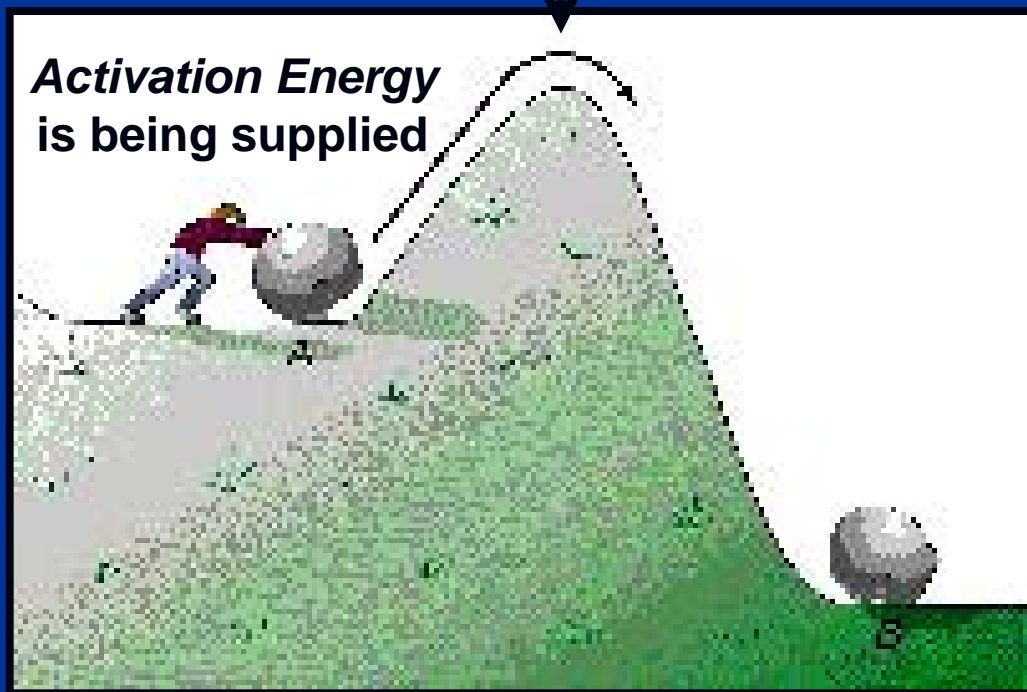


# Chapter 18

## *“Reaction Rates and Equilibrium”*

**Activated Complex**

Read slides 1-28, Stop at  
Equilibrium Constants



Pre-AP Chemistry  
Charles Page High School  
Stephen L. Cotton

# Section 18.1 Rates of Reaction

## ■ OBJECTIVES

- Describe how to **express the *rate*** of a chemical reaction.

# Section 18.1 Rates of Reaction

## ■ OBJECTIVES

- Identify four factors that influence the rate of a chemical reaction.

# Collision Theory

- Reactions can occur:

- Very fast – such as a firecracker



- Very slow – such as the time it took for dead plants to make coal



- Moderately – such as food spoilage



- Figure 18.2, page 542: compare the rates

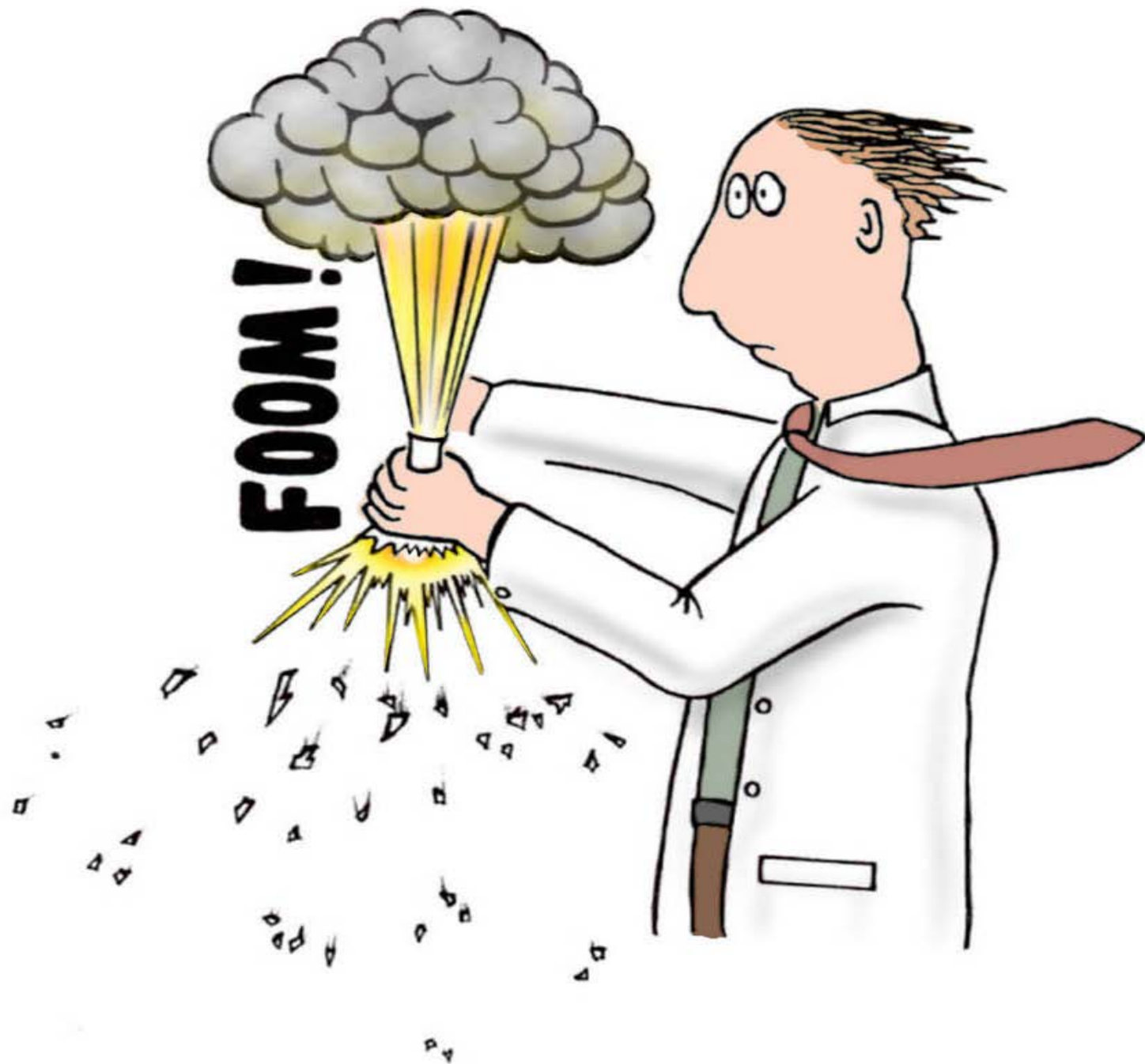
- A “rate” is a measure of the speed of any change that occurs within an interval of time

- In chemistry, reaction rate is expressed as the amount of reactant changing per unit time.

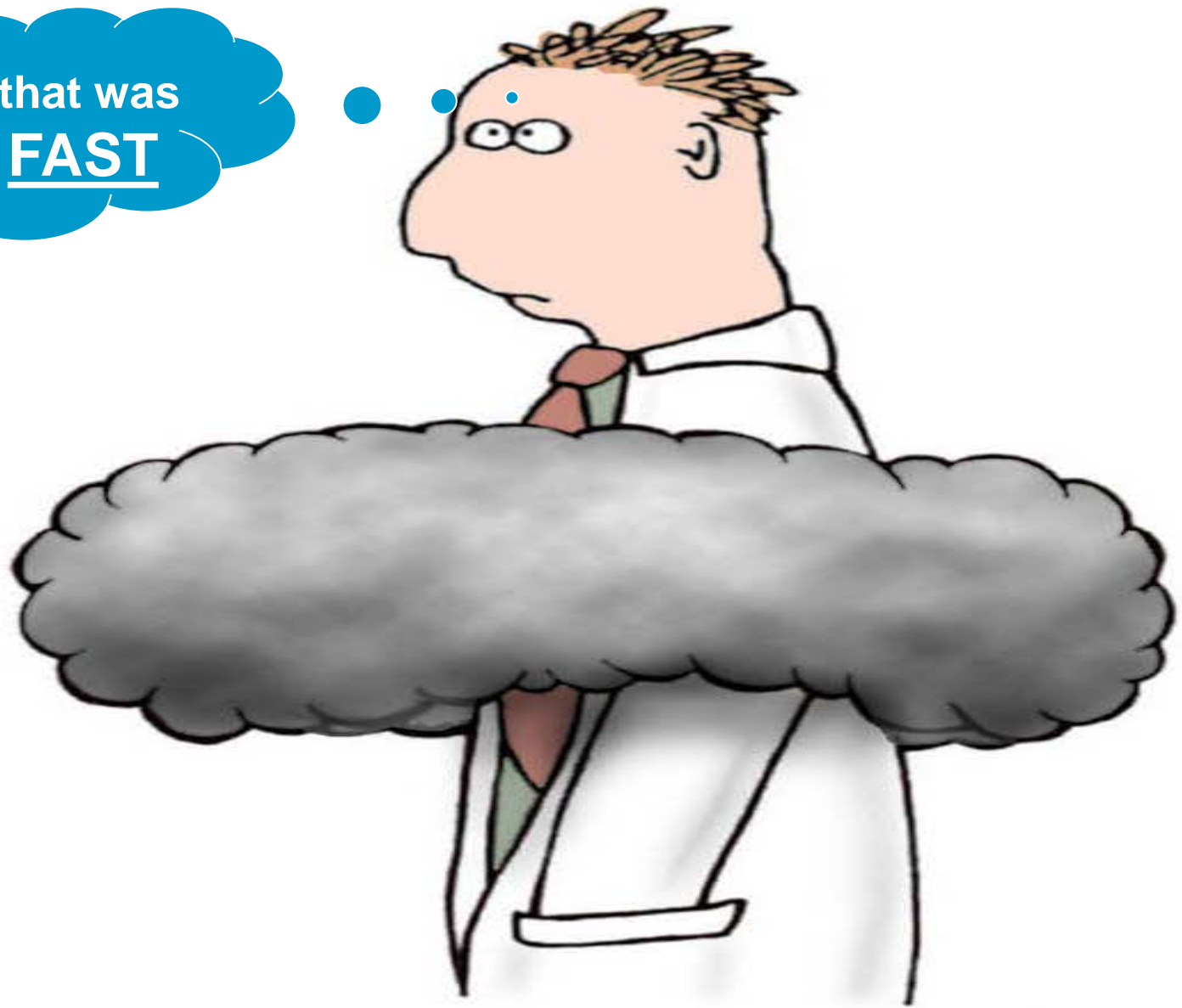
Example: 3 moles/year, or 5 grams/second

I wonder what happens if I mix these two solutions...





WOW, that was  
really FAST



It was also  
really FUN





I wonder if I should  
be wearing my  
goggles?



# Collision Model

- **Key Idea:** The molecules must **touch** (or collide) to react.
- However, only a small fraction of collisions produces a reaction. Why?
- Particles lacking the necessary kinetic energy to react will bounce apart *unchanged* when they collide

# Collision Model

- Collisions must have enough energy to produce the reaction: must equal or exceed the “activation energy”, which is the minimum energy needed to react.
- Will a AA battery start a car?
- Think of clay clumps thrown together *gently* – they don't stick, but if thrown together forcefully, they stick tightly to each other.



# Collision Model

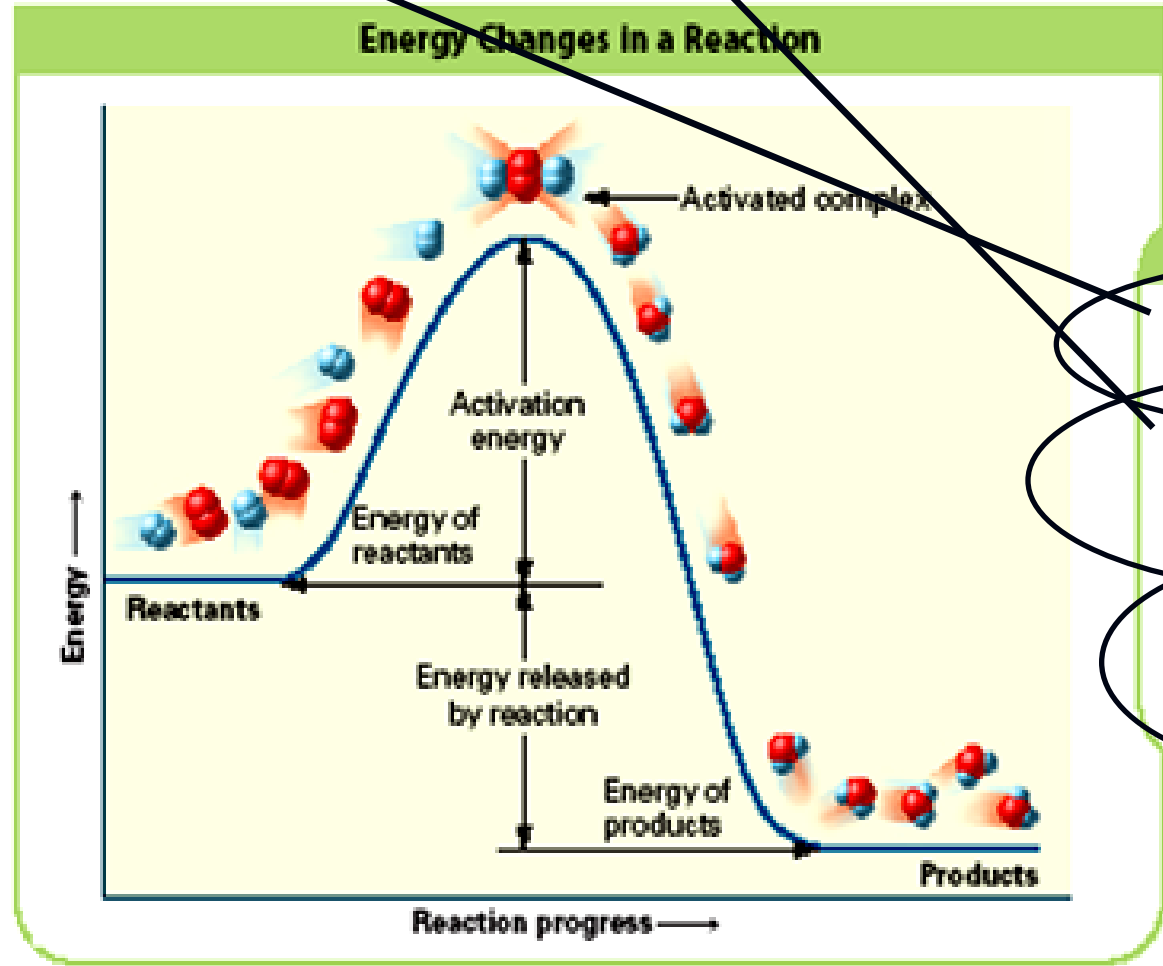
- An “activated complex” is an unstable arrangement of atoms that forms momentarily (typically about  $10^{-13}$  seconds) at the peak of the activation-energy barrier.
  - This is sometimes called the transition state
- Results in either a) forming products, or b) reformation of reactants
  - Both outcomes are equally likely

# Figure 18.5 Interpreting Graphs - Page 543

a. Reactants

b. Absorbed

c. No; it could also revert back to the reactants



**INTERPRETING GRAPHS**

a. **Navigate** Which are at a higher energy, the reactants or products?

b. **Read** Is energy absorbed or released in progressing from the reactants to the activated complex?

c. **Interpret** Once the activated complex is formed, will it always proceed to form products? Explain.

# Collision Model

- The collision theory explains why some naturally occurring reactions are very slow
  - Carbon and oxygen react when charcoal burns, but this has a very high *activation energy* ( $\text{C} + \text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})} + 393.5 \text{ kJ}$ )
  - At room temperature, the collisions between carbon and oxygen are not enough to cause a reaction

# Factors Affecting Rate

## 1) Temperature

Increasing temperature always increases the rate of a reaction.

## 2) Surface Area

Increasing surface area increases the rate of a reaction

## 3) Concentration – example page 545

Increasing concentration USUALLY increases the rate of a reaction

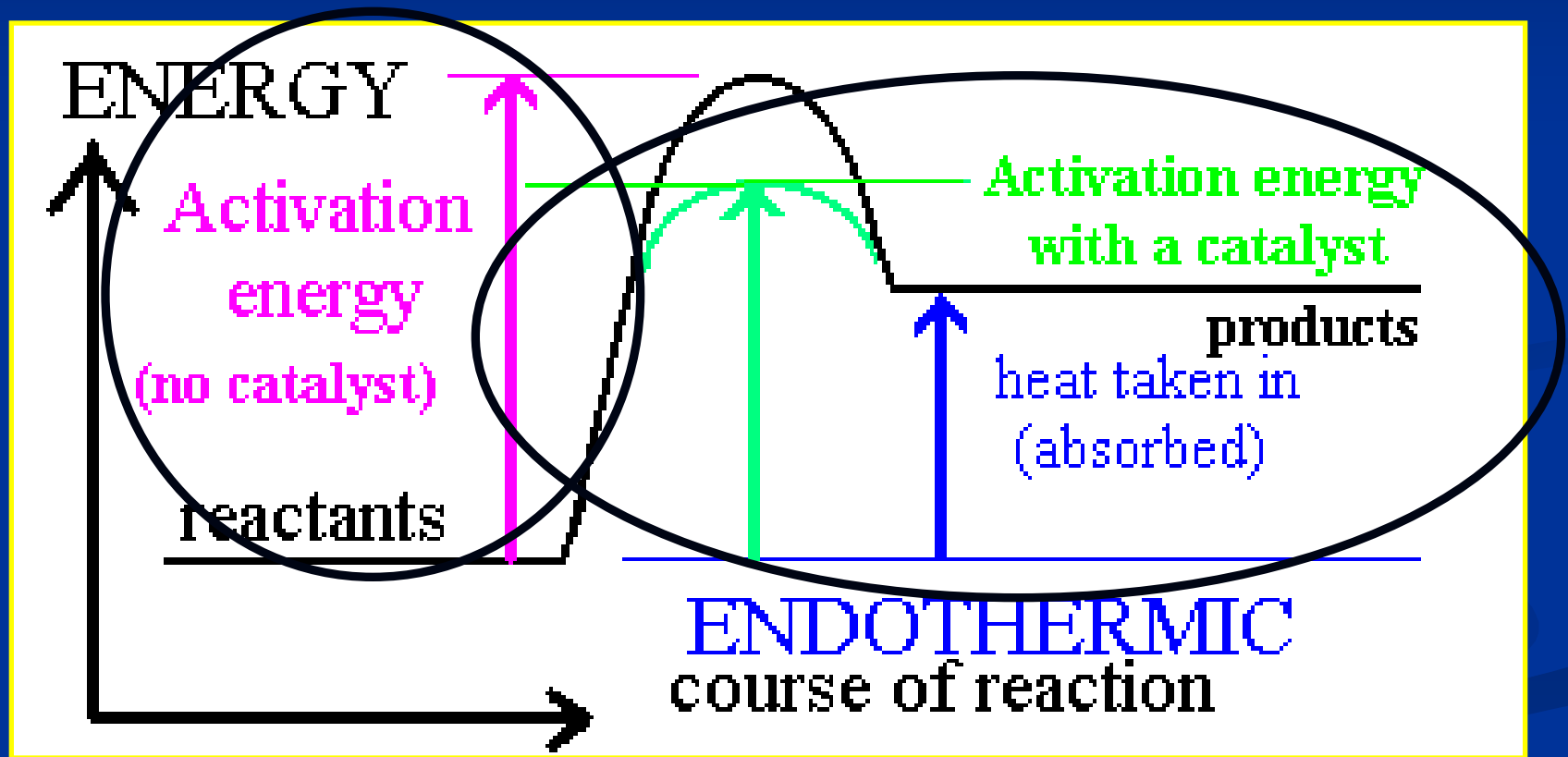
## 4) Presence of Catalyst

# Catalysts

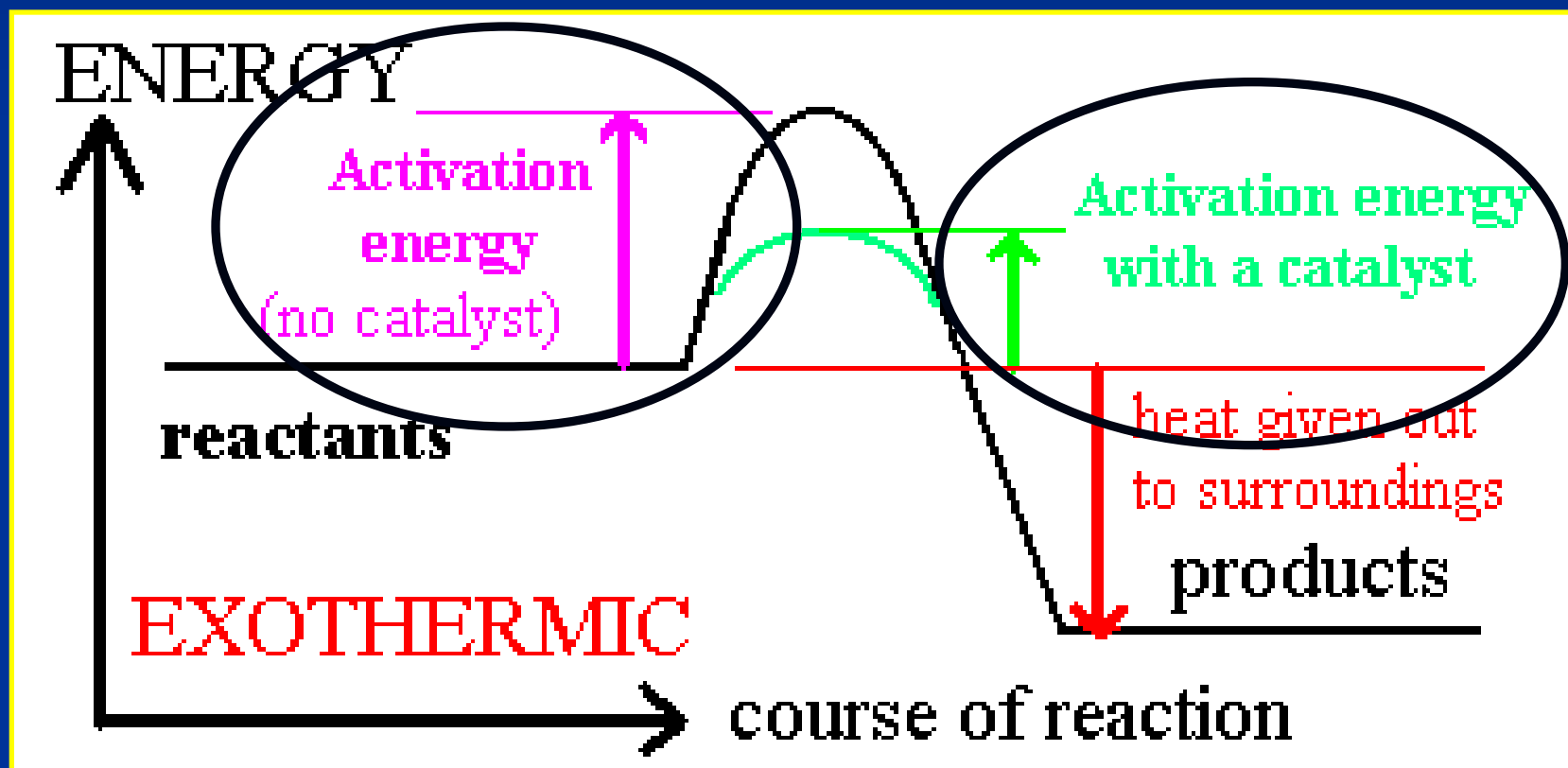
- **Catalyst**: A substance that speeds up a reaction, without being consumed itself in the reaction
- **Enzyme**: A large molecule (usually a protein) that catalyzes biological reactions.
  - Human body temperature =  $37^{\circ}\text{C}$ , much too low for digestion reactions without catalysts.
- **Inhibitors** – interfere with the action of a catalyst; reactions slow or even stop



# Endothermic Reaction with a Catalyst



# Exothermic Reaction with a Catalyst



# Section 18.2 Reversible Reactions and Equilibrium

## ■ OBJECTIVES

- Describe how the *amounts of reactants and products change* in a chemical system at equilibrium.

# Section 18.2 Reversible Reactions and Equilibrium

## ■ OBJECTIVES

- Identify three *stresses* that can change the equilibrium position of a chemical system.

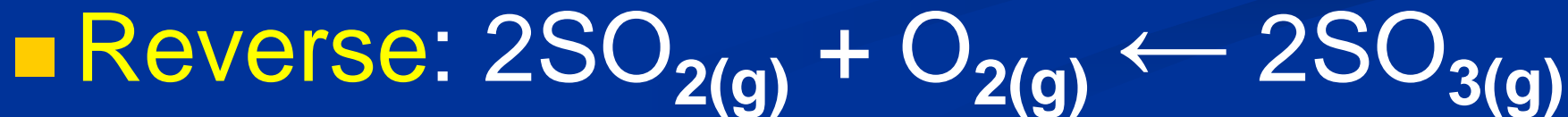
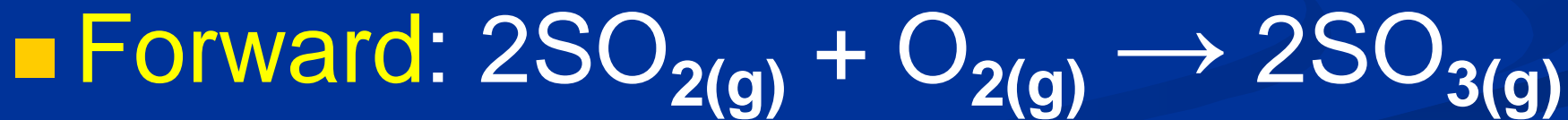
# Section 18.2 Reversible Reactions and Equilibrium

## ■ OBJECTIVES

- Explain what the **value of  $K_{eq}$**  indicates about the position of equilibrium.

# Reversible Reactions

- Some reactions do not go to completion as we have assumed
  - They may be **reversible** – a reaction in which the conversion of reactants to products and the conversion of products to reactants occur simultaneously



# Reversible Reactions

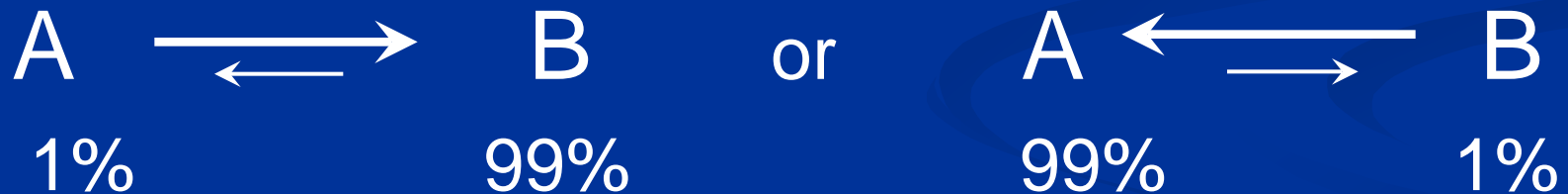
- The two equations can be combined into one, by using a double arrow, which tells us that it is a reversible reaction:



- ✓ A chemical *equilibrium* occurs, and no net change occurs in the actual amounts of the components of the system.

# Reversible Reactions

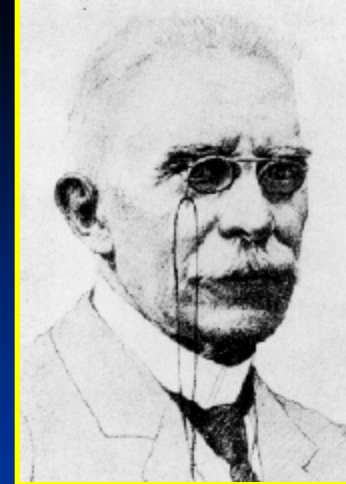
- Even though the *rates* of the forward and reverse are equal, the *concentrations* of components on both sides may not be equal
  - An equilibrium position may be shown:



- ✓ Note the emphasis of the arrows direction
- ✓ It depends on which side is favored; almost all reactions are reversible to some extent



# Le Chatelier's Principle



- The French chemist Henri Le Chatelier (1850-1936) studied how the equilibrium position shifts as a result of changing conditions
- Le Chatelier's principle: If stress is applied to a system in equilibrium, the system changes in a way that relieves the stress

# Le Chatelier's Principle

- What items did he consider to be stress on the equilibrium?
  - 1) Concentration
  - 2) Temperature
  - 3) Pressure

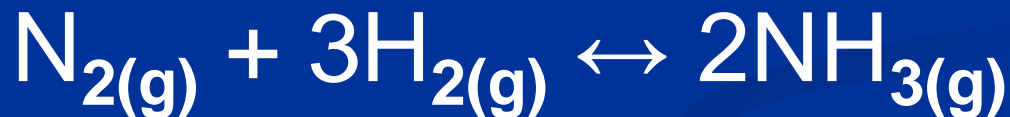
Each of these will now be discussed in detail
- Concentration – adding more reactant produces more product, and removing the product as it forms will produce more product

# Le Chatelier's Principle

- Temperature – increasing the temperature causes the equilibrium position to shift in the direction that absorbs heat
  - If heat is one of the products (just like a chemical), it is part of the equilibrium
  - so cooling an exothermic reaction will produce more product, and heating it would shift the reaction to the reactant side of the equilibrium:  $\text{C} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 393.5 \text{ kJ}$

# Le Chatelier's Principle

- Pressure – changes in pressure will only effect gaseous equilibria
  - Increasing the pressure will usually favor the direction that has *fewer molecules*



- For every two molecules of ammonia made, four molecules of reactant are used up – this equilibrium shifts to the right with an increase in pressure
-

Stop here

# Equilibrium Constants: $K_{eq}$

- Chemists generally express the position of equilibrium in terms of *numerical values*, not just percent
  - These values relate to the amounts (*Molarity*) of reactants and products at equilibrium
  - This is called the equilibrium constant, and abbreviated  $K_{eq}$

# Equilibrium Constants

- consider this reaction (the capital letters are the chemical, and the lower case letters are the balancing coefficient):



- The equilibrium constant ( $K_{eq}$ ) is the ***ratio*** of product concentration to the reactant concentration at equilibrium, with each concentration *raised to a power* (which is the balancing coefficient).

# Equilibrium Constants

- consider this reaction:



- Thus, the “equilibrium constant expression” has this general form:

$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

Note that  $K_{eq}$  has no units on the answer; it is only a *number* because it is a ratio

(brackets: [ ] = molarity concentration)



# Equilibrium Constants

- the equilibrium constants provide valuable information, such as whether products or reactants are favored:

if  $K_{\text{eq}} > 1$ , products favored at equilibrium

if  $K_{\text{eq}} < 1$ , reactants favored at equilibrium

## Expressing and Calculating $K_{eq}$

The colorless gas dinitrogen tetroxide ( $N_2O_4$ ) and the dark brown gas nitrogen dioxide ( $NO_2$ ) exist in equilibrium with each other.



A liter of a gas mixture at equilibrium at  $10^\circ C$  contains 0.0045 mol of  $N_2O_4$  and 0.030 mol of  $NO_2$ . Write the expression for the equilibrium constant and calculate the equilibrium constant ( $K_{eq}$ ) for the reaction.

**1 Analyze** List the knowns and the unknowns.

Knowns

- $[N_2O_4] = 0.0045 \text{ mol/L}$
- $[NO_2] = 0.030 \text{ mol/L}$
- $K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$

Unknowns

- $K_{eq}$  (algebraic expression) = ?
- $K_{eq}$  (numerical value) = ?

**2 Calculate** Solve for the unknowns.

To write the equilibrium constant expressions, place the concentration of the product in the numerator and the concentration of the reactant in the denominator. Raise each to the power equal to its coefficient in the chemical equation. Substitute the given concentrations and calculate  $K_{eq}$ .

$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.030 \text{ mol/L})^2}{0.0045 \text{ mol/L}}$$

$$= \frac{(0.030 \text{ mol/L} \times 0.030 \text{ mol/L})}{0.0045 \text{ mol/L}} = 0.20$$

Does this favor the reactants or products?

# Section 18.3

## Solubility Equilibrium

### ■ OBJECTIVES

- Describe the relationship between the *solubility product constant* and the *solubility* of a compound.

# Section 18.3

## Solubility Equilibrium

### ■ OBJECTIVES

- Predict whether precipitation *will occur* when two salt solutions are mixed.

# Solubility Product Constant

- Ionic compounds (also called *salts*) differ in their solubilities
  - Table 18.1, page 561
- Most “insoluble” salts will actually dissolve to some extent in water
  - Better said to be *slightly*, or *sparingly*, soluble in water

# Solubility Product Constant

- Consider:  $\text{AgCl}_{(s)} \xrightarrow{\text{H}_2\text{O}} \text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)}$
- The “equilibrium expression” is:

$$K_{\text{eq}} = \frac{[\text{Ag}^+] \times [\text{Cl}^-]}{[\text{AgCl}]}$$

What was the physical state of the AgCl?

# Solubility Product Constant

- AgCl existed as a solid material, and is not in a solution = a constant concentration!
- the [ AgCl ] is constant as long as some undissolved solid is present (same with any pure liquid- do not change their conc.)
- By multiplying the two constants, a new constant is developed, and is called the “*solubility product constant*” ( $K_{sp}$ ):



# Solubility Product Constant

- Values of solubility product constants are given for some common slightly soluble salts in Table 18.2, page 562
- $K_{sp} = [Ag^{1+}] \times [Cl^{1-}]$
- $K_{sp} = 1.8 \times 10^{-10}$ 
  - The smaller the numerical value of  $K_{sp}$ , the *lower the solubility* of the compound
  - AgCl is usually considered insoluble because of its low value



# Solubility Product Constant

## ■ To solve problems:

a) write the balanced equation, which splits the chemical into its ions

b) write the “equilibrium expression”, and

c) fill in the values known; calculate answer

## ■ Sample Problem 18.3, page 562

# Solubility Product Constant

- Do not ever include *pure liquids nor solids* in the expression, since their concentrations cannot change (they are constant) – just leave them out!
- Do not include the following in an equilibrium expression:
  1. any substance with a (l) after it such as:  
 $\text{Br}_{2(l)}$ ,  $\text{Hg}_{(l)}$ ,  $\text{H}_2\text{O}_{(l)}$ , or  $\text{CH}_3\text{OH}_{(l)}$
  2. any substance which is a solid (s) such as:  
 $\text{Zn}_{(s)}$ ,  $\text{CaCO}_{3(s)}$ , or  $\text{H}_2\text{O}_{(s)}$

# Solubility Product Constant

- ALWAYS include those substances which can CHANGE concentrations, which are gases and solutions:



# The Common Ion Effect

- A “common ion” is an ion that is found in both salts in a solution
  - example: You have a solution of **lead** (II) chromate. You now add some **lead** (II) nitrate to the solution.
    - The **lead** is a common ion
  - This causes a shift in equilibrium (due to Le Chatelier’s principle regarding **concentration**), and is called the common ion effect

# Common Ion Effect

- Sample Problem 18.4, page 564
- The solubility product constant ( $K_{sp}$ ) can also be used to predict *whether a precipitate will form* or not:
  - if the *calculated* ion-product concentration is *greater* than the *accepted value* for  $K_{sp}$ , then a precipitate will form
- Sample in the text material – page 565

# Section 18.4

## Entropy and Free Energy

### ■ OBJECTIVES

- Identify two characteristics of *spontaneous reactions*.

# Section 18.4

## Entropy and Free Energy

- OBJECTIVES

- Describe the role of *entropy* in chemical reactions.

# Section 18.4

## Entropy and Free Energy

### ■ OBJECTIVES

- Identify two factors that determine the *spontaneity* of a reaction.



# Section 18.4

## Entropy and Free Energy

- OBJECTIVES

- Define *Gibbs free-energy* change.

# Free Energy and Spontaneous Reactions

- Many chemical and physical processes release energy, and that energy can be used to bring about other changes
  - The energy in a chemical reaction can be harnessed to do work, such as moving the pistons in your car's engine
- *Free energy* is energy that is available to do work
  - That does not mean it can be used efficiently

# Free Energy and Spontaneous Reactions

- Your car's engine is only about 30 % efficient, and this is used to propel it
  - The remaining 70 % is **lost as friction and waste heat**
- No process can be made 100 % efficient
  - Even living things, which are among the most efficient users of free energy, are seldom more than 70 % efficient

# Free Energy and Spontaneous Reactions

- We can only get energy from a reaction that *actually occurs*, not just theoretically:



- this is a balanced equation, and is the *reverse of combustion*
- Experience tells us this does not tend to occur, but instead happens in the reverse direction

# Free Energy and Spontaneous Reactions

- The world of balanced chemical equations is divided into two groups:
  - 1) Equations representing reactions that do actually occur
  - 2) Equations representing reactions that do not tend to occur, or at least not efficiently

# Free Energy and Spontaneous Reactions

- The first, (those that actually do occur, and the more important group) involves processes that are *spontaneous*:
  - 1) A spontaneous reaction occurs naturally, and *favors the formation of products* at the specified conditions
  - 2) They produce substantial amounts of product at equilibrium, and release free energy
- Example: a fireworks display – page 567

# Free Energy and Spontaneous Reactions

- In contrast, a *non-spontaneous reaction* is a reaction that does not favor the formation of products at the specified conditions
  - These do not give substantial amounts of product at equilibrium
- Think of soda pop bubbling the  $\text{CO}_2$  out: this is spontaneous, whereas the  $\text{CO}_2$  going back into solution happens very little, and is non-spontaneous

# Spontaneous Reactions

- Do not confuse the words spontaneous and instantaneous. Spontaneous just simply means that it will work by itself, but does not say anything about how fast the reaction will take place – it may take 20 years to react, but it will eventually react.
  - Some spontaneous reactions are very slow:  
sugar + oxygen  $\rightarrow$  carbon dioxide and water, but a bowl of sugar *appears* to be doing nothing (it is reacting, but would take thousands of years)
  - At room temperature, it is very slow; apply heat and the reaction is fast; thus changing the conditions (temp. or pressure) may determine whether or not it is spontaneous

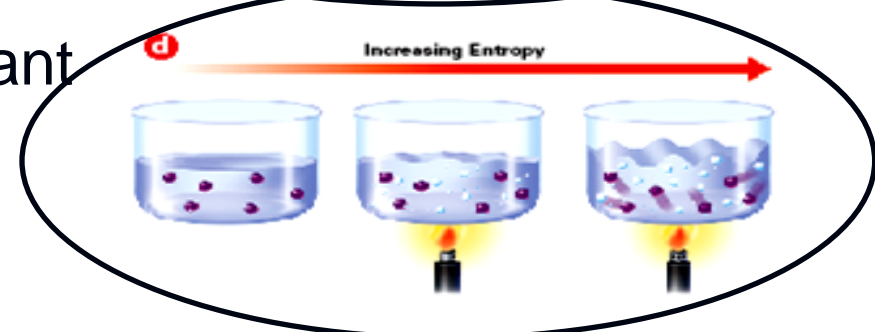
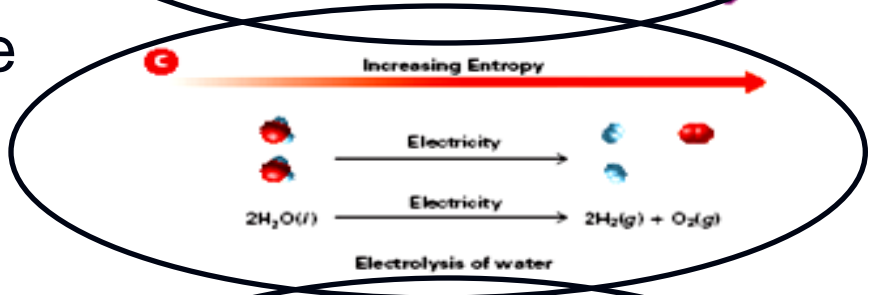
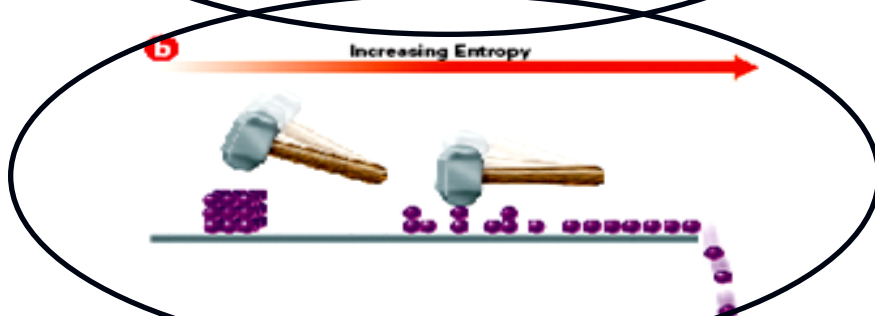
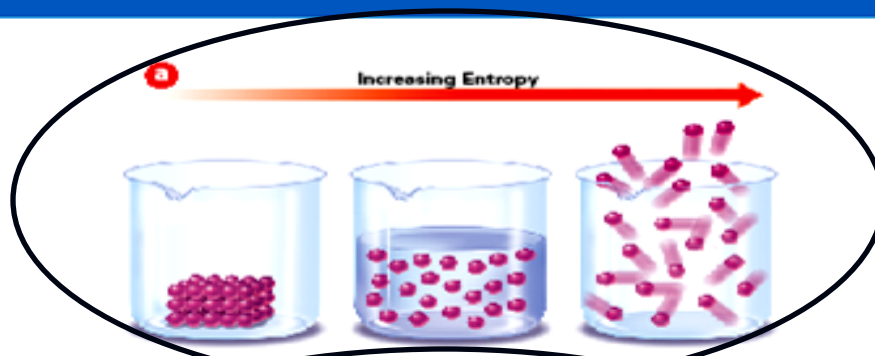


# Entropy (abbreviated “S”)

- Entropy is a measure of disorder, and is measured in units of J/mol·K; and there are no negative values of entropy
- The law of disorder states the natural tendency is for systems to move to the direction of maximum disorder, not vice-versa
  - Your room NEVER cleans itself does it? (disorder to order?)
- An increase in entropy favors the spontaneous chemical reaction
- A decrease in entropy favors the non-spontaneous reaction

Entropy of the gas is greater than the solid or liquid

Entropy increases when there are more product molecules than reactant molecules



Entropy is increased when a substance is divided into parts

Entropy increases when temperature increases

# Enthalpy and Entropy

1) Reactions tend to proceed in the direction that decreases the energy of the system (H, enthalpy).

**and,**

2) Reactions tend to proceed in the direction that increases the disorder of the system (S, entropy).

# Enthalpy and Entropy

- These are the two “drivers” to every equation.
  - If they both AGREE the reaction should be spontaneous, IT WILL be spontaneous at all temperatures, and you will not be able to stop the reaction without separating the reactants
  - If they both AGREE that the reaction should NOT be spontaneous, it will NOT work at ANY temperature, *no matter how much you heat it, add pressure, or anything else!*

# Enthalpy and Entropy

- The size and direction of enthalpy and entropy changes both determine whether a reaction is spontaneous
- If the two drivers disagree on whether or not it should be spontaneous, a third party (Gibb's free energy) is called in to act as the "*judge*" about what temperatures it will be spontaneous, and what the temp. is.
  - But, it WILL work and be spontaneous at some temperature!

# Spontaneity of Reactions

Reactions proceed spontaneously in the direction that lowers their Gibb's free energy, G.

$$\Delta G = \Delta H - T\Delta S \quad (T \text{ is kelvin temp.})$$

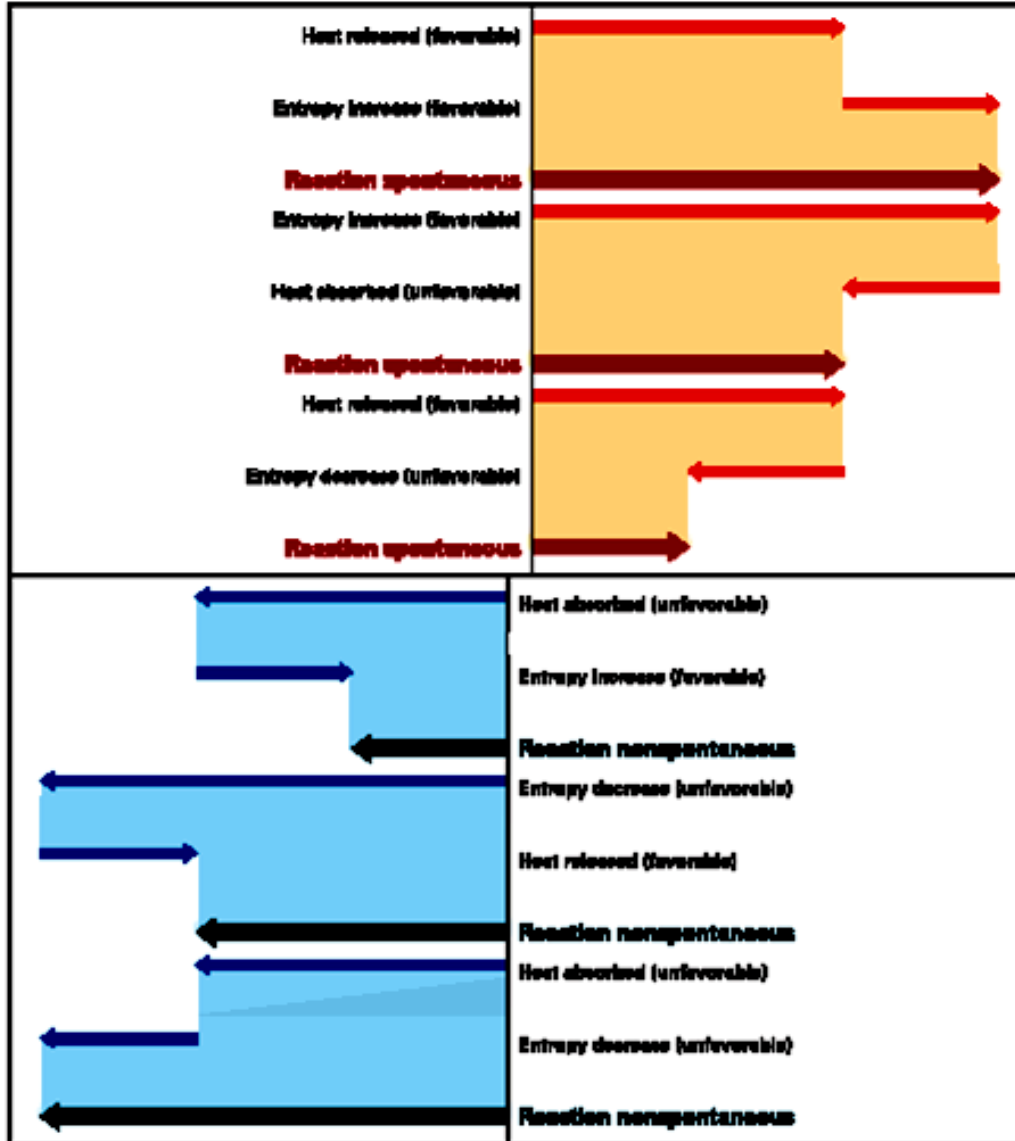
If  $\Delta G$  is negative, the reaction is spontaneous. (system loses free energy)

If  $\Delta G$  is positive, the reaction is NOT spontaneous. (requires work be expended)

# Spontaneity of Reactions

- Therefore, if the enthalpy and entropy do not agree with each other as to what should happen:
  - Gibbs free-energy says that they are both correct, the reaction will occur
  - But the Gibbs free-energy will decide the conditions of temperature that it will happen
- Figure 18.25, page 572 (next slide)

- Page 572





# Section 18.5 The Progress of Chemical Reactions

## ■ OBJECTIVES

- Describe the *general relationship* between the value of the specific rate constant,  $k$ , and the speed of a chemical reaction.

# Section 18.5 The Progress of Chemical Reactions

## ■ OBJECTIVES

- Interpret the hills and valleys in a *reaction progress curve*.

# Rate Laws

- For the equation:  $A \rightarrow B$ , the rate at which A forms B can be expressed as the **change in A (or  $\Delta A$ )** with time, where the beginning concentration  $A_1$  is at time  $t_1$ , and concentration  $A_2$  is at a later time  $t_2$

$$\text{Rate} = - \frac{\Delta A}{\Delta t} = - \frac{\text{concentration } A_2 - \text{concentration } A_1}{t_2 - t_1}$$

# Rate Laws

- Since A is decreasing, its concentration is smaller at a later time than initially, so  $\Delta A$  is negative
  - The negative sign is needed to make the rate positive, as all rates must be.
- The rate of disappearance of A is proportional to concentration of A:

$$-\frac{\Delta A}{\Delta t} \propto [A]$$

# Rate Laws

$$\text{Rate} = - \frac{\Delta A}{\Delta t} = k \times [A]$$

- This equation, called a **rate law**, is an expression for the rate of a reaction in terms of the concentration of reactants.

# Rate Laws

- The **specific rate constant** ( $k$ ) for a reaction is a proportionality constant relating the concentrations of reactants to the rate of reaction
  - The value of the specific rate constant,  $k$ , is **large** if the products form quickly
  - The value of  $k$  is **small** if the products form slowly

# Rate Laws

- The “**order of a reaction**” is the *power to which the concentration of a reactant must be raised* to give the experimentally observed relationship between concentration and rate

For the equation:  $aA + bB \rightarrow cC + dD$ ,

$$\text{Rate} = k[A]^a[B]^b$$

# Rate Laws

$$\text{Rate} = k[A]^a[B]^b$$

Notice that the rate law which governs the speed of a reaction is based on THREE things:

- 1) The **concentration (molarity)** of each of the reactants
- 2) The **power** to which each of these reactants is raised
- 3) The **value of  $k$**  (or the rate constant, which is different for every different equation.)



# Rate Laws

- Rate =  $k[A]^a[B]^b$
- The *powers to which the concentrations are raised* are calculated from experimental data, and the rate constant is also calculated. These powers are called **ORDERS**.
- For example, if the exponent of A was 2, we would say the reaction is 2<sup>nd</sup> order in A; if the exponent of B was 3, we would say the reaction is 3<sup>rd</sup> order in B.
- The overall reaction order is the **SUM** of all the orders of reactants. If the order of A was 2, and B was 3, the overall reaction order is 5.

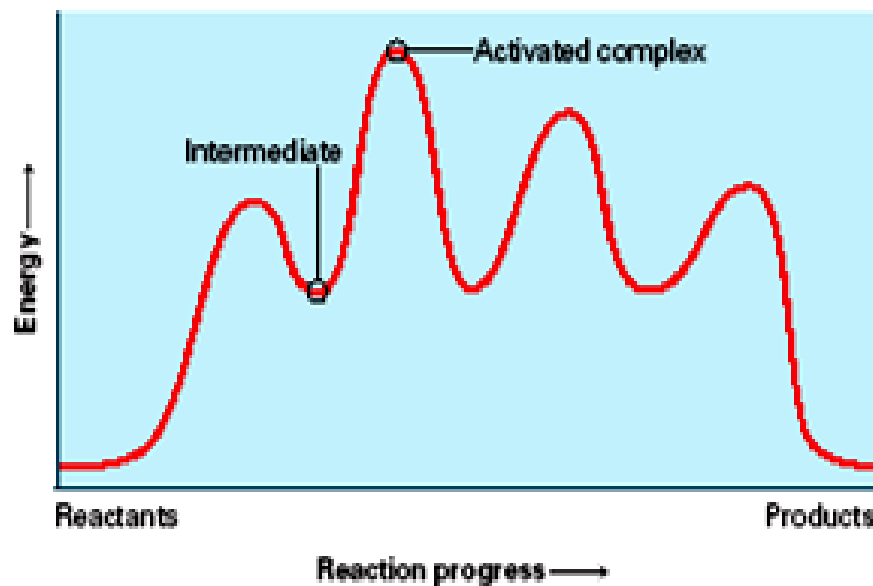
# Reaction Mechanisms

- Figure 18.28, page 578 shows a peak for each “elementary reaction”
  - An elementary reaction is a reaction in which the reactants are converted to products in a single step
  - Only has *one* activation-energy peak between reactants and products
  - Peaks are energies of activated complexes, and valleys are the energy of an intermediate

# Reaction Mechanisms

- An intermediate is a product of *one of the steps* in the reaction mechanism
  - Remember how Hess's law of summation was the total of individual reactions added together to give one equation?

## Energy Changes for a Multi-Step Reaction



## INTERPRETING GRAPHS

a. four

a. **Navigate** How many elementary reactions are part of this reaction?

b. three

b. **Read** How many intermediates are formed?

c. **Interpret** How would a catalyst affect the energy of the reactants and the energy of the products of this reaction?

c. A catalyst would have no effect on the energy, just the rate.

***End of Chapter 18***