

# Kinetics Key

Tuesday, February 28, 2017 1:20 PM

## Chemical Kinetics

**Goal:** Our goal in this activity is to explore some applications of chemical kinetics. We begin by thinking critically about collision theory and the role that it plays in the rate of chemical reactions. We then explore rate laws and integrated rate laws and find useful applications of each.

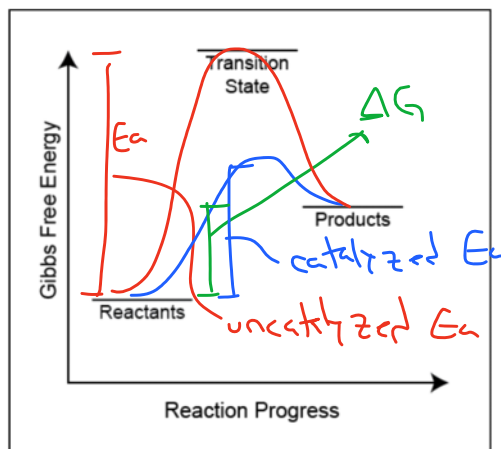
**Arrhenius Equation:**  $k = Ae^{-E_a/RT}$        $\ln \frac{k_2}{k_1} = \frac{-E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$

1. Collision theory requires three things to happen for a chemical reaction to take place. What are these three things?

- Molecules must collide
- Collisions need to occur with the correct molecule orientation
- Molecules must have sufficient energy to overcome activation barrier

2. Consider the reaction coordinate shown.

- Why is the activation energy positive? **The transition state is the highest energy conformation of molecules as they convert from reactants to products – it is not stable.**
- Is this reaction spontaneous? How do you know? **No, the products are at a higher Gibbs Free Energy than reactants ( $\Delta G > 0$ )**
- Is the activation energy for the forward reaction (reactant  $\rightarrow$  products) **larger** or smaller than the activation energy for the reverse reaction (products  $\rightarrow$  reactants)?
- True or false:  $k_{\text{forward}} > k_{\text{reverse}}$ . **False. The reverse is larger since it has a smaller activation energy.**



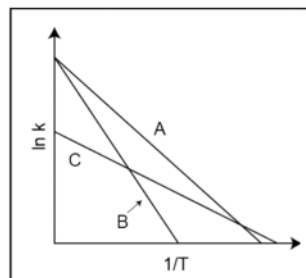
e. Sketch a reaction coordinate if a catalyst is added. How will this affect  $k_{\text{forward}}$ ? **Shown on graph (blue)**

3. The most common form of the Arrhenius equation is  $k = Ae^{-E_a/RT}$ . As discussed, "A" is the pre-exponential factor and  $e^{-E_a/RT}$  is the frequency factor. How does each factor incorporate the requirements of collision theory?

**A includes the orientation effects described in collision theory. The frequency factor addresses the energy requirement (it is the fraction of molecules that have enough energy to overcome the activation energy.**

4. Consider the graph.

- Which reaction (A, B, or C) has the largest pre-exponential factor? **The y-intercept is  $\ln A$  – the more positive these values, the larger A is. A and B have identical pre-exponential factors. They are larger than C.**
- Which has the largest activation energy? **B. The slope is  $-E_a/R$ . Since R is a constant, the steeper the slope, the larger the activation energy. B has the steepest slope.**



calculations using the Arrhenius Equation:

5. If you have 1000 molecules that are ready to react, determine how many have enough energy to overcome the activation barrier under each of these conditions:

a.  $E_a = 15000 \text{ J}$

$T = 250 \text{ K}$

$$e^{-15000 / 8.314(250)} = 0.000734 (1000) = 0.734 \text{ molecules}$$

b.  $E_a = 3.86 \text{ kJ}$

$T = 300 \text{ }^\circ\text{C} = 573.15$

$$e^{-3860 / 8.314(573.15)} = 0.445 (1000) = 445 \text{ molecules}$$

6. Calculate the activation energy of a reaction at 345 K that has a rate constant of  $11 \text{ M}^{-1}\text{s}^{-1}$  and a pre-exponential factor of  $20 \text{ M}^{-1}\text{s}^{-1}$ .

$$11 = 20 e^{-E_a / 8.314(345)}$$

$$-0.5978 = \frac{-E_a}{8.314(345)}$$

$$E_a = 1714.8 \text{ J/mol}$$

7. If the addition of a catalyst decreases the rate constant for the previous problem by 98%, what activation energy for the catalyzed reaction?

$$0.22 = 20 e^{-E_a / 8.314(345)}$$

$$0.011 = e^{-E_a / 8.314(345)}$$

$$-4.51 = \frac{-E_a}{8.314(345)}$$

$$0.98 (11) = 10.78$$

$$k = 11 - 10.78 = 0.22$$

$$E_a = 12935.8 \text{ J/mol}$$

Working on this problem is messy up... but here is the answer if nothing was wrong. New problem

8. Determine the activation energy for a reaction that has a rate constants measured at the following temperatures:

Reaction	Temperature ( $^\circ\text{C}$ )	Rate constant ( $\text{s}^{-1}$ )
1	100 $373.15$	15.86
2	200 $473.15$	198.7

Solution at bottom of key

$$\ln \frac{198.7}{15.86} = \frac{-E_a}{8.314} \left( \frac{1}{473.15} - \frac{1}{373.15} \right)$$

$$2.528 = E_a (6.8125 \times 10^{-5})$$

$$E_a = 37,108.2 \text{ J/mol}$$

9. What is the pre-exponential factor for the reaction in problem 8?

$$15.86 = A e^{-37108.2 / 8.314(373.15)}$$

$$15.86 = 6.39 \times 10^{-6} A$$

$$A = 2482003 \text{ s}^{-1}$$

always has same units as k

**Rate Laws:**

10. For each reaction order, determine the units for the rate constant (use only Molar and seconds)

0 <sup>th</sup>	1 <sup>st</sup>	2 <sup>nd</sup>	5 <sup>th</sup>	7 <sup>th</sup>
$M s^{-1}$	$s^{-1}$	$M^{-1} s^{-1}$	$M^{-4} s^{-1}$	$M^{-6} s^{-1}$

11. The table below has experimental data collected at 25 °C. Using the method of initial rates, determine the rate law for the synthesis of NOBr from NO and Br<sub>2</sub>. Make sure to determine the rate constant.

Reaction	[NO] <sub>0</sub> (M)	[Br <sub>2</sub> ] <sub>0</sub> (M)	Initial rate (M s <sup>-1</sup> )
1	1	1	1.3 × 10 <sup>-3</sup>
2	1.5	1	2.93 × 10 <sup>-3</sup>
3	<del>1.5</del> 1.5	3	8.78 × 10 <sup>-3</sup>

Use method of initial rates

$$\frac{1.3 \times 10^{-3}}{2.93 \times 10^{-3}} = \frac{k}{k} \left(\frac{1}{1.5}\right)^x \left(\frac{1}{1}\right)^y$$

$$0.444 = 0.667^x$$

$$\ln 0.444 = x \ln 0.667$$

$$x = 2$$

$$\text{rate} = k [\text{NO}]^x [\text{Br}_2]^y$$

$$\frac{2.93 \times 10^{-3}}{8.78 \times 10^{-3}} = \frac{k}{k} \left(\frac{1.5}{1.5}\right)^x \left(\frac{1}{3}\right)^y$$

$$0.333 = 0.333^y$$

$$y = 1$$

$$1.3 \times 10^{-3} \frac{M}{s} = k (1 M)^2 (1 M)^1$$

$$k = 1.3 \times 10^{-3} M^{-2} s^{-1}$$

$$\text{rate} = 1.3 \times 10^{-3} M^{-2} s^{-1} [\text{NO}]^2 [\text{Br}_2]$$

12. What is the rate of the synthesis of NOBr at 25 °C when [NO] = 500 μM and [Br<sub>2</sub>] = 2.5 mM?

$$\text{rate} = 1.3 \times 10^{-3} (500 \times 10^{-6} M)^2 (2.5 \times 10^{-3} M)$$

$$\text{rate} = 8.125 \times 10^{-17} \frac{M}{s}$$

13. If the reaction in problem 11 has an activation energy of 10 kJ, determine the rate constant at 100 °C.

$$T_1 = 298.15 K$$

$$T_2 = 373.15 K$$

$$k_1 = 1.3 \times 10^{-3} M^{-2} s^{-1}$$

$$k_2 = ?$$

$$E_a = 10,000 J/mol$$

$$\ln \frac{k_2}{1.3 \times 10^{-3}} = \frac{-10000}{8.314} \left( \frac{1}{373.15} - \frac{1}{298.15} \right)$$

$$\ln \frac{k_2}{1.3 \times 10^{-3}} = 4.035$$

$$\frac{k_2}{1.3 \times 10^{-3}} = 56.51$$

$$k_2 = 0.073 M^{-2} s^{-1}$$

Integrated Rate Laws:

14. Using the information below for the decomposition of  $N_2O_4$  ( $N_2O_4 \rightarrow 2NO + O_2$ ), determine:

- Rate constant with the correct units
- Rate law
- Initial rate
- $[N_2O_4]$  @  $t = 1$  minute
- Rate @  $t = 1$  minute
- $[NO]$  at  $t = 1$  minute
- $[O_2]$  at  $t = 1$  minute

Time (s)	$[N_2O_4]$ (M)
0	0.0345
3.8	0.0245
5.6	0.0212
9.3	0.0154
14	0.0103

plot using Excel (or another software)

$-\ln C$  vs. time is linear  $1^{\text{st}}$  order

$$m = -0.0861$$

$$b = -3.373$$

$$a) k = 0.0861 \text{ s}^{-1} \leftarrow a$$

$$[N_2O_4]_0 = 0.0345 \text{ M}$$

$$b) \text{rate} = 0.0861 \text{ s}^{-1} [N_2O_4]$$

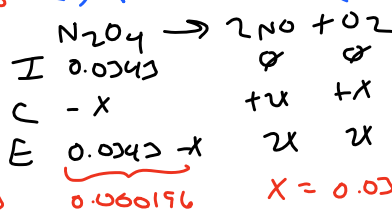
$$\ln [N_2O_4] = -kt + \ln [N_2O_4]_0 \quad c) \text{rate} = 0.0861 (0.0345) = 0.00295 \frac{\text{M}}{\text{s}}$$

$$d) \ln [N_2O_4] = -0.0861 (60 \text{ s}) - 3.373$$

$$\ln [N_2O_4] = -8.539$$

$$[N_2O_4] = 0.000196 \text{ M}$$

$$e) \text{rate} = 0.0861 (0.000196) = 1.69 \times 10^{-5} \text{ M/s}$$



$$f) [NO] = 0.0682 \text{ M}$$

$$g) [O_2] = 0.0341 \text{ M}$$

$$0.000196 \quad x = 0.0341 \text{ M}$$

15. Carbon dating is based on the radioactive decay of  $^{14}C$ . If the rate constant for this process is  $1.2097 \times 10^{-4} \text{ yr}^{-1}$ , how long does it take for 100 grams of  $^{14}C$  to decay to 50 grams?

$$k = 1.2097 \times 10^{-4} \text{ yr}^{-1}$$

$$\ln 50 = -1.2097 \times 10^{-4} \text{ yr}^{-1} t + \ln 100$$

$$t = 0 \rightarrow 100 \text{ g}$$

$$-0.693 = -1.2097 \times 10^{-4} \text{ yr}^{-1} t$$

$$t = x \rightarrow 50 \text{ g}$$

$$t = 5729.9 \text{ yrs}$$

7  $\rightarrow$  corrected problem

$$E_a (\text{uncatalyzed}) = 1714.8 \frac{\text{J}}{\text{mol}}$$

$$E_a (\text{catalyzed}) = 1714.8 - 0.98 (1714.8) = 34.296 \frac{\text{J}}{\text{mol}}$$

$$k = 20 \text{ M}^{-1} \text{ s}^{-1} e^{-\frac{34.296}{8.314 \cdot 345}}$$

$$k = 19.76 \text{ M}^{-1} \text{ s}^{-1}$$

$$k(x) = 19.76$$

$$x = 1.8 \rightarrow 180\% \text{ increase}$$