ $y = mx + b$ form	 A graph with $[A]$ on the vertical axis and time on the horizontal axis. A straight line with a negative slope is plotted, starting from a point on the vertical axis and extending downwards to the right.
1	$r = k[A]$ $\left\{ \begin{array}{l} \text{CALC} \left\{ \begin{array}{l} -\frac{d[A]}{dt} = k[A] \\ -\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_{t_0}^t k dt \end{array} \right. \end{array} \right.$	$\ln[A] = -kt + \ln[A]_0$ $y = mx + b$ form	 A graph with $\ln[A]$ on the vertical axis and time on the horizontal axis. A straight line with a negative slope is plotted, starting from a point on the vertical axis and extending downwards to the right.
2	$r = k[A]^2$ $\left\{ \begin{array}{l} \text{CALC} \left\{ \begin{array}{l} -\frac{d[A]}{dt} = k[A]^2 \\ -\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = \int_{t_0}^t k dt \end{array} \right. \end{array} \right.$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$ $y = mx + b$ form	 A graph with $\frac{1}{[A]}$ on the vertical axis and time on the horizontal axis. A straight line with a positive slope is plotted, starting from a point on the vertical axis and extending upwards to the right.

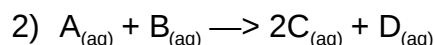
Student Packet: 4.2: Rate Laws: AssessMe question

- 1) Which equation below represents a rate law written in the standard form?
- A) $-d[H_2]/dt = -1/2 d[O_2]/dt$
B) $-d[H_2] = k_{obs}[O_2]dt$
C) $-d[H_2]/dt = k_{obs}[H_2]^{1/2}/[O_2]$
D) $-d[H_2]/d[O_2] = k_{obs}[O_2]$
E) I'm clueless
- 2) Which reaction rate law below has an order of 4?
- A) $d[A]/dt = k_{obs}[A][B]$
B) $d[A]/dt = k_{obs}[A]^2[B]$
C) $d[A]/dt = k_{obs}[A]^4[B]^{-1}$
D) $d[A]/dt = k_{obs}[A]^5/[B]$
E) I'm clueless
- 3) $\text{Log}(0.1) - \text{Log}(0.001) =$
- A) 0.1 B) 100 C) 2 D) 0.01 E) I'm clueless
- 4) $\text{Ln}(x)$ where Ln is a natural logarithm is related to $\text{Log}(x)$ where Log is a base 10 logarithm by:
- A) $\text{Ln}(x) = \text{Log}(x)$
B) $\text{Log}(x)/\text{Ln}(x) = \text{erf}(x)$
C) There is no simple relationship between these two values.
D) $\text{Ln}(x) = 2.303 \cdot \text{Log}(x)$
E) I'm clueless
- 5) The rate of a chemical reaction between substances A and B is found to follow the rate equation $\text{rate} = k[A]^2[B]$ where k is a constant. If the concentration of A is halved, what should be done to the concentration of B to make the reaction go at the same rate as before?
- A) The concentration of B should be kept constant.
B) The concentration of B should be doubled.
C) The concentration of B should be halved.
D) The concentration of B should be quadrupled.
E) I'm clueless
- 6) The rate of the reaction $2\text{NO} + \text{Cl}_2 \longrightarrow 2\text{NOCl}$ is given by the rate equation: $\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$. The value of the rate constant can be increased by:
- A) increasing the concentration of NO.
B) increasing the concentration of Cl_2 .
C) increasing the temperature.
D) doing all of these.
E) I'm clueless

Student Packet: 4.2: Rate Laws: ShowMe questions

- 1) The rate of a chemical reaction $A \rightarrow B + C$ is expressed only in terms of $[A]$. The rate of disappearance of A is $0.002 \text{ mol/l}\cdot\text{s}$ when $[A] = .4 \text{ mol/l}\cdot\text{s}$. Calculate k if the reaction is:

- a) zero order
- b) first order
- c) second order



For the reaction above, carried out in solution at 30°C , the following kinetic data were obtained:

Experiment	Initial concentration of reactants (mol/l)		Initial rate of reaction (mol/l·hr)
	$[A]_0$	$[B]_0$	
1	0.480	0.200	12.00
2	0.480	0.050	3.00
3	0.720	0.100	13.50
4	0.240	0.050	0.75
5	0.480	0.025	1.50

What is the rate law for this reaction?

- 3) The following data give the partial pressure of reactant A as a function of time and were obtained at 150°C for the reaction $A_{(g)} \rightarrow B_{(g)} + C_{(g)}$

$P_A \text{ atm}$	0.0493	0.0248	0.0100	0.0062	0.0042
$t \text{ sec}$	100	200	500	800	1200

Graphically determine the rate expression for the given reaction.

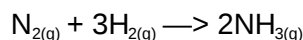
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$P_A \text{ atm}$	0.0493	0.0248	0.0100	0.0062	0.0042
$t \text{ sec}$	100	200	500	800	1200

Algebraically determine the rate expression for the given reaction.

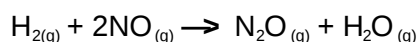
Student Packet: 4.2: Rate Laws: TestMe questions

- 1) Ammonia may be synthesized according to the reaction:



If the rate of disappearance of $\text{N}_{2(g)}$ is $0.001 \text{ mol/l}\cdot\text{s}$, what are the corresponding rates of disappearance of $\text{H}_{2(g)}$ and appearance of $\text{NH}_{3(g)}$?

- A) $-0.001 \text{ mol/l}\cdot\text{s}$ and $0.001 \text{ mol/l}\cdot\text{s}$
 B) $-0.003 \text{ mol/l}\cdot\text{s}$ and $0.002 \text{ mol/l}\cdot\text{s}$
 C) $0.003 \text{ mol/l}\cdot\text{s}$ and $-0.002 \text{ mol/l}\cdot\text{s}$
 D) $0.003 \text{ mol/l}\cdot\text{s}$ and $0.002 \text{ mol/l}\cdot\text{s}$
 E) $0.001 \text{ mol/l}\cdot\text{s}$ and $0.001 \text{ mol/l}\cdot\text{s}$
- 2) Hydrogen reacts with nitric oxide to form nitrous oxide:



The following data were gathered at 25°C :

$[\text{NO}]_0(\text{M})$	$[\text{H}_2]_0(\text{M})$	rate ($\text{mol/l}\cdot\text{s}$)
0.3	0.35	2.835×10^{-3}
0.6	0.35	1.134×10^{-2}
0.6	0.7	2.268×10^{-2}

What is the value of k ?

- A) $1 \text{ mol/l}\cdot\text{s}$
 B) $2.835 \times 10^{-3} \text{ l}^2/\text{mol}^2\cdot\text{s}$
 C) $7.714 \times 10^{-2} \text{ l}^2/\text{mol}^2\cdot\text{s}$
 D) $9.00 \times 10^{-2} \text{ l}^2/\text{mol}^2\cdot\text{s}$
 E) $4.5 \times 10^{-2} \text{ l}^2/\text{mol}^2\cdot\text{s}$
- 3) For a hypothetical chemical reaction that has stoichiometry $2\text{X} + \text{Y} \longrightarrow \text{Z}$, the following rate data were gathered at a constant temperature:

$[\text{X}]^0(\text{M})$	$[\text{Y}]^0(\text{M})$	rate ($\text{mol/l}\cdot\text{s}$)
0.3	0.2	9.0×10^{-5}
0.6	0.4	1.8×10^{-4}
0.6	0.8	3.6×10^{-4}
0.9	1.2	5.4×10^{-4}

What is the rate law for this reaction?

- A) $r = k[\text{X}]$ B) $r = k[\text{Y}]$ C) $r = k$ D) $r = k[\text{X}][\text{Y}]$ E) $r = k[\text{Y}]^2$
- 4) $\text{A} + \text{B} \longrightarrow \text{C} + \text{D}$
 The following data were collected for the concentration of reactant A over time at 25°C . What is the rate law dependence on $[\text{A}]$?

$[\text{A}] (\text{M})$	.0211	.0198	.0176	.0133	.0116	.0096	.0074
$t (\text{min})$	0	10	31	67	100	133	178

- A) zero order B) first order C) second order D) third order E) fourth order
- 5) The proper units for the rate constant of a second order reaction in which concentration is expressed in mol/l are?
- A) s^{-1} B) l^2/mol^2 C) $\text{mol/l}\cdot\text{s}$ D) l/mol E) $\text{l/mol}\cdot\text{s}$