

Chemical Kinetics

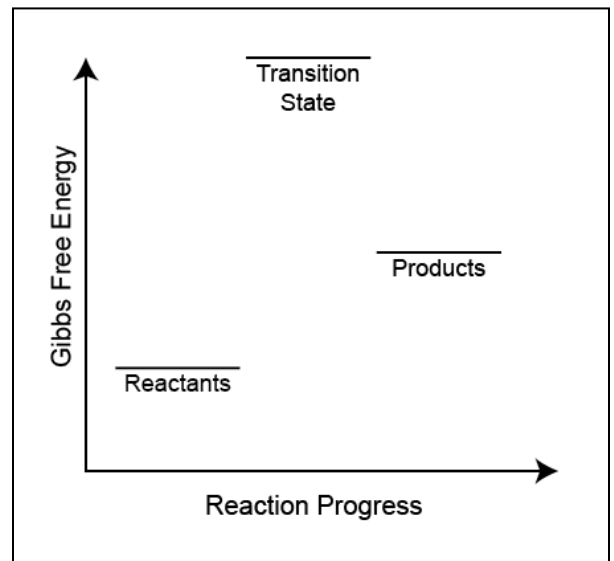
Goal: Our goal in this activity is to explore some applications of chemical kinetics. We begin by thinking critically about collision theory and the role that it plays in the rate of chemical reactions. We then explore rate laws and integrated rate laws and find useful applications of each.

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?

2. Consider the reaction coordinate shown.

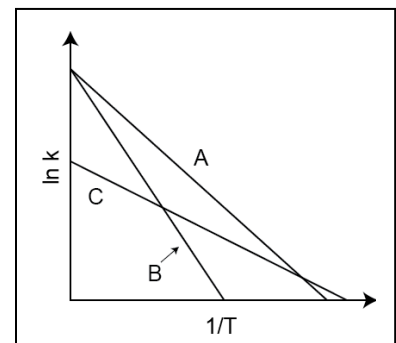
- Why is the activation energy positive?
- Is this reaction spontaneous? How do you know?
- Is the activation energy for the forward reaction (reactant \rightarrow products) larger or smaller than the activation energy for the reverse reaction (products \rightarrow reactants)?
- True or false: $k_{\text{forward}} > k_{\text{reverse}}$.
- Sketch a reaction coordinate if a catalyst is added. How will this affect k_{forward} ?



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?

4. Consider the graph.

- Which reaction (A, B, or C) has the largest pre-exponential factor?
- Which has the largest activation energy?



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. $E_a = 15000 \text{ J}$ $T = 250 \text{ K}$
- b. $E_a = 3.86 \text{ kJ}$ $T = 300 \text{ }^\circ\text{C}$
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 $20 \text{ M}^{-1}\text{s}^{-1}$.
7. The addition of a catalyst decreases the activation energy for the previous problem by 98%. How much will the rate constant be increased?
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 (s^{-1}) |
|----------|----------------------------------|-----------------------------------|
| 1 | 100 | 15.86 |
| 2 | 200 | 198.7 |

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

Rate Laws:

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

0th

1st

2nd

5th

7th

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 Br₂. Make sure to determine the rate constant.

| Reaction | [NO] ₀ (M) | [Br ₂] ₀ (M) | Initial rate (M s ⁻¹) |
|----------|-----------------------|-------------------------------------|-----------------------------------|
| 1 | 1 | 1 | 1.3 x 10 ⁻³ |
| 2 | 1.5 | 1 | 2.93 x 10 ⁻³ |
| 3 | 1.5 | 3 | 8.78 x 10 ⁻³ |

12. What is the rate of the synthesis of NOBr at 25 °C when [NO] = 500 μM and [Br₂] = 2.5 mM?

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

Integrated Rate Laws:

14. Using the information below for the decomposition of N_2O_4 ($\text{N}_2\text{O}_4 \rightarrow 2\text{NO} + \text{O}_2$), determine:

- Rate constant with the correct units
- Rate law
- Initial rate
- $[\text{N}_2\text{O}_4]$ @ $t = 1$ minute
- Rate @ $t = 1$ minute
- $[\text{NO}]$ at $t = 1$ minute
- $[\text{O}_2]$ at $t = 1$ minute

| Time (s) | $[\text{N}_2\text{O}_4]$ (M) |
|----------|------------------------------|
| 0 | 0.0345 |
| 3.8 | 0.0245 |
| 5.6 | 0.0212 |
| 9.3 | 0.0154 |
| 14 | 0.0103 |

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?