

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

I'll hold your hand through the first one! Remember, pages 4 & 5 in the student handout serve as your cheat sheet AND the kids have no fear. They do this kind of stuff a lot in math class. If YOU get stuck, they can probably bail you out!

Experimental values for the temperature dependence of the rate constant for the gas-phase reaction  
 $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$

are as follows: (3 SF)

Calculator screen: Do not be alarmed that it rounded the values!

Before batch transform:

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	$35.5 \times 10^9$

L1	L2	L3	1
195	1.08E9	-----	
230	2.95E9		
260	5.42E9		
298	1.2E10		
369	3.6E10		
-----	-----		
L1(1)=195			

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.

Fast. The  $k$  values are enormous at these relatively low Kelvin temperatures, indicating a very fast reaction. Students should link the magnitude of  $k$  to the magnitude of the temperatures given to receive full credit for this question.

(b.) What is the overall order for this reaction? Justify your answer.

Second order. Examine the units given on  $k$ . Never, ever forget that rate =  $\Delta M / \Delta \text{time}$ . For that to be the case, the units given for  $k$  would have to be multiplied by  $M^2$

$$\therefore \text{rate} = \frac{k \text{ L}}{\text{mol} \cdot \text{s}} [A][A] = \frac{k}{M \cdot \text{s}} [M^2] = k \left( \frac{M}{s} \right)$$

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

First, note that the temperature data is already Kelvin. Batch transform the data so that we have  $1/T$  in L1 and  $\ln k$  in L2. The data screen is shown above. Next, calculate a linear regression (paste the equation into Y1) to determine the slope:

L1	L2	L3	1
.00308	20.8	-----	
.00435	21.805		
.00385	22.413		
.00336	23.208		
.00271	24.293		
-----	-----		
L1(1) = .0051282051...			

The slope is equal to  $-1435.7$  using more than three sig. figs.

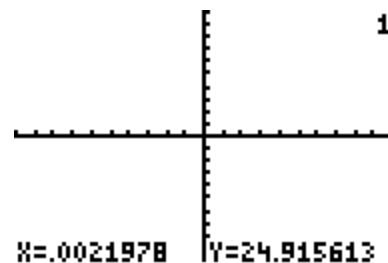
```
LinReg
y=ax+b
a=-1435.715038
b=28.07103087
r2=.9940646537
r=-.9970279102
```

- The  $E_a = -R \times \text{slope}$
- So,  $E_a = -(8.31 \text{ J/mol} \cdot \text{K}) \times (-1435.7 \text{ K})$   
 $= 11,930 \text{ J/mol}$   
 $= 11,900 \text{ J/mol (3SF)} = 11.9 \text{ kJ/mol}$

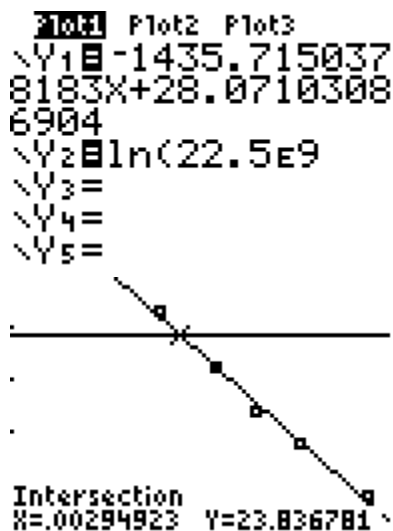
- Note, we ignore the units on  $\ln k$  after taking the natural log—the units become “one”.
- Therefore, the units on the slope are  $(1/(1/K))$  which is plain old units of K which thus cancel, so that  $E_a$  is reported in J/mol.
- Point out to students that this  $E_a$  value makes sense. There is relatively low activation energy required for a reaction occurring at very low temperatures with enormous  $k$ -values.

(d.) What is the value of  $k$  when the temperature is 455 K?

- **QUICK TIP:** Press **ZOOM****[6]** to fit your graph to a standard window. (Notice that the regression line disappears and the graph looks blank, but that’s OK.) We have to do this since the calculation we are asked to make is outside the window range that **ZOOM****[9]** set for us and the calculator can only calculate a value if it is displayed in the graph window.
- Realize that temperatures are  $x$ -values, and more importantly, we need to take the reciprocal of 455 K.
- Press **2nd****TRACE****[ENTER]** and **X=** appears on your screen. Next, enter 455 then press **[x<sup>-1</sup>]** to calculate the reciprocal of 455 K. Finally press **[ENTER]** to get the  $y$ -value on the final screen displayed at right.
- Realize that the  $y$ -value you just found is NOT  $k$ ! It’s the natural log of  $k$ .
- Press **2nd****MODE** to quit the graph screen followed by **2nd****[LN]** 24.92 (I rounded) and press **[ENTER]**.
- Record  $k$  to 3SF and put the proper units (see the table heading from the original data).
- Our  $k$  value is equal to  $6.65 \times 10^{10}$  L/mol • sec.



(e.) What is the temperature when the rate constant has a value of  $22.5 \times 10^9 M^{-1}s^{-1}$ ?



- Now we are looking for  $x$  when we know  $y$ . Remember our  $x$ -values are  $1/T$ , not  $T$ .
- Press **[Y=]** and **[v]** until your cursor arrives at **Y2=**. Press **[LN]** and enter the  $k$  value given in the problem,  $22.5 \times 10^9$ .
- Press **[GRAPH]**. If you see the intersection there is no need to adjust the window.
- If you do NOT see the intersection (because you pressed **ZOOM****[6]** earlier), press **ZOOM****[9]**. If you still do NOT see an intersection, press **WINDOW** and adjust the  $X$  &  $Y$  MIN and MAX until the intersection is displayed.
- Press **2nd****TRACE****[5]****[ENTER]****[ENTER]****[ENTER]** to calculate the  $x$ -value. Record it since it is not the temperature, but rather the reciprocal.

- Press **2nd****MODE** to quit the graph screen.
- Enter the  $x$ -value you recorded and press **[x<sup>-1</sup>]****[ENTER]**.
- Our calculated temperature is  $339.07 = 339$  K (3SF).

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

The following data were collected for a reaction. (3\* SF—T's are 2SF, but become 3 when converted to Kelvins)

$k$ (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.

Slow. The value for the rate constant,  $k$  is very small at these VERY high Celsius temperatures. Students should link the magnitude of  $k$  to the magnitude of the temperatures given to receive full credit for this question.

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

- Be careful entering this into the calculator. The columns are reversed! Also note the given temperatures are Celsius.

L1	L2	L3	1
000149	-8.153	-----	
.00163	-7.627		
.00158	-7.136		
.00153	-6.677		
.00149	-6.245		
-----	-----		

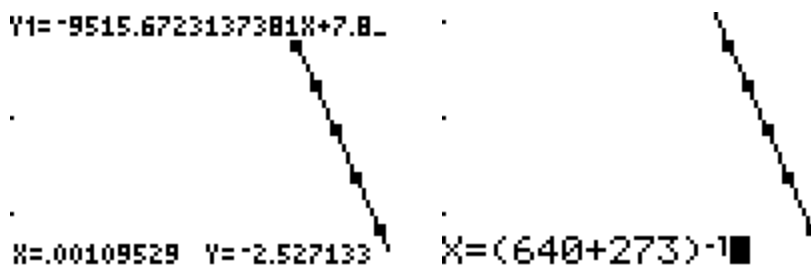
L1() = .0016863406...

```
LinReg
y=ax+b
a=-9515.672314
b=7.895289812
r2=.9999976668
r=-.9999988334
```

- So,  $E_a = -R$  (slope) = 79,075 J/mol = 79.1 kJ/mol (2 SF). This makes sense since it is an enormous activation energy at VERY high temperatures with small  $k$  values.

(c.) What is the value of  $k$  when the temperature is  $640^\circ\text{C}$ ?

- $640^\circ\text{C}$  is way outside our range. Its KELVIN reciprocal is  $0.001095\dots$ . You must change the window.



- $Y = -2.527\dots$ , but that's  $\ln k$
- $k = 0.07989\dots = 0.0799 \text{ L mol}^{-1} \text{ s}^{-1}$  which is much faster since we doubled the initial starting temperature!

(d.) What is the temperature when the rate constant has a value of  $50.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ ?

- You'll have to adjust the window to display this intersection.  $\ln(50.5 \times 10^{-4}) = -5.3$ , so adjust the window to display that y-value.
- **QUICK TIP:** If you have trouble adjusting the window, or are simply in a hurry, press  $\boxed{\text{ZOOM}}\boxed{6}$ . This gives you the standard 4 quadrant graph and allows you to see your intersections (at least most of the time) so you can skip setting your window entirely!
- The x-value is  $0.001386\dots$  which is  $1/T$ .
- $T = 721.5 \text{ K} = 722 \text{ K}$  or better yet,  $449^\circ\text{C}$  since the original temperatures were recorded in degrees Celsius.

### 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 (°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

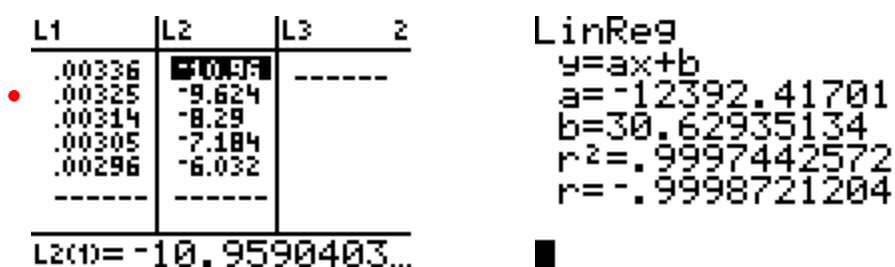
Show all work and pay particular attention to sig. figs. and units when reporting your answers.

(a.) Is this reaction fast or slow? Justify your answer.

Slow. The value for the rate constant,  $k$  is very small at these relatively low Celsius temperatures. Students should link the magnitude of  $k$  to the magnitude of the temperatures given to receive full credit for this question.

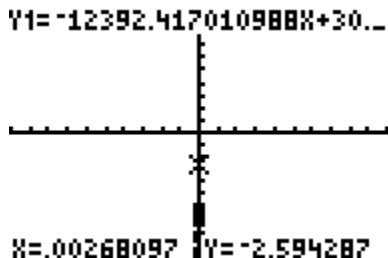
(b.) What is the activation energy for this reaction?

- Be careful entering this into the calculator. The columns are reversed! Also note the given temperatures are Celsius.



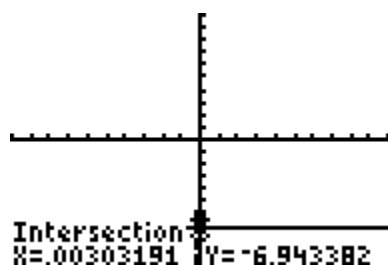
- So,  $E_a = -R(\text{slope}) = 102,980 \text{ J/mol} = 103 \text{ kJ/mol}$  (3 SF, since Kelvin temperatures were used for the graph). This activation energy is reasonable since it is a large value at relatively low Celsius temperatures for a reaction with small  $k$  values.

(c.) What is the value of  $k$  when the temperature is  $100^\circ\text{C}$ ?



- The Kelvin reciprocal of 100 degrees Celsius is equal to 0.00268
- Using zoom 6,  $y = \ln k = -2.594287...$  so,  $k = 0.0747 \text{ s}^{-1}$

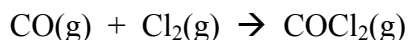
(d.) What is the temperature when the rate constant has a value of  $9.65 \times 10^{-4} \text{ s}^{-1}$ ?



- The  $y$ -value is  $\ln k$ , so enter that value into Y2=
- Find the intersection and realize that the  $x$ -value is the reciprocal Kelvin temperature.
- $x = 0.00303191 = 1/K$  ;  $K = 329.825 = 56.8^\circ\text{C}$  (3 SF).

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

Given the same reactant concentrations, the reaction



at  $250^\circ\text{C}$  is  $1.50 \times 10^3$  times as fast as the same reaction at  $150^\circ\text{C}$ .

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

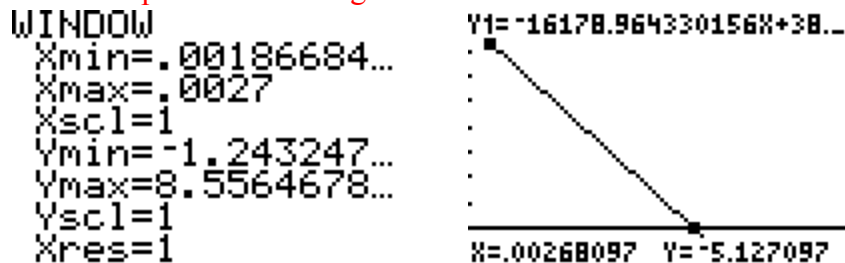
- Students may have a difficult time getting started. Since the problem states "...times as fast as..." students should assign a value of 1 as the  $k$ -value for the slow reaction and 1,500 as a  $k$ -value for the fast reaction.
- The Celsius temperatures are given but must be converted to Kelvin and also converted to reciprocals. Notice the perfect r. No surprise since we only have two points to plot!

```
LinReg
y=ax+b
a=-16178.96433
b=38.24814262
r^2=1
r=-1
```

- The slope =  $-16,179$ , so  $E_a = -R(\text{slope}) = 134,447 \text{ J/mol} = 134 \text{ kJ/mol}$ .

(b.) What is the value of  $k$  when the temperature is  $100^\circ\text{C}$ ?

- The reciprocal of 100 degrees Celsius = 0.00268. Reset the window or just use zoom 6.



- $y = -5.127 = \ln k$ , so  $k = 5.93 \times 10^{-3}$ .

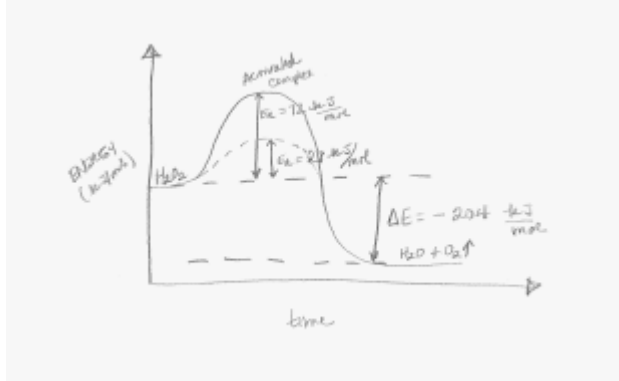
### Arrhenius #5 (Adapted from Whitten, Davis, Peck 5<sup>th</sup> edition #51)

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  $72 \text{ kJ/mol}$  (uncatalyzed) to  $28 \text{ kJ/mol}$  (catalyzed) at  $25^\circ\text{C}$ . The total  $\Delta E$  for the reaction is  $-204 \text{ kJ/mol}$ .

(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  $25^\circ\text{C}$ .



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

- The amount of energy required for the reverse reaction is the sum of the energy released plus the activation energy for the *uncatalyzed* reaction, therefore,  $276 \text{ kJ/mol}$

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

- The amount of energy required for the reverse reaction is the sum of the energy released plus the activation energy for the *catalyzed* reaction, therefore,  $232 \text{ kJ/mol}$

## #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
$3.50 \times 10^{-5}$	0.0960	?

(a.) Calculate the initial concentration of the colored species.

$$A = \epsilon l c = abc$$

- $\epsilon = 2.75 \times 10^3$

$$c = \frac{A}{\epsilon l} = \frac{0.330}{(2.75 \times 10^3 \text{ cm}^{-1}\text{M}^{-1})(1.00 \text{ cm})} = 1.20 \times 10^{-4} \text{ M}$$

(b.) Use the data given for concentration and time to determine the order of the reaction. Justify your answer.

- Using concentration-time data: Perform three linear regressions—L1,L2; L1,L3; L1,L4.
- L1, L4 yields the best r value  $\therefore$  the reaction is second order since the graph of 1/concentration vs. time is linear.

```
LinReg
y=ax+b
a=776.1904762
b=8309.52381
r^2=.9998870992
r=.999943548
```

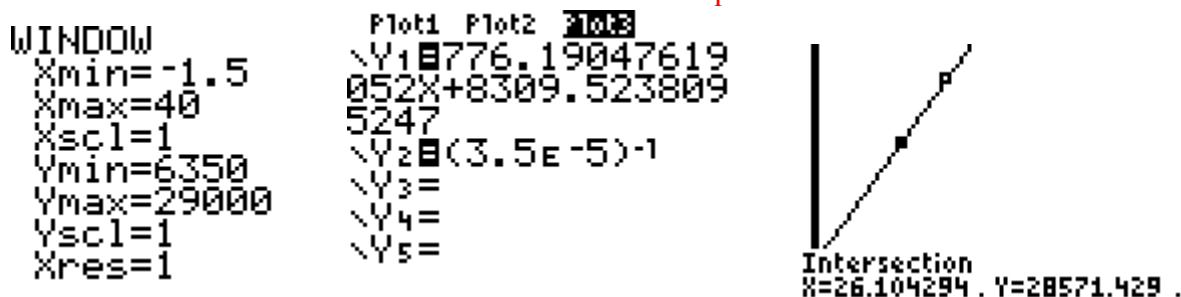


(c.) What is the value of the rate constant? Specify its units.

- The value of  $k = |\text{slope}| = 776.19 = 776 \text{ M}^{-1} \text{ min}^{-1}$

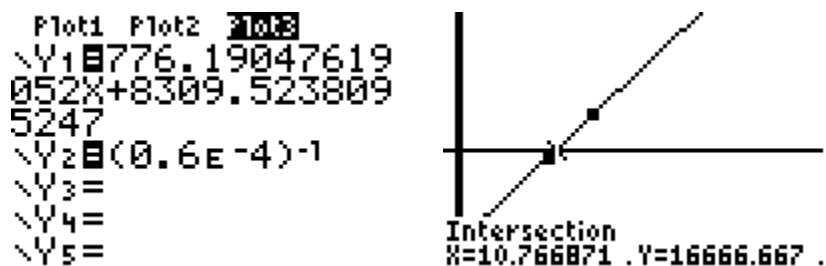
(d.) Calculate the number of minutes it takes for the absorbance to drop from 0.330 to 0.096.

- Be sure you have only one stat plot on and that it is set L1, L4 for the  $x, y$  values.
- An absorbance of 0.096 corresponds to a concentration of  $3.50 \times 10^{-5} \text{ M}$ .
- Our last time entered is 15 minutes, obviously the reaction proceeds further to reach an absorbance as low as 0.0960.
- The window must be adjusted for the increase in time. This is trial and error. I used 40 minutes as a starting point.
- Write an equation in  $y2=$  to the reciprocal of  $3.50 \times 10^{-5}$  or 28,571.
- Calculate the intersection of the two lines. The time required is 26.1 minutes.



(e.) Calculate the half-life of the reaction. Include units with your answer.

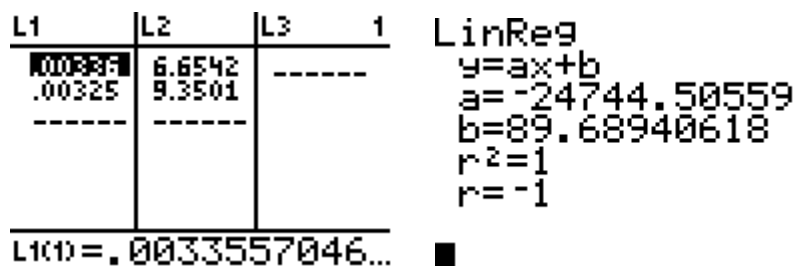
- The  $\frac{1}{2}$ -life is the time it takes for a given concentration to be halved.
- $\frac{1}{2}$  of the original concentration is  $0.60 \times 10^{-4}$ , so reset  $Y2=$  to the reciprocal of that value.
- Calculate the intersection. The  $\frac{1}{2}$ -life is equal to 10.8 minutes



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?

- Be sure and re-set your stat plot to L1,L2.
- Use the  $k$  from part c and this one to construct a graph of  $\ln k$  vs.  $1/\text{Kelvin temperature}$ . The slope of the line is equal to  $-24,744$  as shown below.
- $E_a = -R (\text{slope}) = 205,623 \text{ J/mol} = 206 \text{ kJ/mol}$



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

- The Kelvin reciprocal of 45 degrees Celsius is 0.0031, so the window must be adjusted.
- $\ln k = 11.876 \therefore k = 143,774 = 1.44 \times 10^5 \text{ M}^{-1} \text{ min}^{-1}$

