Name ____________________________________Chem 163 Section: ______ Team Number: ______

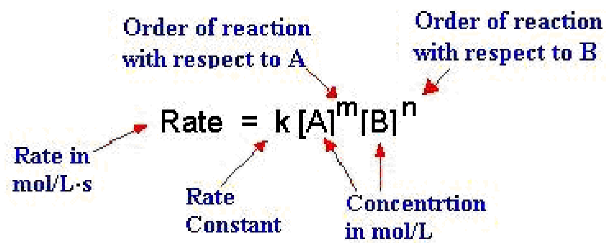
ALE 4. Effect of Temperature and Catalysts on the Rate of a Chemical Reaction

(Reference: 16.5 – 16.6 & 16.8 *Silberberg 5th edition*)

Why do reaction rates increase as temperature increases?

The Model: Temperature and the Rate of a Reaction

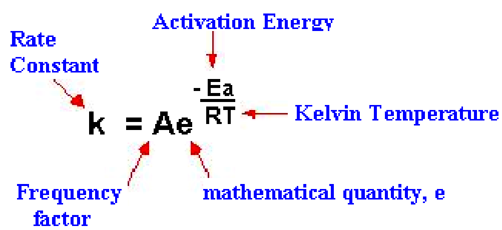
As we've seen in previous ALE's, the rate law for a reaction between two substances **A** and **B** looks like this:



The rate law shows the effect of changing the concentrations of the reactants on the rate of the reaction. What about all the other things (like temperature and catalysts, for example) which also change affect the rate of reaction? Where do these fit into this equation? All of these factors fit into the so-called **rate constant**—<u>*which is only constant if the only thing that changes is the concentration of the reactants*</u>.

<u>If you change the temperature or add a catalyst, for example, the rate constant changes.</u> This is shown mathematically in the Arrhenius equation.

The Arrhenius equation



What the various symbols mean:

- ***Temperature, T***, measured in Kelvin.
- ***The gas constant, R***, the same constant in the ideal gas law (PV=nRT), but with a value and units of **8.314 J/mol·K**
- ***Activation energy, E_a,*** the minimum energy needed for the reaction to occur, with the units **J/mol**.
- ***e*** = 2.71828, is a mathematical number, a bit like pi. You don't need to worry exactly what it means, although when you do calculations with the Arrhenius equation, you will have to find it on your calculator. You should find an e^x button—probably on the same key as "Ln".
- ***The expression, $e^{-(Ea\,/\,RT)}$*** For reasons that are beyond the scope of this class, this is related to the <u>*fraction of the molecules that have a kinetic energy equal to or greater the activation energy at a particular temperature*</u>.
- ***The frequency factor, A***, a term that takes into account how often the reactant molecules collide and the orientation of the molecules as they collide. It varies slightly with temperature, although not much. It is often taken as constant across small temperature ranges.

By this time you've probably forgotten what the original Arrhenius equation looked like! Here it is again:

The Arrhenius Equation: $k = A e^{-\frac{Ea}{RT}}$

Below are alternate forms of the Arrhenius equation that are created by a taking the natural log, Ln, of the Arrhenius equation :

$$\text{Ln}\,k = \text{Ln}\,A - \frac{E_a}{RT} \quad \text{or} \quad \text{Ln}\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{or} \quad \text{Ln}\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

"Ln" is a form of logarithm. Don't worry about what it means. If you need to use this equation, just find the "Ln" button on your calculator.

Using the Arrhenius equation

The Arrhenius equation quantifies the effect of a change of temperature on the rate constant—and therefore on the rate of the reaction. If the rate constant doubles, for example, so also will the rate of the reaction. Look back at the rate law equation if you aren't sure why that is.

What happens if you increase the temperature by 10°C from, say, 20°C to 30°C? Since the **frequency factor, A**, in the equation is approximately constant for small changes in temperature, we only need to look at how $\mathbf{e^{-(Ea / RT)}}$ *changes the fraction of molecules with energies equal to or in excess of the activation energy*.

Key Questions

1. The activation energy of a typical reaction is in the range of 0 to 330 kJ/mol. If the activation energy of a reaction is 50. kJ/mol, what is the approximate fraction of reactant molecules at 20.0°C with kinetic energy equal to or greater than the activation energy? Be careful with units—use units for all numbers!

2. What is the approximate fraction of reactant molecules at 30.0°C with kinetic energy equal to or greater than the activation energy?

3. By approximately what factor will the rate of the reaction increase when the temperature is increased from 20.0°C to 30.0°C? Use your responses to the previous two questions to answer this question. Is your answer reasonable and what you would expect? Explain.

4. A catalyst provides an alternate route with lower activation energy for the reaction. Suppose that in the presence of a catalyst the activation decreases from 50. to 25 kJ/mol. What is the approximate fraction of reactant molecules at 20.0°C with kinetic energy equal to or greater than the activation energy in the presence of the catalyst? How many times faster is the reaction in presence of the catalyst at 20.0°C?

Exercises involving the effect of temperature on the rate of reaction

5. The reaction 2 NOCl (g) $\rightarrow$ 2 NO (g) + Cl_2 (g) has an E_a of 1.00 x 10^2 kJ/mol and a rate constant of 0.286 L $mol^{-1}s^{-1}$ at 500. K. What is the rate constant at 490. K?

6. Understanding the high-temperature formation and breakdown of the nitrogen oxides is essential for controlling the pollutants generated by car engines. The second-order reaction for the breakdown of nitric oxide, NO, to its elements has rate constants of 0.0796 L $mol^{-1}s^{-1}$ at 737 ^oC and 0.0815 L $mol^{-1}s^{-1}$ at 947 ^oC. What is the activation energy of this reaction?

Model: the collision theory

It is clear that in a reaction between two particles (particles = molecules, ions, atoms or free radicals), the particles must come in contact with each in order to react. But although the particles collide, they may not react. It isn't enough for the two species to collide—they must collide the right way around, and must collide with enough energy for bonds to break.

The chance of a reaction involving three particles colliding simultaneously with the correct orientation is very remote. All three (or more) particles would have to arrive at exactly the same point in space at the same time, with everything lined up exactly right, and having enough energy to react. That's not likely to happen very often!

Consider a simple reaction involving a collision between two molecules—ethene, $CH_2{=}CH_2$, and hydrogen chloride gas, HCl, for example. These react to give chloroethane.

$$CH_2{=}CH_{2(g)} \ + \ HCl_{(g)} \rightarrow CH_3CH_2Cl_{(g)}$$

As a result of a successful collision between the two molecules, the double bond between the two carbons is converted into a single bond. A hydrogen atom gets attached to one of the carbons and a chlorine atom to the other. However, not all collisions between ethene and hydrogen result in a chemical reaction.

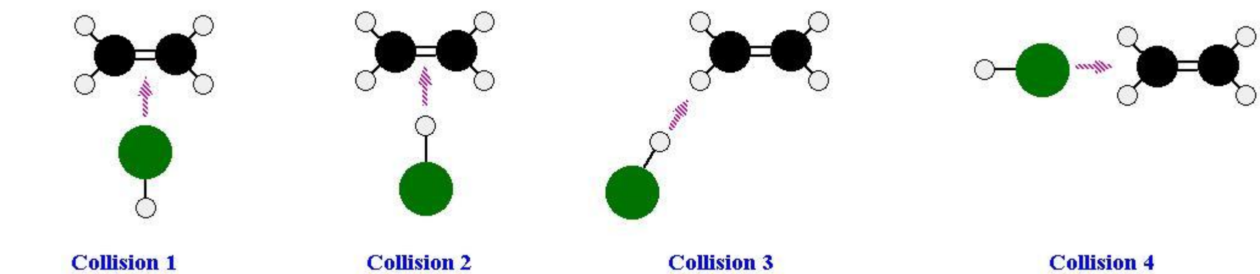


Figure 1. Possible collisions between HCl and ethene, C_2H_4.

Key Questions

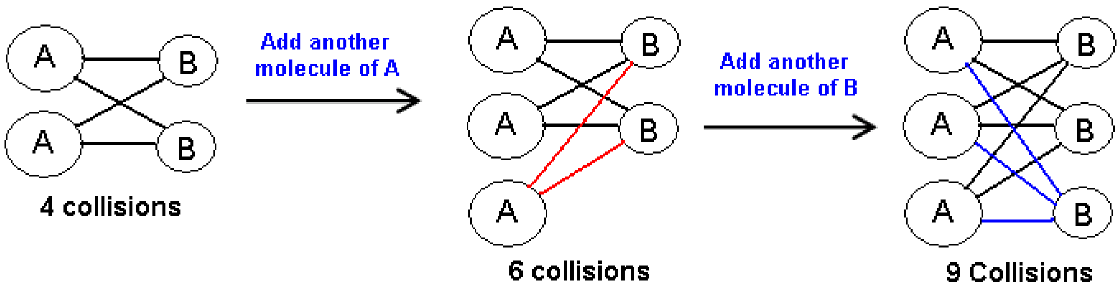
7. Give at two reasons why some, but not all, collisions between reactant molecules result in a chemical reaction.

8. Label the partial charge of all atoms represented in figure 1, above. Use δ+ to indicate a partial positive charge and δ- for a partial negative charge. Electronegativities: C = 2.5, H = 2.1, Cl = 3.0

9. Which of the collisions in figure 1 do you think might lead to a chemical reaction? *Explain*.

Model: Effect Concentration on the number of collisions

In a reaction between substances A and B, the reactant molecules must collide with sufficient energy to react. The figure below illustrates the total number of unique collisions possible as the number of reactant molecules increases.



Key Questions

10. Looking at the model above, does it make sense that the concentrations of the reactants are multiplied in the rate law, rather than added? *<u>Use the model above as to support your response</u>*.

11. In a reaction between A and B, how many unique collisions are possible if there were 5 molecules of A and 25 molecules of B?

12. How does the collision theory explain the effect of concentration on reaction rate?

Exercises

13. For the reaction $A_{(g)} + B_{(g)} \rightarrow AB_{(g)}$, how many unique collisions between A and B are possible if 1.01 mole $A_{(g)}$ reacts with 2.12 mole $B_{(g)}$ in a closed reaction vessel?

14. Consider the two reactions below occurring at 50°C.

Reaction #1: $NH_{3\,(g)}$ + $HCl_{(g)}$ → $NH_4Cl_{(s)}$

Reaction #2: $N(CH_3)_{3\,(g)}$ + $HCl_{(g)}$ → $(CH_3)_3NHCl\,(s)$

a. At 50°C, compare the relative kinetic energies and molecular velocities of ammonia, NH_3, and trimethylamine, $N(CH_3)_3$. *Explain your reasoning.*

b. Assuming the activation energies are equal, which reaction, #1 or #2 would you expect to occur at a higher rate at 50°C? Explain your reasoning in terms of molecular velocity and molecular complexity

Model: The energy of the collision between reactants

Even if the species are orientated properly, you still won't get a reaction unless the particles collide with a certain minimum energy called the ***activation energy*** of the reaction. All chemical reactions involve the breaking of chemical bonds (needing energy) and the making of new ones (releasing energy)—chemical bonds have to be broken before new ones can be made. *Activation energy is involved in breaking some of the original bonds in the reactant molecules. Activation energy is the minimum energy required before a reaction can occur*. You can show this on an ***energy profile*** (a.k.a. reaction energy diagram) for the reaction as shown in figure 2, below.

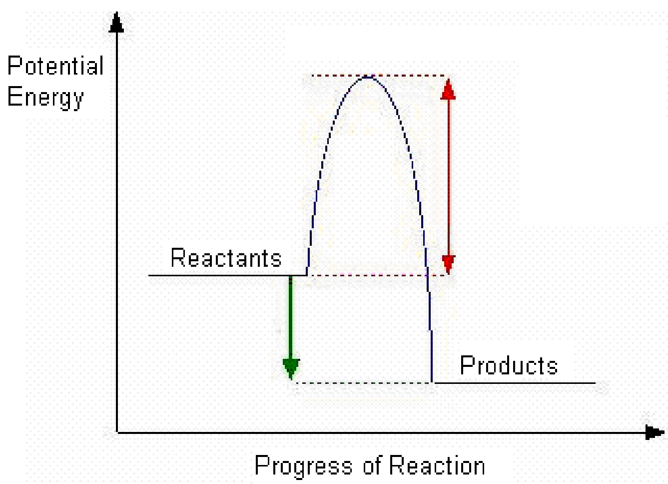


Figure 2. Reaction energy diagram showing the relative energies of the reactants, transition state and products.

Key Questions

15. Label each of the following in figure 2: transition state, activation energy (E_a) and heat of reaction (ΔH_{rxn}).

16. What does the transition state represent?

17. What will happen if the particles collide with less energy than the activation energy? Why?

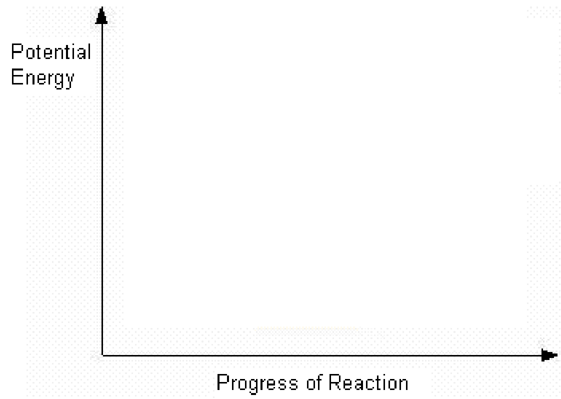
18. Is the reaction in figure 2 exothermic or endothermic? Explain.

19. Why does an increase in temperature increase the rate of a chemical reaction?

Exercises

20. For the reaction $A_{2\,(g)}$ + $B_{2\,(g)}$ → 2 $AB_{(g)}$, $E_{a(\mathrm{fwd})}$ = 125 kJ/mol and $E_{a(\mathrm{rev})}$ = 85 kJ/mol. Assuming the reaction occurs in one step…

    a. Draw the reaction energy diagram. Label: the axes, reactants, products, $E_{a(\mathrm{fwd})}$, $E_{a(\mathrm{rev})}$, ΔH_{rxn}, transition state



    b. Calculate ΔH_{rxn}. Is the reaction endo- or exothermic?

    c. Sketch the structure of a possible transition state for the reaction between A_2 and B_2.

Model: Catalysts decrease the energy of activation

A **catalyst** is a substance that speeds up a chemical reaction, but is chemically unchanged at the end of the reaction. When the reaction has finished, there is exactly the same mass of catalyst as was present at the beginning. A catalyst provides an alternative route for the reaction with **lower activation energy**.

An **enzyme** is a protein catalyst that speeds up a specific chemical reaction. The reactant molecule is called a **substrate**, and the enzyme converts the substrate molecule(s) into one or more products. Almost all processes in a cell need enzymes in order to occur at a life sustaining rate. Since most enzymes act on only one kind of substrate molecule and speed up only one kind of reaction from the many 100's that occur in any given cell, the set of enzymes made in a cell determines which metabolic pathways occur in that cell.

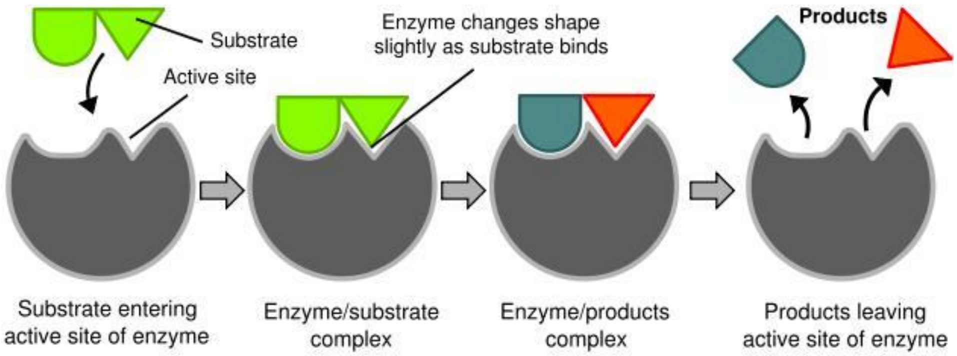
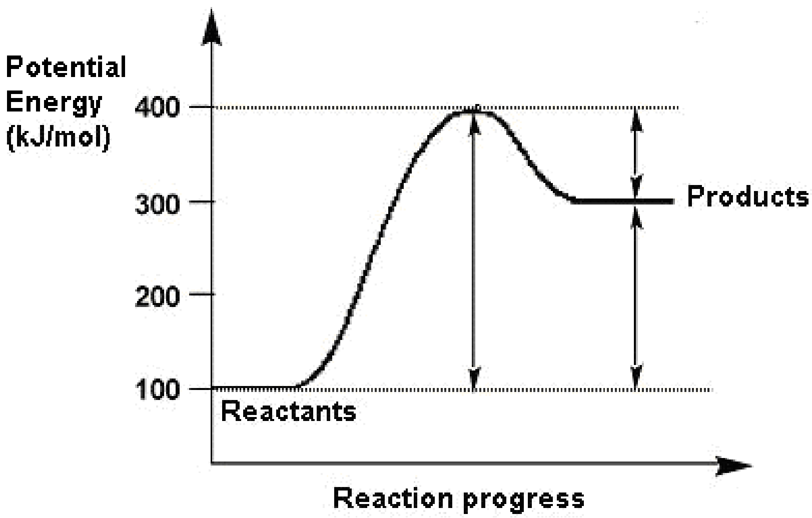


Figure 3. The catalytic cycle of an enzyme: once finished converting one substrate molecule into products the enzyme is free to act on another substrate molecule.

Key Questions

21. In the figure below draw an alternate pathway for the reaction in the presence of a catalyst that changes the activation energy by **25 kJ/mol** and label each of the following: transition state without catalyst, transition state with catalyst, E_a without catalyst, E_a with catalyst and ΔH_{rxn}.



22. Use the information and figure in the previous question to calculate each of the following in kJ/mol:

	With Catalyst	Without Catalyst
E_a (kJ/mol)		
ΔH_{rxn} (kJ/mol)		

23. Does a catalyst increase reaction rate by the same means as a rise in temperature does? Explain.

24. Consider the acid catalyzed hydrolysis of an organic ester to produce a carboxylic acid and an alcohol: R—COO—R' + H_2O → R-COOH + R—OH, an *exothermic reaction*. On the *same* set of axes, below, sketch the reaction energy diagrams for the catalyzed and uncatalyzed reactions. In addition to labeling the axes, for the catalyzed and uncatalyzed reactions, label: the reactants, products, ΔH^o_{rxn}, $E_{a(\mathrm{fwd})}$, $E_{a(\mathrm{rev})}$ and transition state(s)

25. Enzymes are remarkably efficient catalysts that can increase reaction rates by as many as 20 orders of magnitude. One of the fastest acting enzymes is carbonic anhydrase, an enzyme in red blood cells that converts CO_2 and water to carbonic acid, H_2CO_3. Carbonic anhydrase can act on 10 million carbon dioxide molecules per second!
    a. How do enzymes affect the transition state of a reaction, and why does this affect the reaction rate?

    b. What characteristics of enzymes give them this tremendous effectiveness as catalysts?