

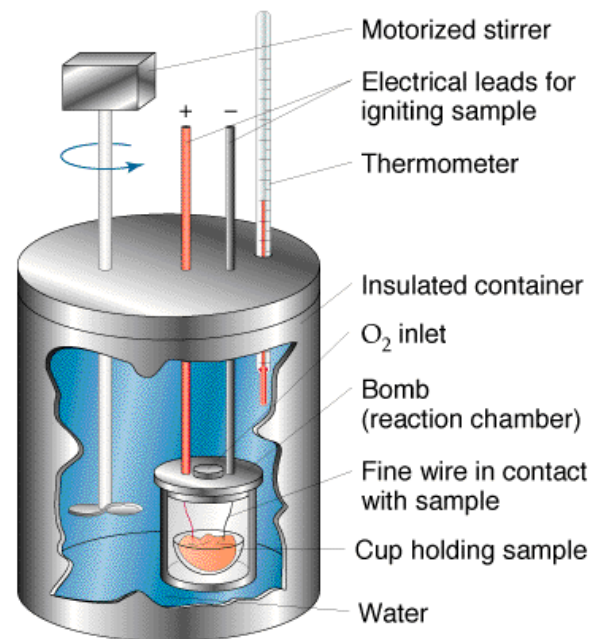
CHAPTER 16: REACTION ENERGY  
AND  
CHAPTER 17: REACTION KINETICS

Honors Chemistry

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# 16.1 – Thermochemistry

- Definition: study of the transfers of energy as heat that accompany chemical reactions and physical changes
- Measured by a calorimeter



# Measuring Heat (Review)

- Units that measure heat/energy: **CALORIES!**
- **Calorie (cal)**: the quantity of heat that raises the temperature of 1 g of pure water by 1°C
- 1 **C**alorie = 1000 **calories** = 1 **kilocalorie**
- SI Units: **joule (J)**
- **Conversion:**  
 $1 \text{ J} = 0.239 \text{ cal}$  or  $1 \text{ cal} = 4.184 \text{ J}$

# Specific Heat (c) (Review)

- How the quantity of heat is actually measured
- **Specific Heat (c)** – amount of energy required to raise the heat 1 gram of a substance by 1 degree Celsius

$$q = m \cdot c \cdot \Delta T$$

(heat quantity) = (mass)(spec. heat)(temp change)

or rearranged to be:  $c = \frac{q}{m \cdot \Delta T}$

# Specific Heat

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- Water has a high specific heat and metals have low specific heat
- Therefore it takes less energy to heat up a metal than a nonmetal like water!
- That is why the beach is cooler in the summer than the city!

# Heat of Reaction

Definition: Quantity of heat released or absorbed during a chemical reaction

- Enthalpy (H): heat content of a system
- Enthalpy Change ( $\Delta H$ ): amount of heat absorbed or lost by a system during a process
  - ▣ Can have Exothermic and Endothermic reactions

# Enthalpy of Reaction

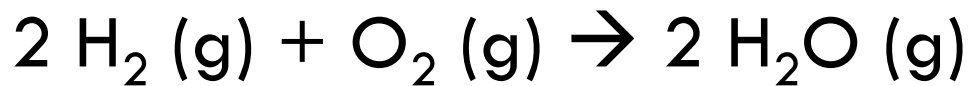
Thermochemical Equation: equation that includes the quantity of heat released or absorbed during the reaction as written

□ Depends on the amounts of reactants and products:

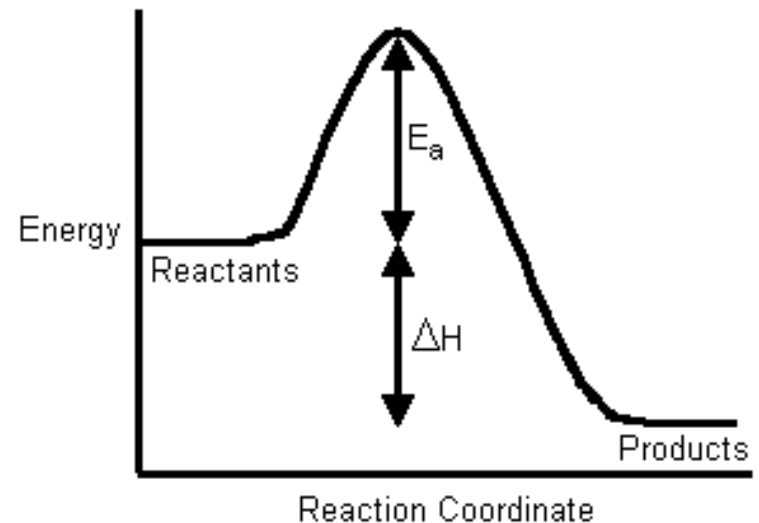


# Exothermic Reactions

- Energy is **released** to surroundings
- Products have LESS energy than reactants
- $\Delta H$  is negative



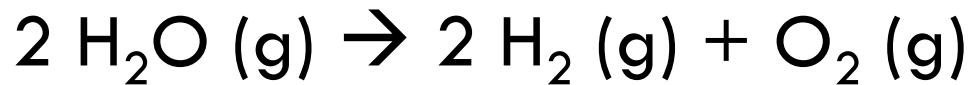
$$\Delta H = - 483.6 \text{ kJ}$$



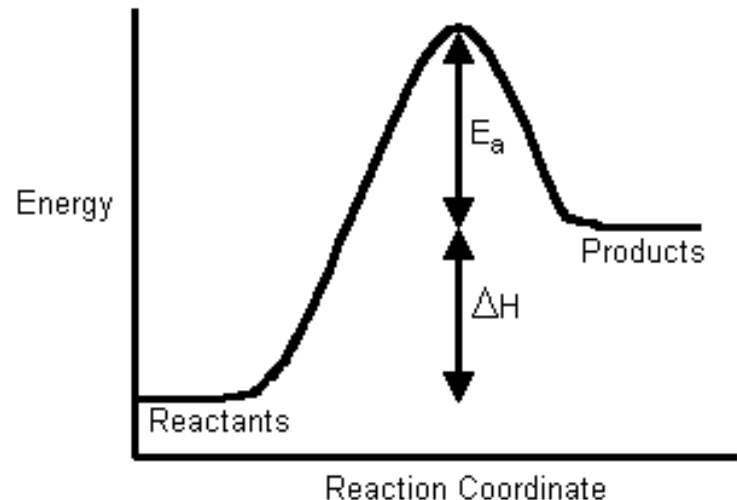


# Endothermic Reactions

- Energy is **absorbed** from surroundings
- Products have **MORE** energy than reactants
- $\Delta H$  is positive



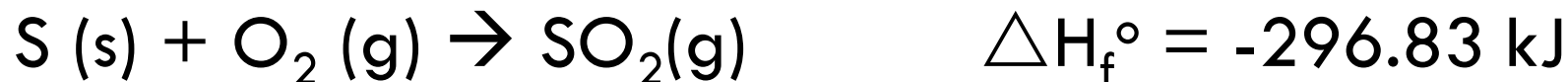
$$\Delta H = + 483.6 \text{ kJ}$$



# Standard Molar Heat of Formation ( $\Delta H_f^\circ$ )

Definition: heat released or absorbed when one mole of a compound is formed by combination of its elements at standard room temperature of 25°C

## Appendix Table A-14 p. 862



- Elements in their standard states have  $\Delta H_f^\circ = 0 \text{ kJ}$
- A negative  $\Delta H_f^\circ$  indicates a substance is more stable than the free elements

# Standard Heats of Formation

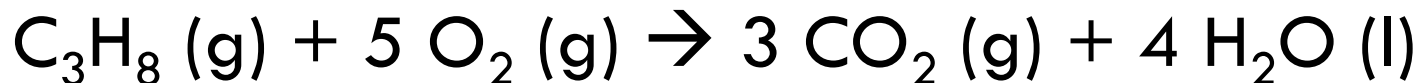
**Table 6.2** • Selected Standard Molar Enthalpies of Formation at 298 K

Substance	Name	Standard Molar Enthalpy of Formation (kJ/mol)
C(graphite)	graphite	0
C(diamond)	diamond	+1.8
CH <sub>4</sub> (g)	methane	-74.87
C <sub>2</sub> H <sub>6</sub> (g)	ethane	-83.85
C <sub>3</sub> H <sub>8</sub> (g)	propane	-104.7
C <sub>4</sub> H <sub>10</sub> (g)	butane	-127.1
C <sub>2</sub> H <sub>4</sub> (g)	ethene (ethylene)	+52.47
CH <sub>3</sub> OH( <i>ℓ</i> )	methanol	-238.4
C <sub>2</sub> H <sub>5</sub> OH( <i>ℓ</i> )	ethanol	-277.0
C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> (s)	sucrose	-2,221.2
CO(g)	carbon monoxide	-110.53
CO <sub>2</sub> (g)	carbon dioxide	-393.51
CaCO <sub>3</sub> (s)*	calcium carbonate	-1207.6
CaO(s)	calcium oxide	-635.0
H <sub>2</sub> (g)	hydrogen	0
HCl(g)	hydrogen chloride	-92.31
HCl(aq)*	hydrochloric acid (1 M)	-167.2

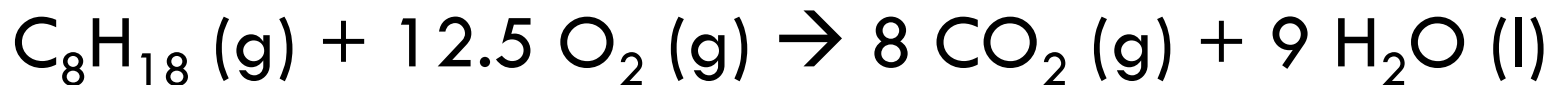
# Molar Heat of Combustion ( $\Delta H_{\text{comb}}$ )

Definition: heat released when one mole of a compound combusts

**Appendix Table A-5, p. 856**



$$\Delta H_{\text{comb}} = -2219.9 \text{ kJ}$$



$$\Delta H_{\text{comb}} = -5450.5 \text{ kJ}$$

# Calculating Heats of Reaction

**Hess's Law**: the overall enthalpy change in a reaction is equal to the sum of enthalpy changes for the individual steps in the process

**In order for a reaction to occur:**

- ▣ all reactants must have their bonds broken
- ▣ all products must have their bonds formed

# Calculating Heats of Reactions

**Hess's Law of Heat Summation:** *If you add two or more thermochemical equations to give a final equation, then you can also add the heats of reaction to give the final heat of reaction*

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

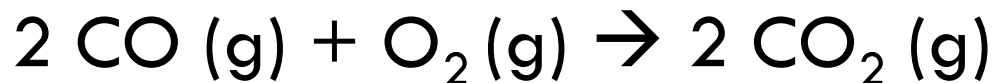
( $\Sigma$  = sum)

- This will also show if the net reaction is exothermic (-) or endothermic (+).

# Sample Problem

What is the  $\Delta H_f^\circ$  for the reaction between gaseous carbon monoxide with oxygen to form gaseous carbon dioxide?

Balanced equation:

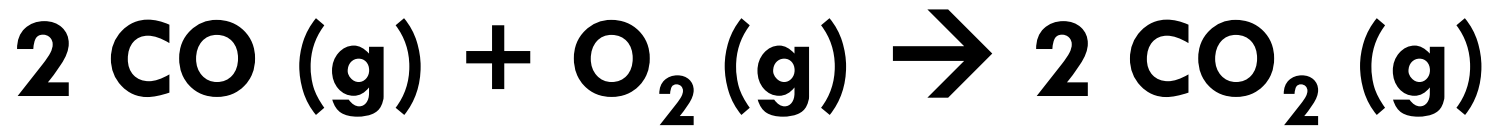


**LOOK UP...**

$$\Delta H_f^\circ \text{CO (g)} = -110.5 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{O}_2 \text{(g)} = 0 \text{ kJ/mol (free element)}$$

$$\Delta H_f^\circ \text{CO}_2 \text{(g)} = -393.5 \text{ kJ/mol}$$



$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta H^\circ = [2 \text{ mol} \times -395.5 \text{ kJ/mol}] - [2 \text{ mol} \times -110.5 \text{ kJ/mol}]$$

$$\Delta H^\circ = [-787 \text{ kJ}] - [-221 \text{ kJ}]$$

$$\Delta H^\circ = -566 \text{ kJ}$$

Therefore, this reaction is an exothermic process!

Appendix A-5 Enthalpy of combustion for CO:

$$\Delta H_c = -283.0 \text{ kJ/mol} \times 2 \text{ mol} = -566.0 \text{ kJ}$$



# Calculating $\Delta H_{\text{Reaction}}$ from the Heats of Formation Reactions



**Look up:**

$$\Delta H_f^\circ \text{PbCl}_2 = -359.4 \text{ kJ/mol}$$

Reaction of the formation:  $\text{Pb} + \text{Cl}_2 \rightarrow \text{PbCl}_2$

$\Delta H_f^\circ \text{Cl}_2 = 0 \text{ kJ/mol}$  because it's an element

$$\Delta H_f^\circ \text{PbCl}_4 = -329.2 \text{ kJ/mol}$$

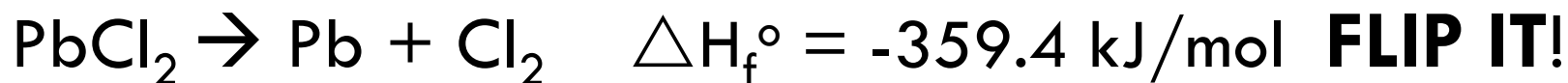
Reaction of the formation:  $\text{Pb} + 2 \text{Cl}_2 \rightarrow \text{PbCl}_4$

**In the reaction:**

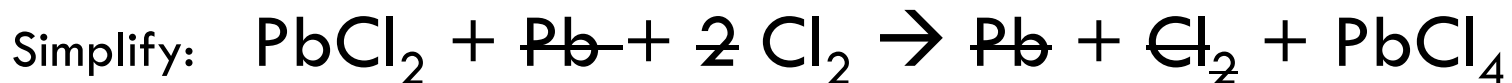
$\text{PbCl}_2$  has to be broken, so reverse the reaction

$\text{PbCl}_4$  has to be made, keep the reaction as written

# Calculating $\Delta H_{\text{Reaction}}$ from the Heats of Formation Reactions



**Now add the equations together:**



$$\text{Add } \Delta H_f^\circ = +359.4 \text{ kJ} + -392.2 \text{ kJ} = 30.2 \text{ kJ}$$

# Calculating $\Delta H_{\text{Reaction}}$ from the Heats of Formation Reactions

**Check Answer with the summation equation:**

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta H^\circ = [1 \text{ mol} \times -329.2 \text{ kJ/mol}] - [1 \text{ mol} \times -359.4 \text{ kJ/mol}]$$

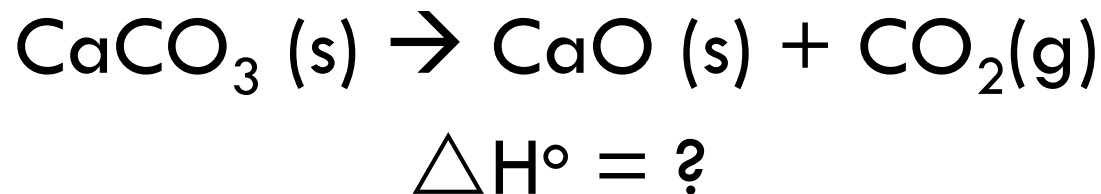
$$\Delta H^\circ = [-329.2 \text{ kJ}] - [-359.4 \text{ kJ}]$$

$$\Delta H^\circ = +30.2 \text{ kJ}$$

Therefore, this reaction is an endothermic process!

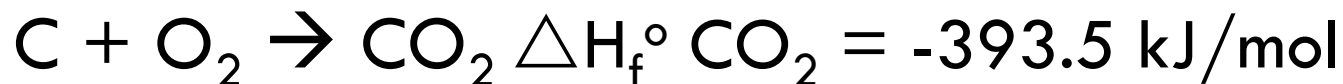
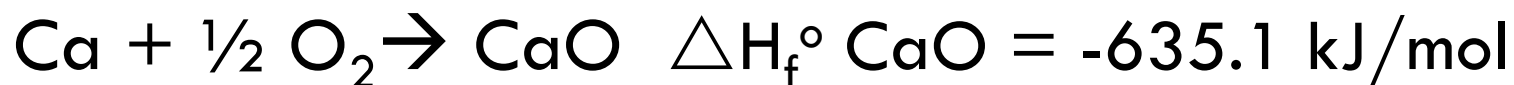
# Calculating $\Delta H_{\text{Reaction}}$ from the Heats of Formation Reactions

Now calculate the heat of reaction for the decomposition of calcium carbonate when heated:





**Look up:**



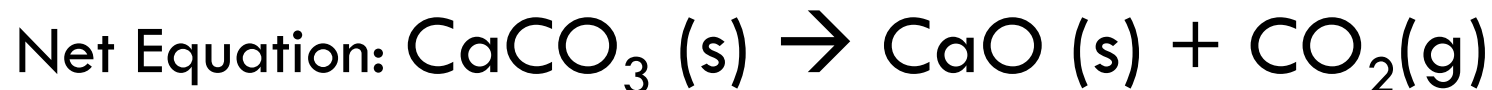
**In the reaction:**

$\text{CaCO}_3$  has to be broken, **so reverse the reaction**

$\text{CaO}$  &  $\text{CO}_2$  has to be made, keep the reactions as written

# Answer:

## Complete equation:



## Add up heats of formation:

CaCO<sub>3</sub> is reversed: +1207 kJ

CaO is the same: -635.1 kJ

CO<sub>2</sub> is the same: -393.5 kJ

TOTAL: 178.4 kJ, endothermic

# Answer:

**Check your answer:**

$$\Delta H = \text{products} - \text{reactants}$$

$$= [-635.1 \text{ kJ} + -393.5 \text{ kJ}] - [-1207 \text{ kJ}]$$

$$= 178.4 \text{ kJ}$$

# Section 16.2 – Driving Force of Reactions

## What makes a reaction spontaneous?

Ex: Ball rolls down a hill – obvious, but why?

Driving force: Potential energy is too high, so nature wants to lower it....

### **SPONTANEOUS!**

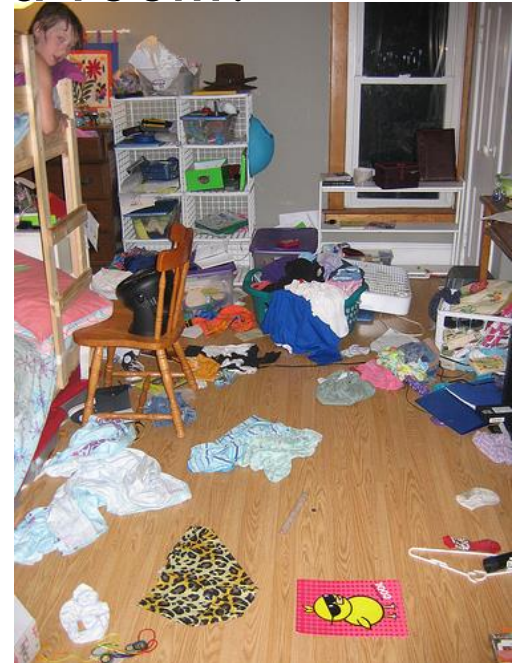
- ▣ Nature has a tendency of reactions to occur that lead to a lower energy state
- ▣ Therefore: ball will NOT roll up a hill!





# Entropy (S)

- Definition: property that describes the order of a system
- Nature tends toward **disorder**
- *Hint*: easier to mess up or to clean up a room?
- We measure  $\Delta S$  in J/K·mol
- *Temperature can effect S*



# Free Energy

Depends on two things:

- ▣ Enthalpy:  $\Delta H$
- ▣ Entropy:  $\Delta S$  and the Temperature of the system

Gibb's Free Energy: combined enthalpy-entropy of a system

$$\Delta G = \Delta H - T\Delta S$$

If  $\Delta G = (-)$  = reaction will be favorable/spontaneous

If  $\Delta G = (+)$  = reaction will be unfavorable/nonspontaneous

**Note:**  $\Delta G^\circ$ ,  $\Delta H^\circ$ , &  $\Delta S^\circ$  = at standard temperature

# Enthalpy, Entropy & Free Energy

$\Delta H$	$\Delta S$	$\Delta G$
- Value (exothermic)	+ Value (more random)	Always negative
- Value (exothermic)	- Value (less random)	Negative @ lower temperatures
+ Value (endothermic)	+ Value (more random)	Negative @ higher temps
+ Value (endothermic)	- Value (less random)	Never negative

# Free Energy Sample Problem

For the reaction  $\text{NH}_4\text{Cl (s)} \rightarrow \text{NH}_3 \text{ (g)} + \text{HCl (g)}$ , at 298.15 K,  $\Delta H^\circ = 176 \text{ kJ/mol}$  and  $\Delta S^\circ = 0.285 \text{ kJ/(mol}\cdot\text{K)}$ . Calculate  $\Delta G^\circ$ , and tell whether this reaction is spontaneous in the forward direction at this temperature.

# Free Energy Sample Problem

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = 176 \text{ kJ/mol} - [298 \text{ K} \times 0.285 \text{ kJ}/(\text{mol}\cdot\text{K})]$$

$$\Delta G = 176 \text{ kJ/mol} - 84.9 \text{ kJ/mol}$$

$$\Delta G = 91.0 \text{ kJ/mol}$$

**Non spontaneous because  $\Delta G =$  positive!**

## Chapter 17: Reaction Kinetics



# Collision Theory



# Section 17.1 – The Reaction Process

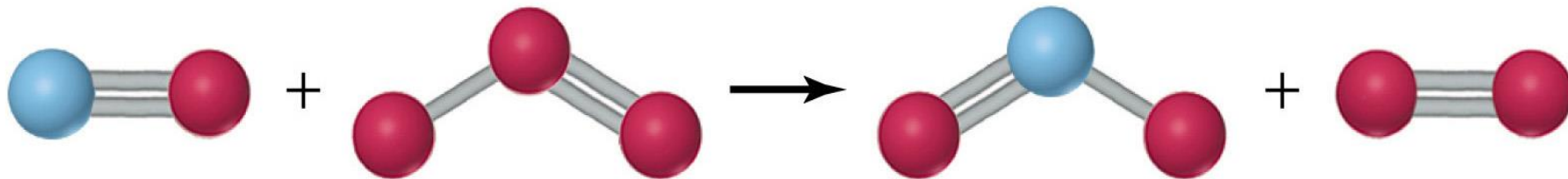
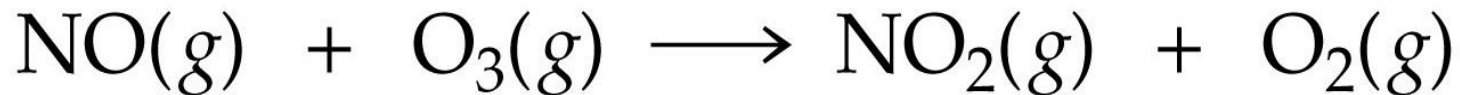
- Reaction Mechanism: step-by-step sequence of reactions by which the overall chemical change occurs
- Why does the rate of chemical reactions vary so widely?
- Collision Theory:
  - ▣ Reactant molecules must collide in the proper orientation and with sufficient energy
  - ▣ Only a fraction of collisions meet these requirements



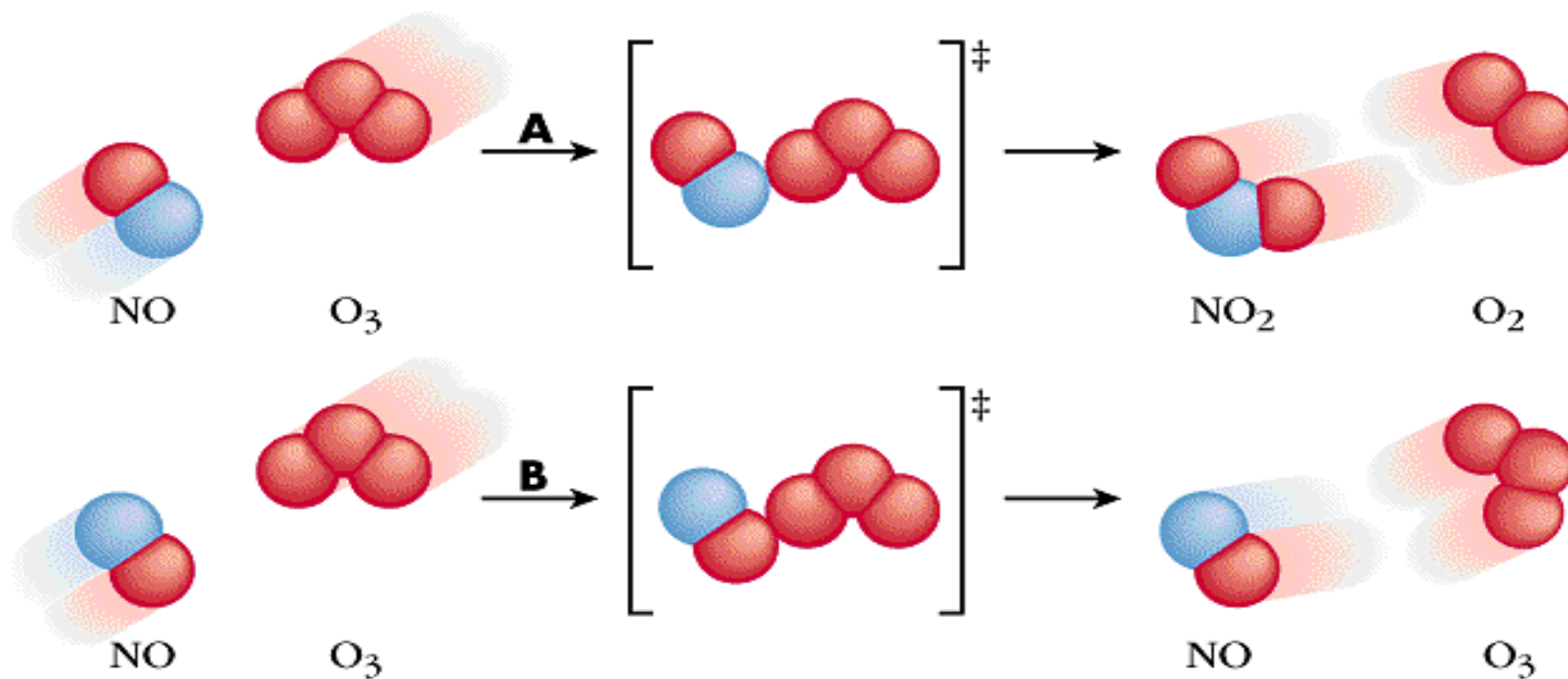
# Collision Theory

Consider:

▣ Ozone + smog  $\rightarrow$  nitrogen dioxide + oxygen



# Collisions of NO and O<sub>3</sub>

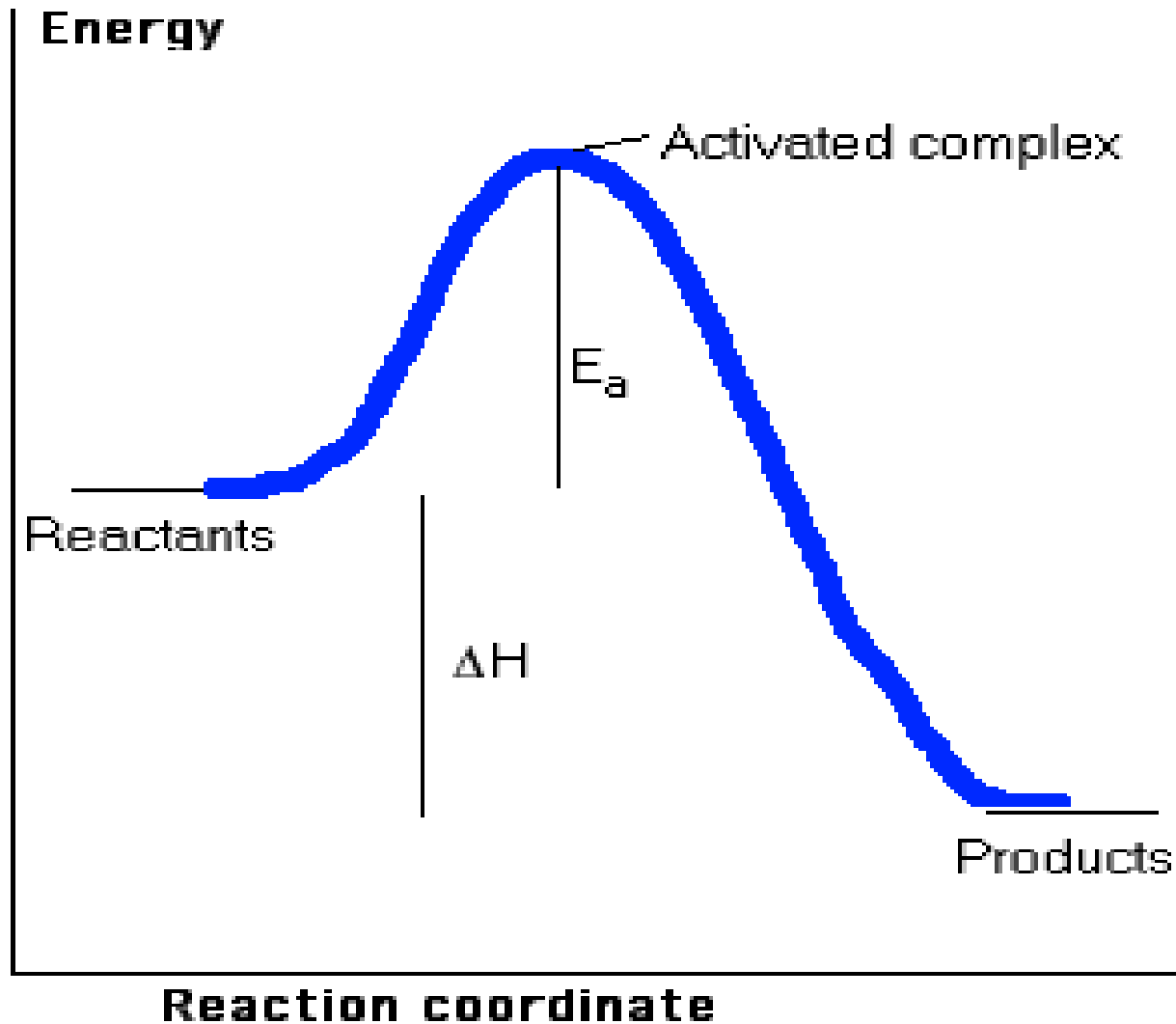


# Energy Diagrams

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- Reactants must overcome an energy barrier before they can change to products
- Activation Energy ( $E_a$ ):
  - ▣ Minimum amount of energy that reactants must have before they can be converted to products

# Energy Diagrams

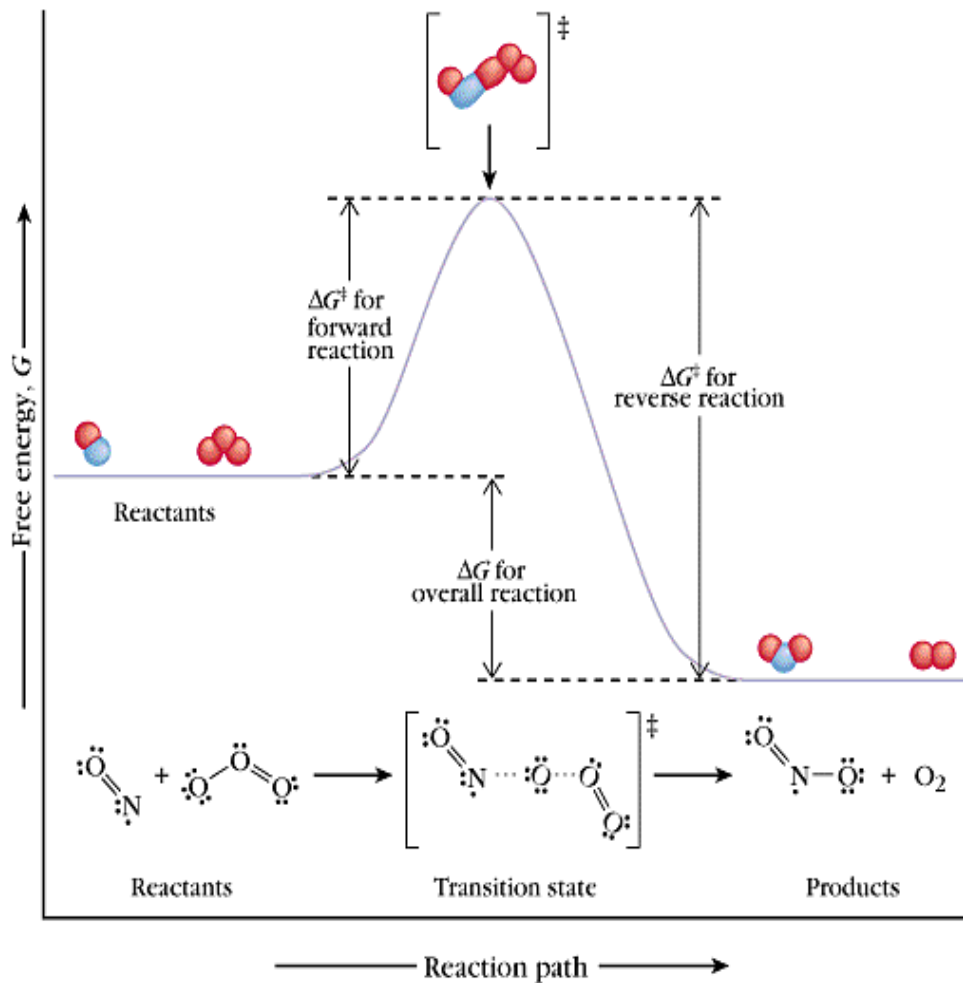


# Energy Diagrams

## Activated Complex:

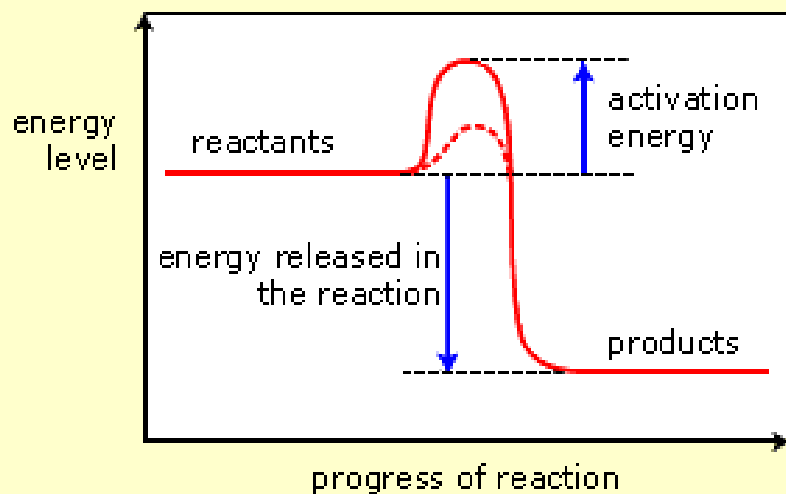
- ▣ An unstable, high-energy chemical species that must be formed as reactants convert to products
- ▣ The in-between stage....
- ▣ Designated with a double superscript dagger ( $\ddagger$ )
  - such as  $\{\text{O}_3\text{NO}\}^\ddagger$

# Energy Diagram for NO and O<sub>3</sub>

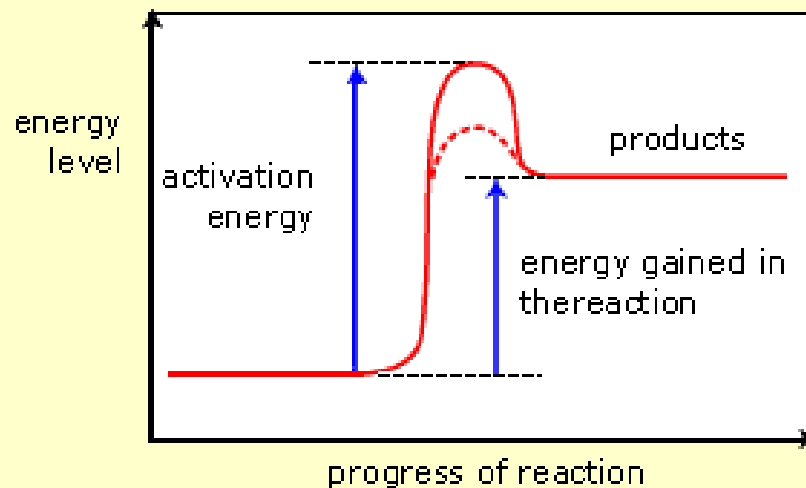


# Exothermic vs. Endothermic

Energy levels in an exothermic reaction



Energy levels in an endothermic reaction



# Energy Diagrams with Activated Complexes

**Example:** The following is exothermic:

- $2 \text{HI} (\text{g}) \rightarrow \text{H}_2 (\text{g}) + \text{I}_2 (\text{g})$
- Draw an energy diagram that shows the relative energies of the reactants, products and the activated complex.
- Label the diagram with molecular representations of the reactants, products, and a possible structure for the activated complex.



# Section 17.2 - Reaction Rates

- What makes milk and other foods spoil more quickly?
- What happens if you accidentally add a drop of bleach to a dark wash? A cup?
- What dissolves faster granulated sugar or a sugar cube?



# Reaction Rates

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## **Factors that influence reaction rates**

1. Temperature
2. Reaction concentration
3. Surface area
4. Presence of a catalyst

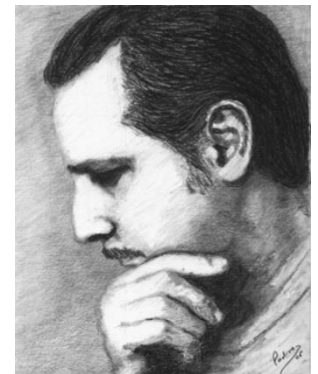
Looking at each in the terms of Collision Theory!

# Temperature

- The average kinetic energy of a substance increases when the temperature rises
- Increases the fraction of collisions that are effective
- Molecules move faster at higher temperatures, so they collide more frequently
- More molecules attain the required activation energy
- For a typical reaction, the rate approximately doubles for every  $10^{\circ}\text{C}$  increase in temperature

# Concentration

- Reactions go faster when the concentration of one or more of the reactants increases
- Increases in concentration increases the number of reactants per unit volume
- Because molecules are closer together, the number of collisions per unit time increases

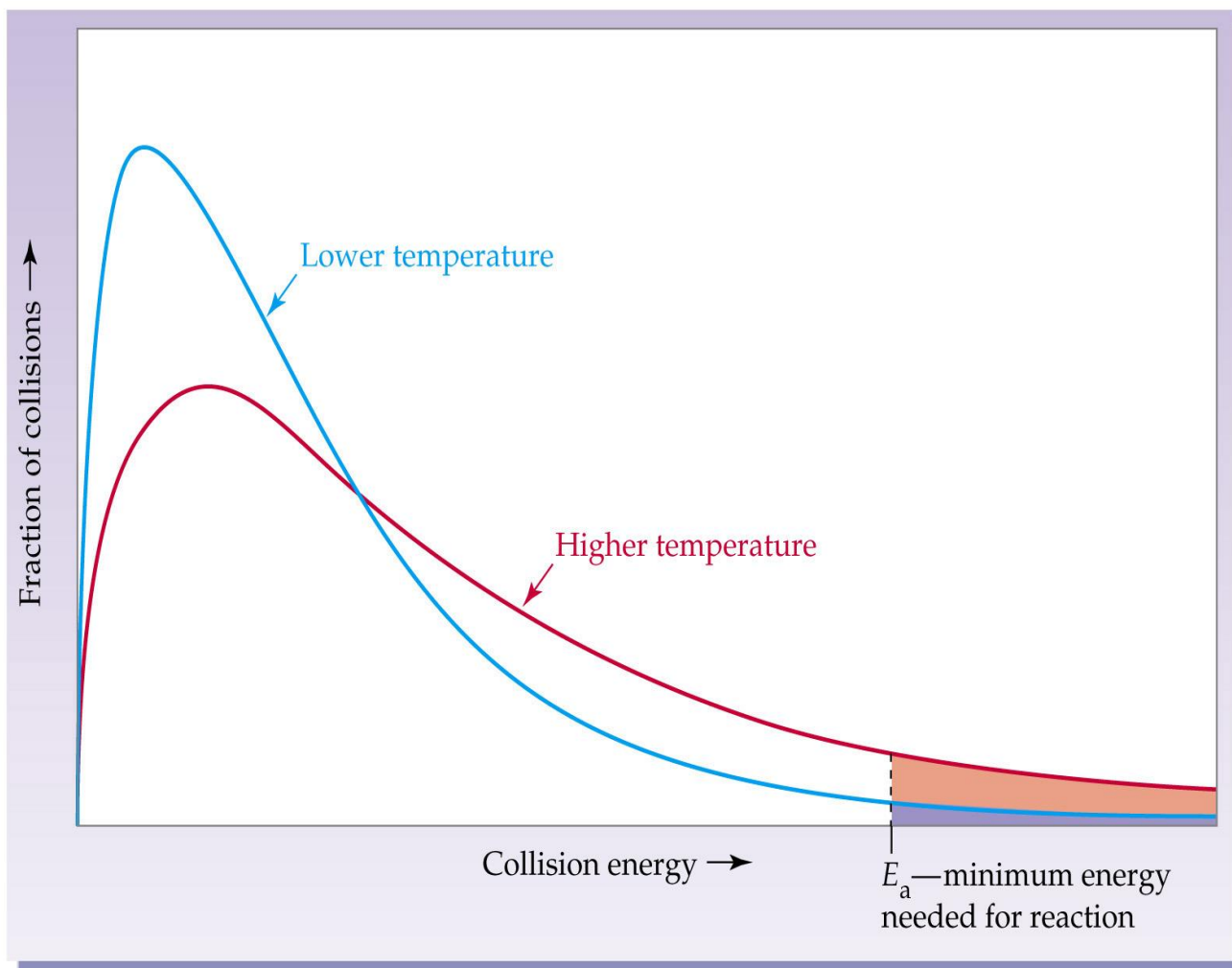


# Surface Area

- Similar to increase concentration
- More surface area means more molecules or atoms exposed to the reaction collisions
- Ex) granulated sugar vs. sugar cubes



# Fraction of Collisions vs. Collision Energy @ Different Temperatures

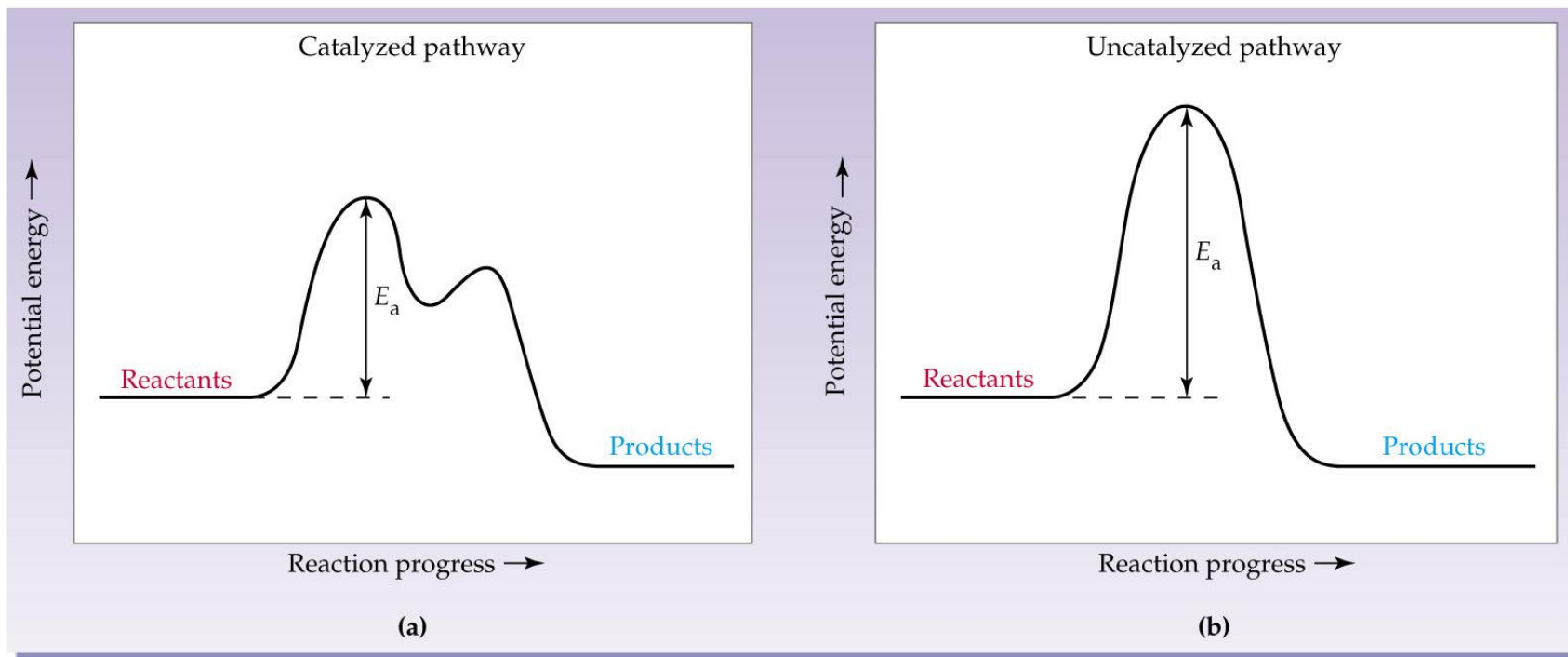


# Catalysts

## Catalyst:

- ▣ A substance that alters the pathway in which a reaction occurs without itself being consumed in the reaction
- ▣ Lower-energy pathway with lower activation energy
- ▣ This way, increases the rate of a reaction
  - Greater fraction of reactants can achieve the new minimum energy requirement

# Catalyst





# Rate Laws for Reactions

**Rate Law**: an equation that relates reaction rate and concentrations of reactants

- Specific Rate Laws for the directions of reactions
  - ▣ Forward rate law is different than the reverse reaction rate law

# Rate Laws for Reactions



□ Rate Law of the forward reaction:

□ Depends on concentrations of  $\text{H}_2$  and  $\text{NO}$

□ Depends on temperature

$$R = k [\text{reactants}]^{\text{coefficient}}$$

□  $R$  = reaction rate

□  $k$  = rate constant (takes into account temperature)

□  $R = k [\text{H}_2]^2 [\text{NO}]^2$