



# AP\* Chemistry

## Arrhenius Made Easy

(At Least As Easy As It's Ever Going To Get!)

Chemistry is defined as the study of matter and energy. Unfortunately, the study of matter consumes most of our class time. Why? It's easier. Matter is tangible; the amount of matter present is easily measured with a balance or other simple device. Students can directly observe matter in the case of liquids and solids or at least observe its effects in the case of gases. Students can also easily observe changes in matter as chemical reactions take place. The study of energy, on the other hand, is far more challenging since *only* the effects of energy changes can be measured. Consequently, two sets of measurements must be made, final and initial, and calculations are sure to follow.

How do we know that the study of matter dominates AP\* Chemistry classrooms? Simple, at the reading of the exams, year after year, students do a fine job of explaining changes in matter, but rarely tie the changes in matter to the changes in energy. Valuable points are lost. Students don't realize that the changes in matter are a direct result of the changes in energy and that it is a cause and effect relationship. Students simply dwell on the effect and neglect the cause. This topic within the kinetics unit focuses on the cause, the energy cause. Additionally, it provides the essential link between the study of kinetics and the study of thermodynamics.

### The Collision Model

What we know so far:

- The rate of a chemical reaction depends on the concentration of the reactants.
- The order of each reactant depends on the detailed reaction mechanism.
- The temperature of the reaction affects the value of the rate constant.
- The general rule of thumb is that a 10°C increase in temperature doubles the reaction rate.
- The molecules must collide in order to react, but that's not all—they must collide with sufficient energy and the correct orientation (geometry) so that the collisions are *effective*.

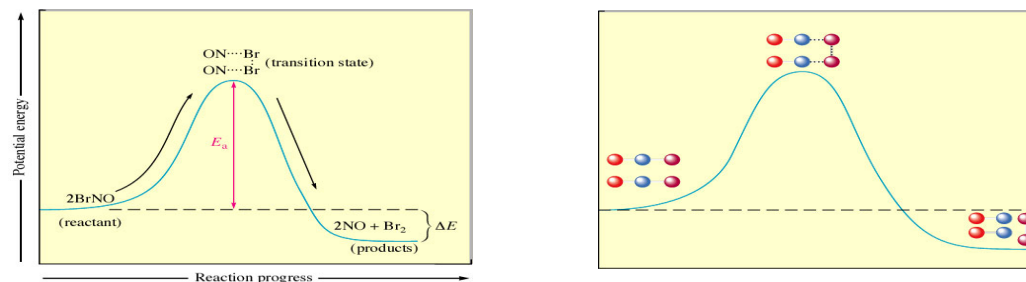
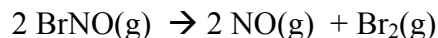
What else do we *need* to know?

- Why the relationship between an increase in temperature and an increase in rate is *not* a direct relationship.
- Why thermodynamically spontaneous reactions such as combustion reactions or  $C_{(\text{graphite})} \rightarrow C_{(\text{diamond})}$  don't just happen "spontaneously".
- Why the activation energy is so very important to both kinetics and thermodynamics.

### The Relationship Between Energy and Speed

In the 1880s, Svante Arrhenius (the acid guy) first proposed the existence of threshold energy, called the **activation energy**, which must be overcome to produce a chemical reaction. The collision model is simple, the kinetic energy of the molecules before collision is converted to potential energy as the molecules are distorted during a collision to break bonds and rearrange the atoms into the product molecules.

Consider this reaction:



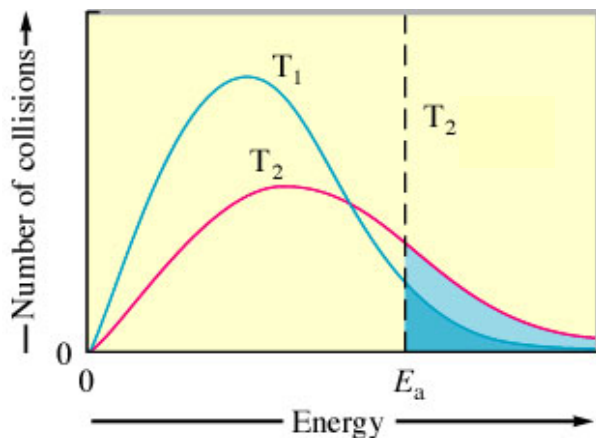
We envision reaction progress as shown above.

- Never be surprised if the words “transition state” are replaced with “activated complex”. These two terms describe the highly unstable collection of atoms bound together at the top of the energy hump.
- The next collision occurring between the activated complex and any other molecule will supply more energy to the unstable species and can break bonds. Which bonds are broken determines whether it slides back to re-form reactants or slides forward to create products.
- Likewise, “reaction progress” can be replaced with “time”.
- The activation energy,  $E_a$ , is the threshold energy and must be overcome if the reaction is to proceed. **If you are asked to compare graphs of this shape, remember that the taller the hump, the larger the  $E_a$ , the smaller the value of the rate constant,  $k$ , and the slower the rate.**
- $\Delta E$  is the net energy change and represents the enthalpy,  $\Delta H$ , of the reaction. Is the above reaction exothermic or endothermic?

How does temperature affect  $E_a$ ?

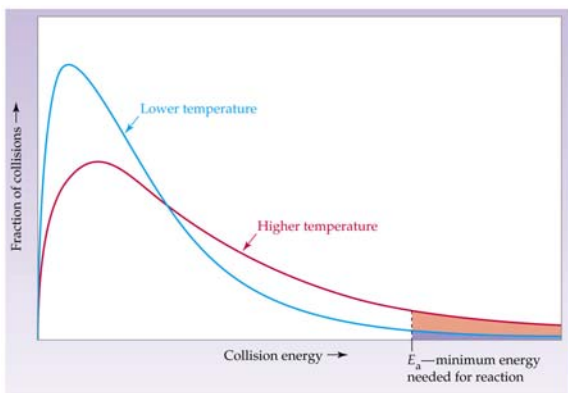
- Temperature is defined as the average kinetic energy of the molecules.
- The higher the temperature, the higher the average KE, the more energetic the molecules. Think “heat ‘em up, speed ‘em up”.
- The more energetic the molecules, the more energetic the collisions!

Examine this graph:



Which temperature is greater?

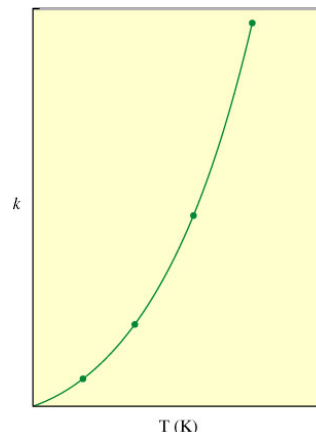
Which temperature has more molecules with enough energy to overcome the activation energy?



Generally, when the temperature is doubled, the fraction of molecules having high enough  $E$  to overcome  $E_a$ , WAY MORE than doubles, which explains WHY the relationship between reaction rate and temperature is NOT linear. It is exponential! Need proof?

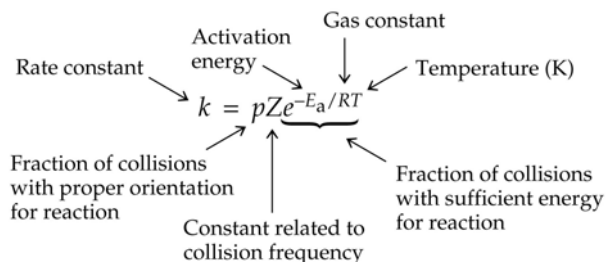
If we graph the value of the rate constant,  $k$ , versus the Kelvin temperature, we get the graph pictured right. See? Not linear, but rather, *exponential*. That means that the natural log function is in your immediate future [again].

Double the Kelvin temperature and you more than double the rate constant. Since Calculus is not a pre-requisite for AP Chemistry, we linearize the data, just as we did for integrated rate law, so we can deal with the mathematics more simply. Slope is your friend!



## The Arrhenius Equation

Arrhenius derived the following equation, which is way too complicated:



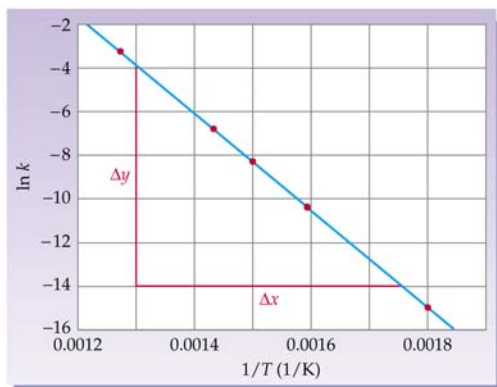
Scary, huh? Relax; you don't have to memorize that one! I'll spare you the derivations that allow us to arrive at the one you do need to know:

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

Labels for the simplified equation:

- $\ln k$ :  $y$
- $\frac{-E_a}{R}$ :  $m$
- $\frac{1}{T}$ :  $x$
- $\ln A$ :  $b$

This version allows us to simplify the relationship between the rate constant and Kelvin temperature.  $A$  replaces the constants  $p$  and  $Z$  in the original equation—you'll be asked to solve for  $k$ ,  $E_a$ , or  $T$ .



To summarize, if you plot  $\ln k$  vs. the reciprocal of Kelvin temperature, you get a straight line with a slope equal to  $\frac{-E_a}{R}$ .

That means  $E_a = -R \times \text{slope}$ .

This is activation ENERGY, so use the ENERGY “R” which is  $\frac{8.31 \text{ J}}{\text{K} \cdot \text{mole}}$ . If you prefer Algebra methods over graphical

methods, there is a two-point formula as well which is:  $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ .

## Graphing Calculator Tutorial (Not intended to insult your intelligence.)

First, you need to recognize when you have an Arrhenius equation problem on your hands! It is when you are given  $k$ -time data OR are asked to calculate the activation energy,  $E_a$ .

### ENTERING DATA INTO LISTS

- Press  $\boxed{2\text{nd}}\boxed{+}\boxed{4}\boxed{\text{ENTER}}$  to clear all lists.
- Press  $\boxed{\text{STAT}}\boxed{\text{ENTER}}$  and arrow to the first cell in L1 if necessary.
- Enter your temperature data in L1 and your  $k$  values in L2.

### PERFORMING A BATCH TRANSFORM

To obtain reciprocal Kelvin temperatures:

- Press  $\boxed{\leftarrow}$  and/or  $\boxed{\uparrow}$  repeatedly until L1 is highlighted (Go to the “tippy top” of L1).
- Press  $\boxed{(}\boxed{2\text{nd}}\boxed{1}\boxed{+}\boxed{2}\boxed{7}\boxed{3}\boxed{)}\boxed{x^{-1}}\boxed{\text{ENTER}}$  to convert the Celsius temperatures to reciprocal Kelvin temperatures. If Kelvin temperatures were given in the problem, then simply press  $\boxed{2\text{nd}}\boxed{1}\boxed{x^{-1}}\boxed{\text{ENTER}}$  to calculate the reciprocals of the Kelvin temperatures.

To obtain the natural log of the  $k$  values:

- Press  $\boxed{\rightarrow}$  and/or  $\boxed{\uparrow}$  repeatedly until L2 is highlighted (Go to the “tippy top” of L2).
- Press  $\boxed{\text{LN}}\boxed{2\text{nd}}\boxed{2}\boxed{\text{ENTER}}$  to convert the rate constant values to  $\ln k$ .

### RUNNING A LINEAR REGRESSION & GRAPHING THE DATA

To run the linear regression, view the statistics and paste the equation into  $Y=$  :

Press  $\boxed{\text{STAT}}\boxed{\rightarrow}$  (to get to CALC)  $\boxed{4}\boxed{2\text{nd}}\boxed{1}\boxed{,}\boxed{2\text{nd}}\boxed{2}\boxed{,}\boxed{\text{VARS}}\boxed{\rightarrow}$  (to YVARS)  $\boxed{\text{ENTER}}\boxed{\text{ENTER}}\boxed{\text{ENTER}}$ . The statistics relating to the linear regression (line of best fit) will be displayed. Record the slope!

Remember  $E_a = -R \times \text{slope}$ .

- Press  $\boxed{2\text{nd}}\boxed{Y=}$  and make sure only one plot is ON. Set the plot to  $\text{L1}$   $\text{L2}$ .
- To view the graph, press  $\boxed{2\text{nd}}\boxed{\text{GRAPH}}$ . If additional equations are being graphed, press  $\boxed{2\text{nd}}\boxed{Y=}$  to clear them out.

## DETERMINING $y$ WHEN GIVEN $x$

To calculate  $k$  when given the Kelvin temperature:

- First realize that your graph is  $\ln k$  vs.  $1/T$ .
- Press  $\boxed{2\text{nd}}\boxed{\text{TRACE}}\boxed{\text{ENTER}}$  to get to CALCULATE and select VALUE.
- Enter the Kelvin temperature given and press  $\boxed{x^{-1}}\boxed{\text{ENTER}}$ .
  - If you get an error message, it's because your window is not set properly. The calculator can only calculate what is displayed on the graphing screen.
  - Stop. Ask yourself if your  $x$ -value is within the data you graphed (if so, you are interpolating) or outside the range (if so, you are extrapolating). If interpolating, try again—you should not get an error!
  - If extrapolating, you may need to quit the graph screen ( $\boxed{2\text{nd}}\boxed{\text{MODE}}$ ) and calculate the reciprocal Kelvin temperature. Once you have that value, press  $\boxed{\text{WINDOW}}$  to examine your Xmin and Xmax. Use your arrow keys to adjust the values so that your desired value is *included within* the values displayed on the graph.
  - Once you've adjusted the window, press  $\boxed{2\text{nd}}\boxed{\text{TRACE}}$  and enter the Kelvin temperature given and press  $\boxed{x^{-1}}\boxed{\text{ENTER}}$ .
- The  $y$ -value displayed is the natural log of  $k$ , NOT the value of  $k$ . Record the  $y$ -value.
- Quit the graph screen by pressing  $\boxed{2\text{nd}}\boxed{\text{MODE}}$  and then press  $\boxed{2\text{nd}}\boxed{\text{LN}}$  and enter the number you recorded followed by  $\boxed{\text{ENTER}}$ .

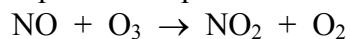
## DETERMINING $x$ WHEN GIVEN $y$

To calculate the Kelvin temperature when given  $k$ :

- First realize that your graph is  $\ln k$  vs.  $1/T$ .
- Press  $\boxed{Y=}$  and  $\boxed{\nabla}$  to Y2. Press  $\boxed{\text{LN}}$  and enter the  $k$  value given in the question.
- Press  $\boxed{\text{GRAPH}}$ . If you see the intersection of the two lines, Press  $\boxed{2\text{nd}}\boxed{\text{TRACE}}\boxed{5}\boxed{\text{ENTER}}\boxed{\text{ENTER}}\boxed{\text{ENTER}}$  to get to CALCULATE, select INTERSECTION and calculate the ordered pair of the point of intersection. You are interested in the  $x$ -value, but remember the  $x$ -value displayed is the reciprocal of the Kelvin temperature you seek. Record the  $x$ -value displayed on the screen.
  - If you do NOT see the point of intersection, then press  $\boxed{\text{WINDOW}}$  and adjust your window until you do. This may require some trial and error. The calculator can only calculate what is displayed on the graph, so the intersection must be displayed.
- Quit the graph screen by pressing  $\boxed{2\text{nd}}\boxed{\text{MODE}}$  and calculate the inverse of the reciprocal Kelvin temperature displayed by entering the  $x$ -value you recorded and pressing  $\boxed{x^{-1}}\boxed{\text{ENTER}}$ . Record the Kelvin temperature. Convert back to Celsius if the problem requires.

## Arrhenius #1 (Adapted from Zumdahl, 5<sup>th</sup> edition #53)

Experimental values for the temperature dependence of the rate constant for the gas-phase reaction



are as follows:

T (K)	$k$ (L/mol • s)
195	$1.08 \times 10^9$
230.	$2.95 \times 10^9$
260.	$5.42 \times 10^9$
298	$12.0 \times 10^9$
369	$35.5 \times 10^9$

Show all work and pay particular attention to sig. figs. and units when reporting your answers.

- Is this reaction fast or slow? Justify your answer.
- What is the overall order of this reaction? Justify your answer.
- What is the activation energy for this reaction?
- What is the value of  $k$  when the temperature is 455 K?
- What is the temperature when the rate constant has a value of  $22.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ?

## Arrhenius #2 (Adapted from Brady, 4<sup>th</sup> edition #96)

The following data were collected for a reaction.

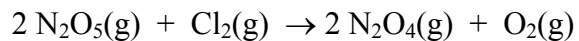
$k$ (L mol <sup>-1</sup> s <sup>-1</sup> )	T (°C)
$2.88 \times 10^{-4}$	320
$4.87 \times 10^{-4}$	340
$7.96 \times 10^{-4}$	360
$1.26 \times 10^{-3}$	380
$1.94 \times 10^{-3}$	400

Show all work and pay particular attention to sig. figs. and units when reporting your answers.

- (a.) Is this reaction fast or slow? Justify your answer.
- (b.) What is the activation energy for this reaction?
- (c.) What is the value of  $k$  when the temperature is 640 K?
- (d.) What is the temperature when the rate constant has a value of  $50.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ ?

### Arrhenius #3 (Adapted from Chang, 6th edition #37)

Variation of the rate constant with temperature for the first-order reaction



is given in the following table.

$k$ ( $\text{s}^{-1}$ )	$T$ ( $^{\circ}\text{C}$ )
$1.74 \times 10^{-5}$	25
$6.61 \times 10^{-5}$	35
$2.51 \times 10^{-4}$	45
$7.59 \times 10^{-4}$	55
$2.40 \times 10^{-3}$	65

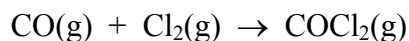
Show all work and pay particular attention to sig. figs. and units when reporting your answers.

- Is this reaction fast or slow? Justify your answer.
- What is the activation energy for this reaction?
- What is the value of  $k$  when the temperature is  $100^{\circ}\text{C}$ ?
- What is the temperature when the rate constant has a value of  $9.65 \times 10^{-4} \text{ s}^{-1}$ ?



#### Arrhenius #4 (Adapted from Chang, 6<sup>th</sup> edition #39)

Given the same reactant concentrations, the reaction



at 250°C is  $1.50 \times 10^3$  times as fast as the same reaction at 150° C.

(a.) Calculate the activation energy for this reaction.

(b.) What is the value of  $k$  when the temperature is 100°C?

#### Arrhenius #5 (Adapted from Whitten, Davis, Peck 5<sup>th</sup> edition #51)

Biological reactions nearly always occur in the presence of enzymes as catalysts. The enzyme catalase, which acts on the decomposition of hydrogen peroxide, reduces the  $E_a$  for the reaction from 72 kJ/mol (uncatalyzed) to 28 kJ/mol (catalyzed) at 25°C. The total  $\Delta E$  for the reaction is -204 kJ/mol.

(a.) Write the balanced chemical equation for the decomposition of hydrogen peroxide.

(b.) Draw and label a reaction coordinate (potential energy) diagram for this reaction at 25°C.

(c.) What is the activation energy of the uncatalyzed reverse reaction?

(d.) What is the activation energy for the catalyzed reverse reaction?

## #6 (adapted from the 2004 AP Chemistry Exam)

The following data was collected during the decomposition reaction of a colored chemical species, X, into colorless products monitored with a spectrophotometer by measuring changes in absorbance over time. The reaction was carried out at 25°C and 1atm pressure. Species X has a molar absorptivity constant of  $2.75 \times 10^3 \text{ cm}^{-1}\text{M}^{-1}$  and the path length of the cuvette containing the reaction mixture is 1.00 cm. The data for the experiment are given in the table below.

[X] (M)	Absorbance	Time (min)
?	0.330	0.0
$6.25 \times 10^{-5}$	0.172	10.0
$5.00 \times 10^{-5}$	0.138	15.0
$3.50 \times 10^{-5}$	0.096	?

- (a.) Calculate the initial concentration of the colored species.
- (b.) Use the data given for concentration and time to determine the order of the reaction. Justify your answer.
- (c.) What is the value of the rate constant? Specify its units.
- (d.) Calculate the number of minutes it takes for the absorbance to drop from 0.330 to 0.096.
- (e.) Calculate the half-life of the reaction. Include units with your answer.

An additional experiment was performed to determine the value of the rate constant for this reaction. It was determined that the reaction had a rate constant of  $1.15 \times 10^4$  at  $35^\circ\text{C}$ .

(f.) What is the activation energy for this reaction?

(g.) What is the value of  $k$  when the temperature is  $45^\circ\text{C}$ ?

# Kinetics Concept Map

