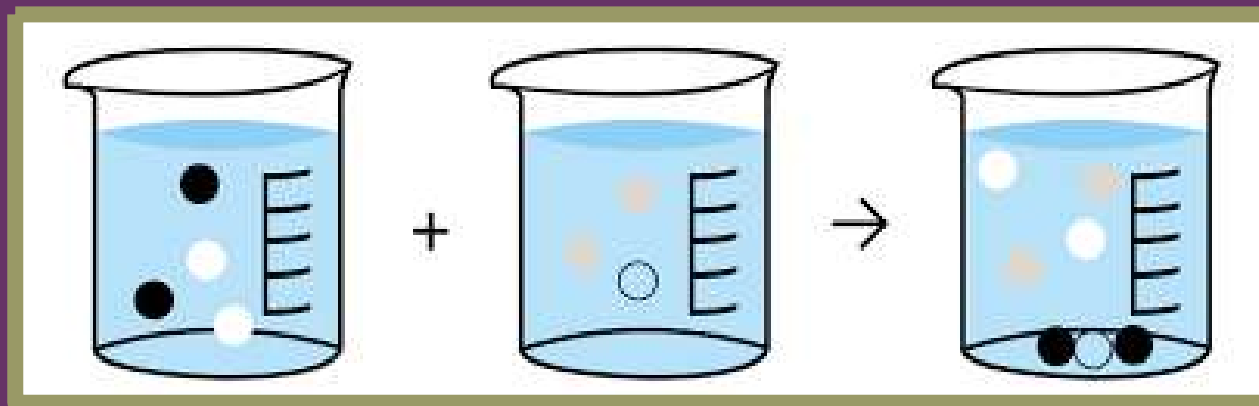


# AP Chemistry Exam Review



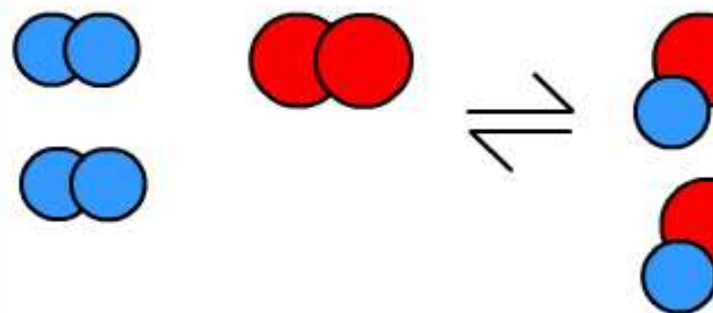
+

Big Idea #3

Chemical Reactions

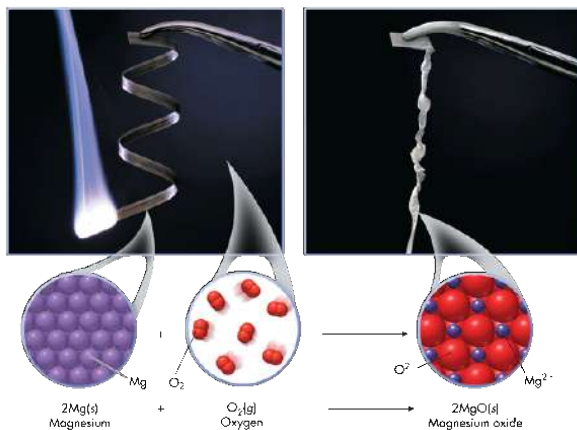
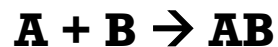


Changes in matter involve the rearrangement and/or reorganizations of atoms and/or the transfer of electrons

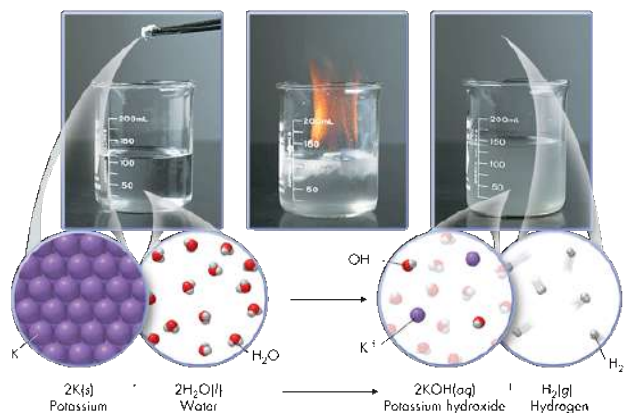


# + Types of Chemical Reactions

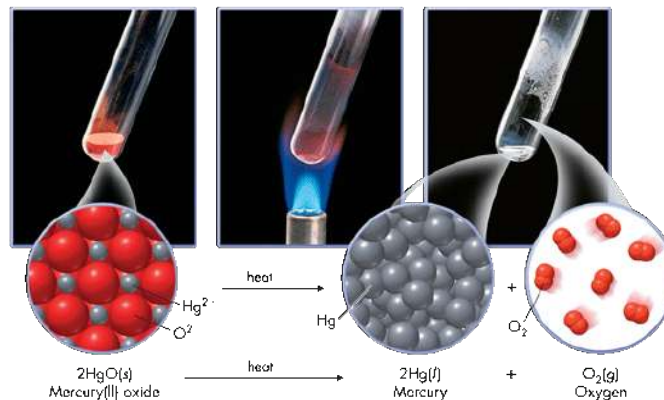
## Synthesis



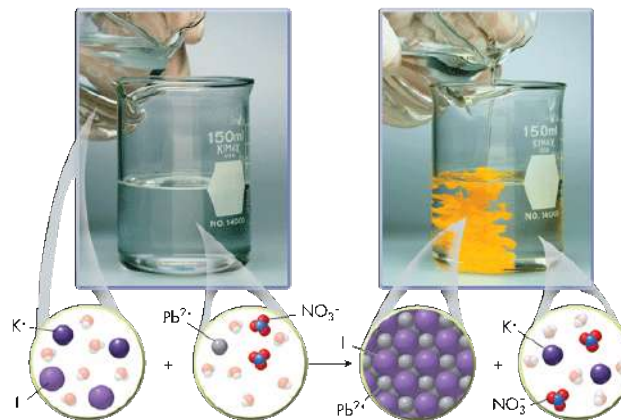
## Single Displacement



## Decomposition



## Double Displacement

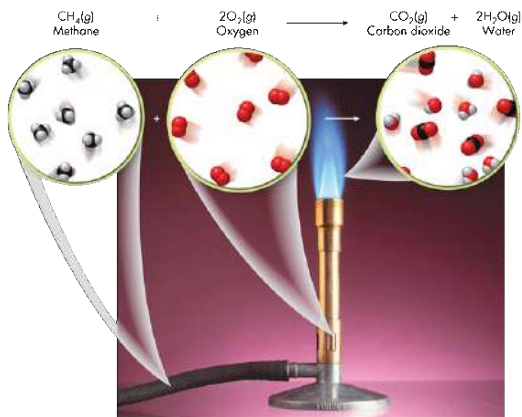


Images from: Wilbraham, Antony C. *Pearson Chemistry*. Boston, MA: Pearson, 2012. Print.

LO 3.1: Students can translate among macroscopic observations of change, chemical equations, and particle views.

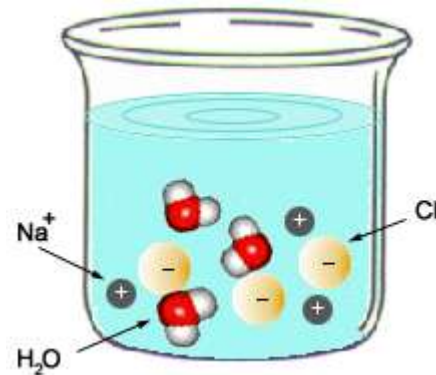
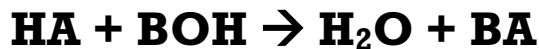
# + Types of Chemical Reactions

## Combustion



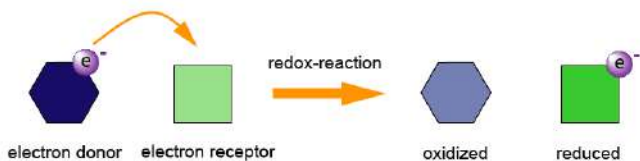
C. Pearson Chemistry.  
Boston, MA: Pearson, 2012.  
Print.

## Acid-Base (Neutralization)



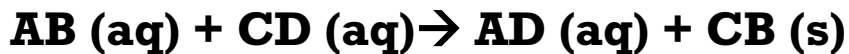
[Video](#)

## Oxidation-Reduction



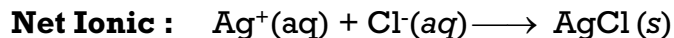
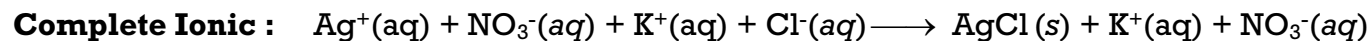
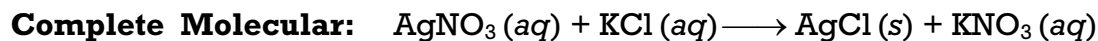
- electron
- molecule A
- molecule B

## Precipitation



LO 3.1: Students can translate among macroscopic observations of change, chemical equations, and particle views.

# + Balanced Equations



Source

[Video Quizlet](#)

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

**TABLE 4.2** Solubility Rules for Common Ionic Compounds in Water at 25°C

Soluble Compounds	Insoluble Exceptions
Compounds containing alkali metal ions ( $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Rb}^+$ , $\text{Cs}^+$ ) and the ammonium ion ( $\text{NH}_4^+$ )	
Nitrates ( $\text{NO}_3^-$ ), bicarbonates ( $\text{HCO}_3^-$ ), and chlorates ( $\text{ClO}_3^-$ )	
Halides ( $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ )	Halides of $\text{Ag}^+$ , $\text{Hg}_2^{2+}$ , and $\text{Pb}^{2+}$
Sulfates ( $\text{SO}_4^{2-}$ )	Sulfates of $\text{Ag}^+$ , $\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Hg}_2^{2+}$ , and $\text{Pb}^{2+}$
Insoluble Compounds	Soluble Exceptions
Carbonates ( $\text{CO}_3^{2-}$ ), phosphates ( $\text{PO}_4^{3-}$ ), chromates ( $\text{CrO}_4^{2-}$ ), sulfides ( $\text{S}^{2-}$ )	Compounds containing alkali metal ions and the ammonium ion
Hydroxides ( $\text{OH}^-$ )	Compounds containing alkali metal ions and the $\text{Ba}^{2+}$ ion

Spectator ions should not be included in your balanced equations.

Remember, the point of a Net Ionic Reaction is to show only those ions that are involved in the reaction. Chemists are able to substitute reactants containing the same species to create the intended product.

*You only need to memorize that compounds with nitrate, ammonium, halides and alkali metals are soluble.*

**LO 3.2:** The student can translate an observed chemical change into a balanced chemical equation and justify the choice of equation type (molecular, ionic, or net ionic) in terms of utility for the given circumstances.

# + Making Predictions

Solid copper carbonate is heated strongly:

Click reveals answer and explanation.

What evidence of a chemical change would be observed with this reaction?

Click reveals answer and explanation.

What is the percent yield of  $\text{CO}_2$  if you had originally heated 10.0g  $\text{CuCO}_3$  and captured 3.2g  $\text{CO}_2$  ?

Click reveals answer and explanation.

How could you improve your percent yield?

Click reveals answer and explanation.

[Video](#)

**LO 3.3: The student is able to use stoichiometric calculations to predict the results of performing a reaction in the laboratory and/or to analyze deviations from the expected results.**

# + Limiting Reactants – D.A.



15.00 g aluminum sulfide and 10.00 g water react

a) Identify the Limiting Reactant

Click reveals answer and explanation.

b) What is the maximum mass of  $\text{H}_2\text{S}$  which can be formed from these reagents?

Click reveals answer and explanation.

c) How much excess reactant is left in the container?

Click reveals answer and explanation.

*\*\*Dimensional Analysis is not the only way to solve these problems. You can also use BCA tables (modified ICE charts), which may save time on the exam →*

Source

[Video](#)  
[Sim](#)  
[pHet](#)

LO 3.4: The student is able to relate quantities (measured mass of substances, volumes of solutions, or volumes and pressures of gases) to identify stoichiometric relationships for a reaction, including situations involving limiting reactants and situations in which the reaction has not gone to completion.



# + Limiting Reactants – BCA Table

15.00 g aluminum sulfide and 10.00 g water react according to the following equation:



a) Identify the Limiting Reactant

Click reveals answer and explanation.

b) What is the maximum mass of  $\text{H}_2\text{S}$  which can be formed from these reagents?

Click reveals answer and explanation.

c) How much excess reactant is left in the container?

Click reveals answer and explanation.

[Video](#)

# + Experimental Design

## Synthesis

A sample of pure Cu is heated in excess pure oxygen. Design an experiment to determine quantitatively whether the product is CuO or Cu<sub>2</sub>O.

[Video](#)

Click reveals basic steps

## Decomposition



Design a plan to prove experimentally that this reaction illustrates conservation of mass.

Click reveals basic steps

LO3.5: The student is able to design a plan in order to collect data on the synthesis or decomposition of a compound to confirm the conservation of matter and the law of definite proportions.

# + Data Analysis

When tin is treated with concentrated nitric acid, and the resulting mixture is strongly heated, the only remaining product is an oxide of tin. A student wishes to find out whether it is SnO or SnO<sub>2</sub>.

Mass of pure tin 5.200 grams.  
Mass of dry crucible 18.650 g  
Mass of crucible + oxide after first heating 25.500 g  
Mass after second heating 25.253 g  
Mass after third heating 25.252 g

**How can you use this data, and the law of conservation of mass, to determine the formula of the product?**

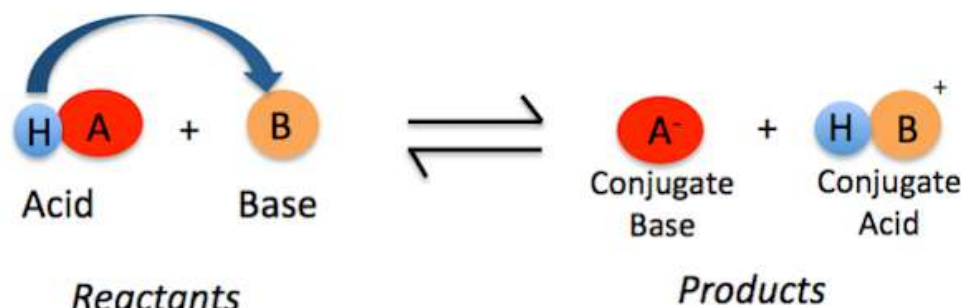
Click reveals answer and explanation.

# + Bronsted-Lowry Acids & Bases

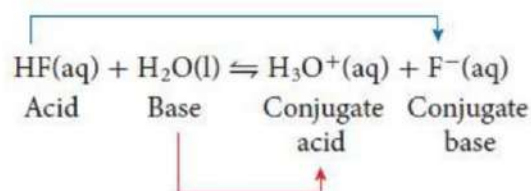
According to Bronsted-Lowry (B.L.) an acid is a "proton donor" and a base is a "proton acceptor." The proton here is shown as a hydrogen.

The acid's conjugate base is the anion.

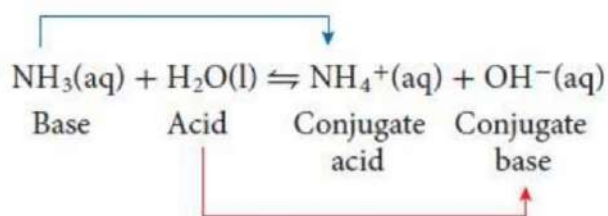
The base's conjugate acid now has the proton (hydrogen ion).



## ▶ Hydrogen fluoride: A Brønsted-Lowry acid

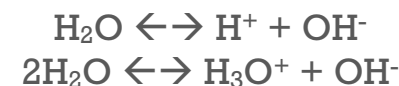
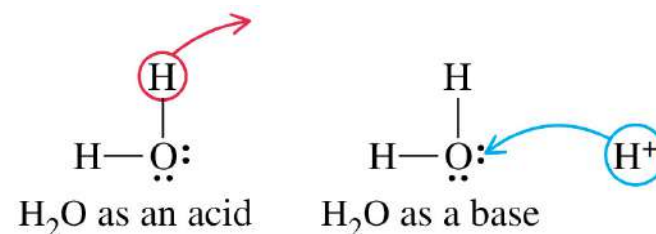


## ▶ Ammonia: A Brønsted-Lowry base



## Amphoteric nature of water

Water acts as both an acid & a base.

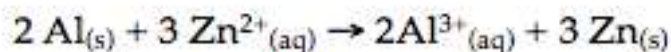


LO 3.7: The student is able to identify compounds as Bronsted-Lowry acids, bases and/or conjugate acid-base pairs, using proton-transfer reactions to justify the identification.

# + Redox Reactions

- When an electron is transferred, it is called a **redox reaction**. When something is reduced, the RED part of redox, it gains electrons. You may have a difficult time with this definition because when something is reduced, it

inc ions will react with aluminum metal according to the following chemical reaction:



Based on this chemical reaction how many moles of electrons would be transferred

when 1.0 mole of  $\text{Zn}^{2+}$  is reduced to  $\text{Zn}_{(s)}$ .  
 Reduced compound A      Oxidized compound B

Answer:

- The correct answer is "c" 2.0 moles. For each  $\text{Zn}^{2+}$  ion 2 electrons are needed to convert it in to a Zn atom. If we are consuming 1 mole of  $\text{Zn}^{2+}$  we will need to transfer 2 moles of electrons.
- 0.33 moles
- 2.0 moles
- 0.67 moles
- 0.33 moles

©2011, Aaron Glimme, LearnAPChemistry.com

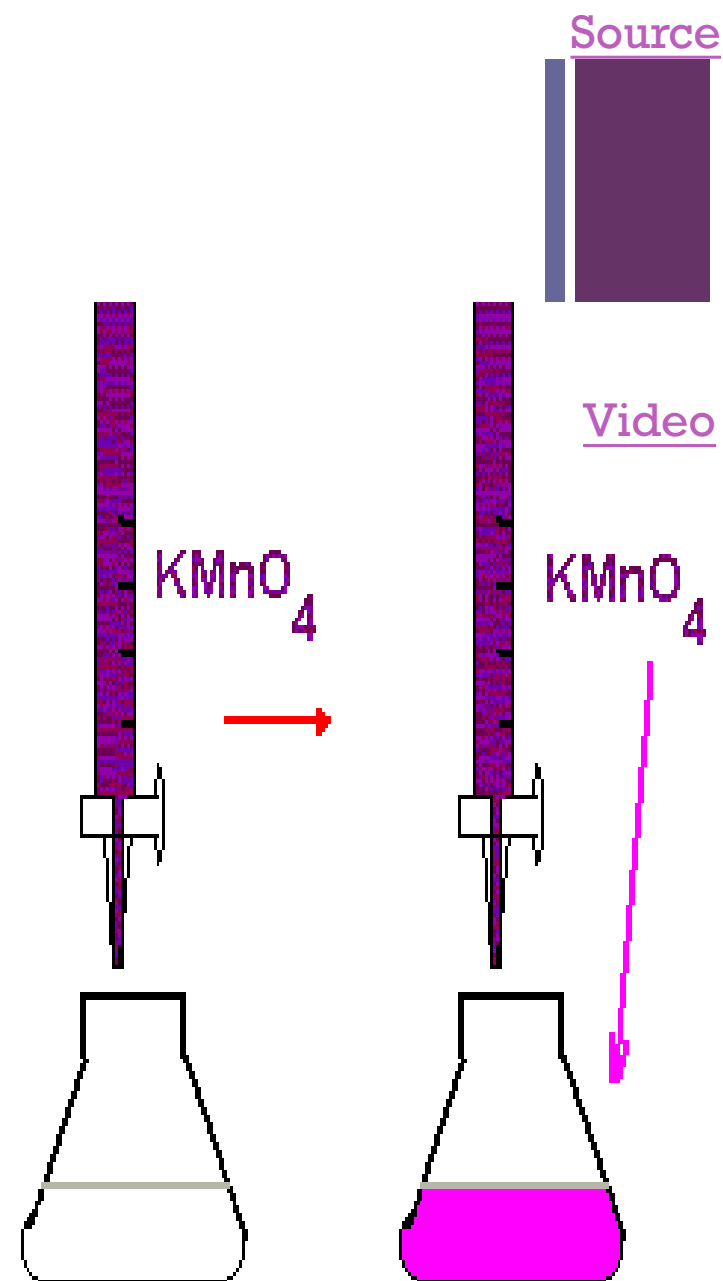
LO 3.8: The student is able to identify redox reactions and justify the identification in terms of electron transfer

# + Redox Titrations

A redox titration (also called an oxidation-reduction titration) can accurately determine the concentration of an unknown analyte by measuring it against a standardized titrant. A common example is the redox titration of a standardized solution of potassium permanganate ( $\text{KMnO}_4$ ) against an analyte containing an unknown concentration of iron (II) ions ( $\text{Fe}^{2+}$ ). The balanced reaction in acidic solution is as follows:



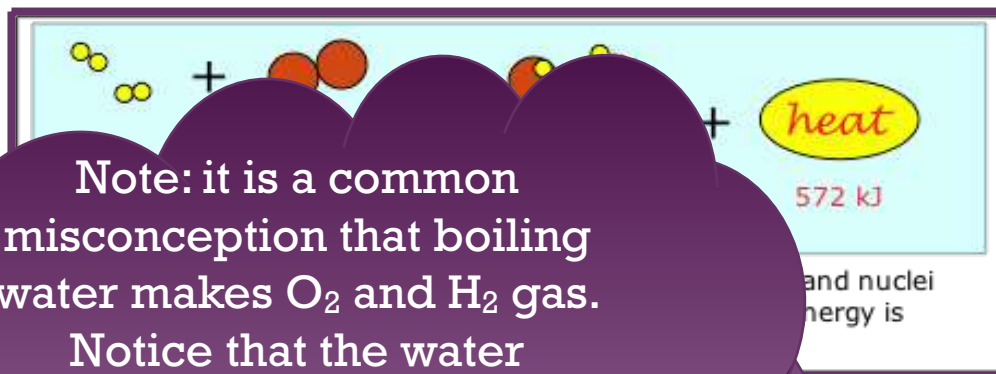
In this case, the use of  $\text{KMnO}_4$  as a titrant is particularly useful, because it can act as its own indicator; this is due to the fact that the  $\text{KMnO}_4$  solution is bright purple, while the  $\text{Fe}^{2+}$  solution is colorless. It is therefore possible to see when the titration has reached its endpoint, because the solution will remain slightly purple from the unreacted  $\text{KMnO}_4$



LO 3.9: The student is able to design and/or interpret the results of an experiment involving a redox titration

# Evidence of Chemical Change

+



Note: it is a common misconception that boiling water makes O<sub>2</sub> and H<sub>2</sub> gas.

Notice that the water molecule stays intact as the water boils. Covalent bonds are not broken with this physical change- only intermolecular attractions (hydrogen bonds) between water molecules.

Source

[Video](#)  
[Video](#)  
[Video](#)

## Chemical Changes:

Production of gas:

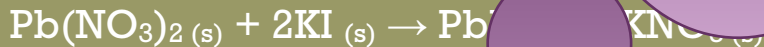


Formation of a precipitate:



Change in color:

Two white solids react to form a yellow and a white solid. This is a chemical change!



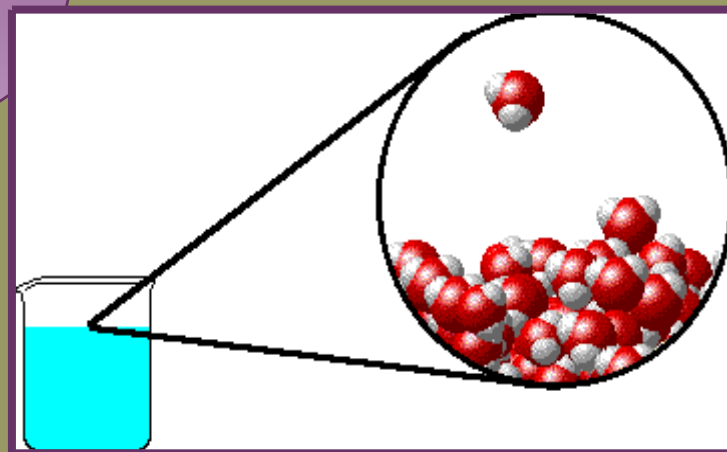
Production of heat\*:



\*can also include the absorption of heat

## Signs:

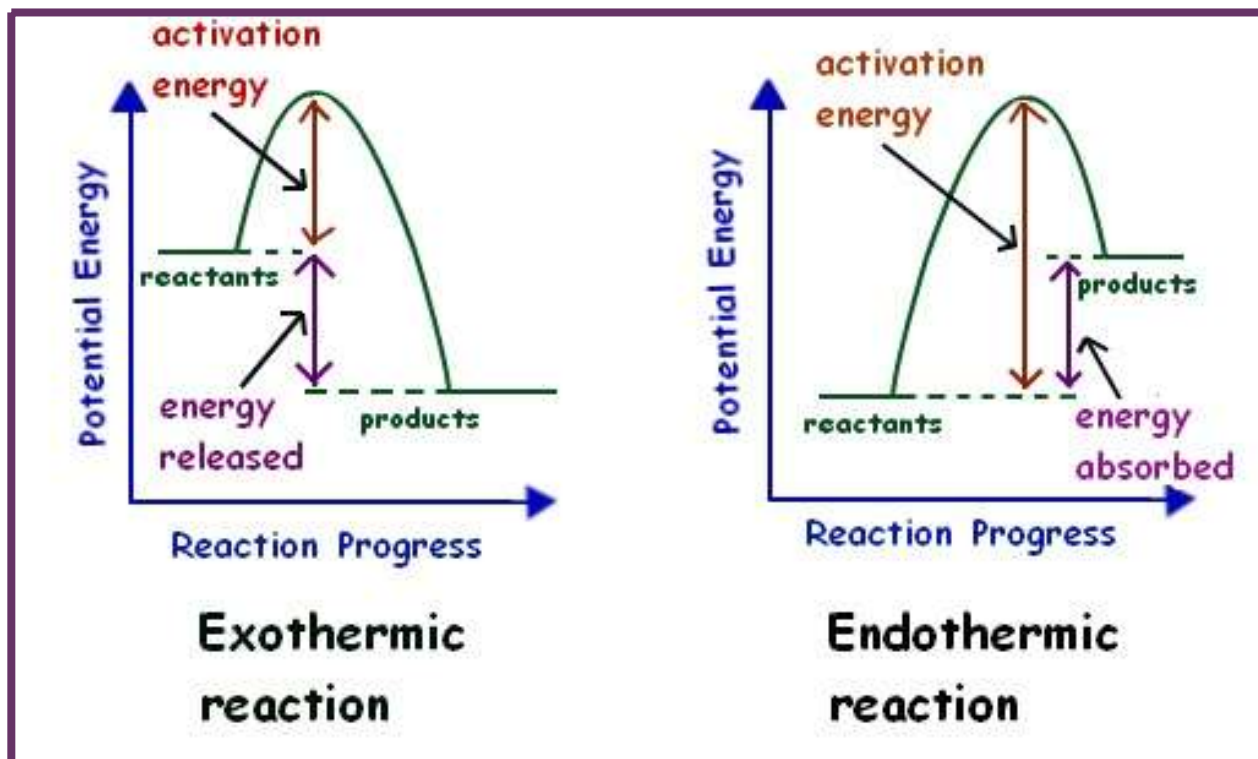
Similar visible evidence (i.e. bubbles) creates “bubbles,” but bonds are not broken and reformed. No new substances are formed.



LO 3.10: Evaluate the classification of a process as a physical, chemical, or ambiguous change based on both macroscopic observations and the distinction between rearrangement of covalent interactions and noncovalent interactions.

# + Energy Changes

- Chemical reactions involve the formation of new products
- Bonds between atoms or ions in the reactants must be **BROKEN** (the enthalpy of the system is increasing ... **ENDOTHERMIC** process)
- Bonds are then **FORMED** between atoms or ions to make the products of the reaction. (the enthalpy of the system is decreasing...**EXOTHERMIC** process)

[Video](#)[Video](#)

LO 3.11: The student is able to interpret observations regarding macroscopic energy changes associated with a reaction or process to generate a relevant symbolic and/or graphical representation of the energy changes.

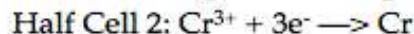
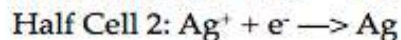
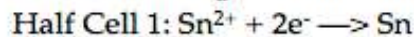


+

# Galvanic Cell Potential

## Question:

The following question is based on combining the three different half cells listed below:



Galvanic Cell	Half Cells	Reaction	$E^{\circ}_{\text{cell}}$ (V)
X	1 & 2	$\text{Sn} + 2\text{Ag}^{+} \longrightarrow 2\text{Ag} + \text{Sn}^{2+}$	0.94
Y	2 & 3	$\text{Cr} + 3\text{Ag}^{+} \longrightarrow 3\text{Ag} + \text{Cr}^{3+}$	1.54
Z	1 & 3	$2\text{Cr} + 3\text{Sn}^{2+} \longrightarrow 3\text{Sn} + 2\text{Cr}^{3+}$	?

What is the cell potential of galvanic cell Z?

- a. 0.26 V
- b. 0.60 V
- c. 2.48 V
- d. 5.90 V

©2014, Aaron Glimme, LearnAPChemistry.com

Click reveals answer and explanation.

Source

[Video](#)

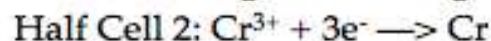
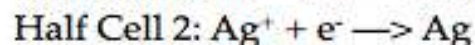
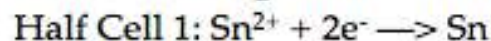
[Video](#)

LO 3.12: Make qualitative or quantitative predictions about galvanic or electrolytic reactions based on half-cell reactions and potentials and/or Faraday's laws.

# + Redox Reactions and Half Cells

## Question:

The following question is based on combining the three different half cells listed below:



Galvanic Cell	Half Cells	Reaction	$E^{\circ}_{\text{cell}}$ (V)
X	1 & 2	$\text{Sn} + 2\text{Ag}^{+} \longrightarrow 2\text{Ag} + \text{Sn}^{2+}$	0.94
Y	2 & 3	$\text{Cr} + 3\text{Ag}^{+} \longrightarrow 3\text{Ag} + \text{Cr}^{3+}$	1.54

## Answer:

The correct answer is "c", oxidation occurs in cell X and reduction in cell Z. In galvanic cell X the tin is losing electrons to form the  $\text{Sn}^{2+}$  ion, this is oxidation. In galvanic cell Z the  $\text{Sn}^{2+}$  is gaining electrons to form Sn, this is reduction.

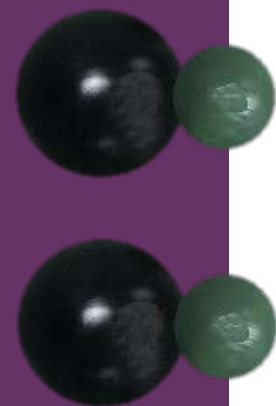
d. Reduction occurs in cell X and oxidation in cell Z.

©2014, Aaron Glimme, LearnAPChemistry.com

[Video](#)

[Video](#)

LO 3.13: The student can analyze data regarding galvanic or electrolytic cells to identify properties of the underlying redox reactions

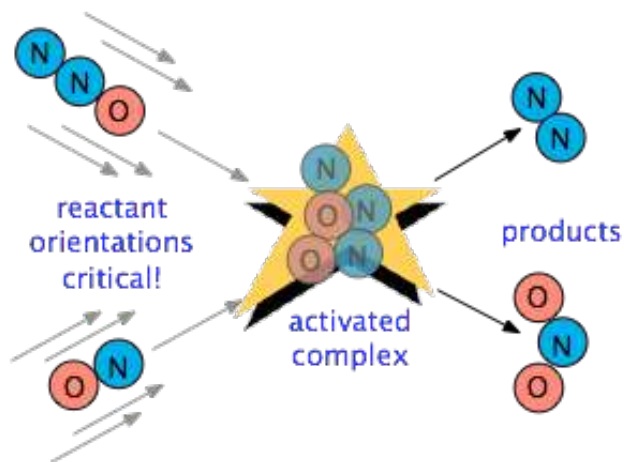


+

# Big Idea #4

# Kinetics

# + Factors Affecting Reaction Rate



*Collision theory states that reactants must collide in the correct orientation and with enough energy for the molecules to react; changing the number of collisions will affect the reaction rate*

Rate is the change in concentration over time

$$\Delta[\mathbf{A}] / t$$

## ■ Factors that Affect Reaction Rate

### ■ State of reactants

■ Rate increases as state changes from solid  $\rightarrow$  gas as increased molecular movement allows for more opportunity for collision

■ Greater surface area of solids will increase rate as more reactant is exposed and able to participate in collisions

■ **Temperature** - more kinetic energy leads to more successful collisions between molecules

■ **Concentration** - more reactants  $\rightarrow$  more collisions

■ **Use of a catalyst** - affect the mechanism of reaction leading to faster rate

LO 4.1: The student is able to design and/or interpret the results of an experiment regarding the factors (i.e., temperature, concentration, surface area) that may influence the rate of a reaction.

# + Determining Rate Order

Rate law for a reaction has the form:  $\text{rate} = k [\text{A}]^m [\text{B}]^n \dots$  (only reactants are part of the rate law)

Exponents ( $m, n, \text{etc.}$ ) are determined from examining data, not coefficients:



Trial	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial Rate (mol/(L·s))
1	0.100	0.100	0.002
2	0.200	0.100	0.002
3	0.200	0.200	0.004

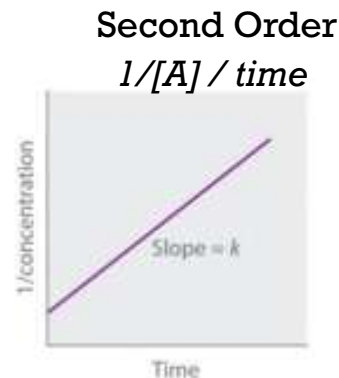
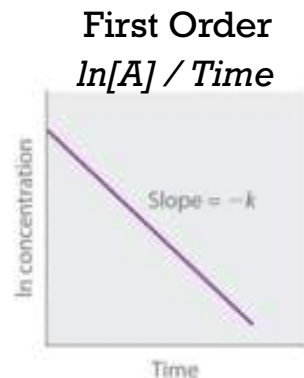
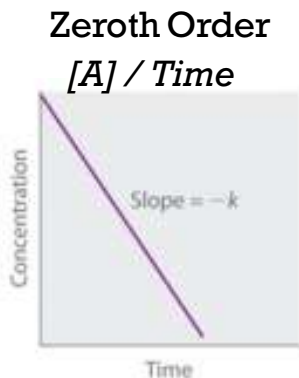
When [A] is doubled, the rate do not change, so the reaction is zero order with respect to A

When [B] is doubled, the rate doubles, so the reaction is first order with respect to B

The overall rate expression for the reaction is  $\text{rate} = k [\text{B}]$

$k$  is the rate constant and is determined experimentally by plugging in data into the rate expression

Plot to create a straight line graph:



The first and second order integrated rate laws can be found on the Kinetics section of the AP Equations Sheet

LO 4.2: The student is able to analyze concentration vs. time data to determine the rate law for a zeroth-, first-, or second-order reaction.

# + Half-life (First Order)

$$\ln[A] = -kt + \ln[A]_0$$

$$\ln \frac{[A]_0}{2} = -kt + \ln[A]_0$$

$$\ln[A]_0 - \ln 2 = -kt + \ln[A]_0$$

$$\ln[A]_0 - \ln[A]_0 - \ln 2 = -kt$$

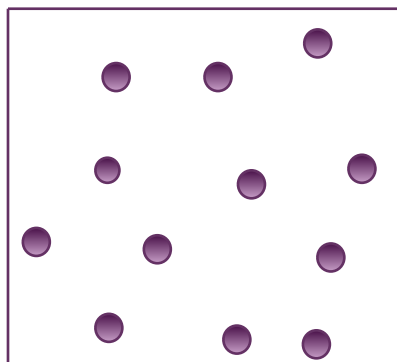
$$-\ln 2 = -kt$$

$$\ln 2 = kt$$

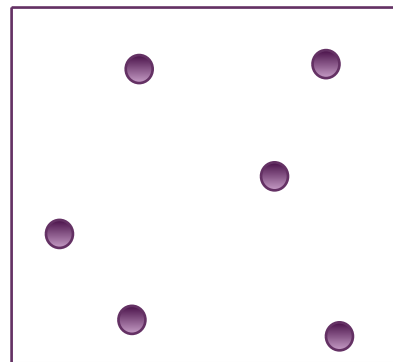
$$t_{1/2} = \frac{\ln 2}{k}$$

The first order half life equation is derived from the first order integrated rate law

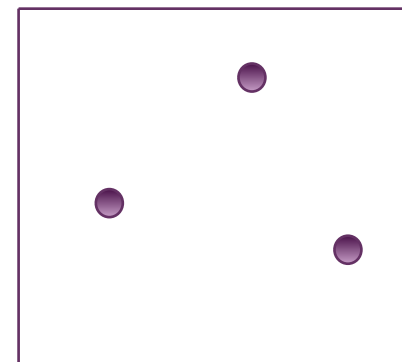
- Time needed for the concentration of reactant to reach half its initial value
- Time to reach half concentration is dependent on  $k$ , not initial concentration
- Half life remains constant in a first order reaction
- **Example:** when  $t_{1/2} = 30$  sec, the concentration is halved each 30 seconds



Initial Conditions  
(12 molecules)



After 30 seconds  
(6 molecules)



After 60 seconds  
(3 molecules)

LO 4.3: The student is able to connect the half-life of a reaction to the rate constant of a first-order reaction and justify the use of this relation in terms of the reaction being a first-order reaction.

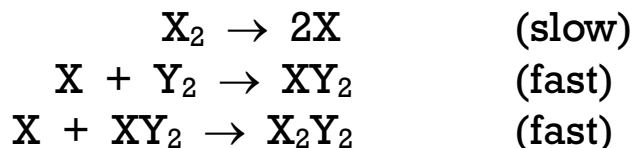
# + Reaction Mechanisms



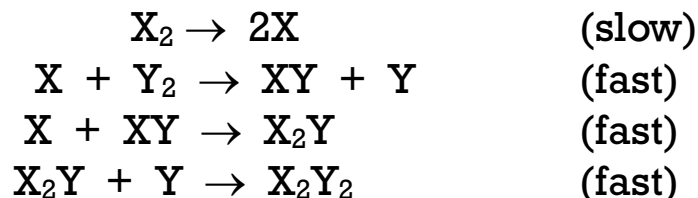
A reaction and its experimentally determined rate law are represented above. A chemist proposes two different possible mechanisms for the reaction, which are given below.

[Video](#)

## Mechanism 1



## Mechanism 2



Based on the information above, which of the mechanisms is/are consistent with the rate law? List the intermediates in each mechanism:

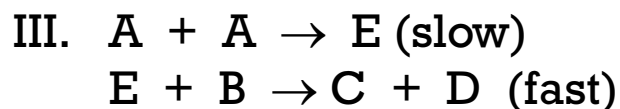
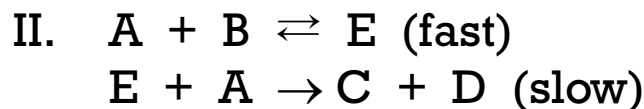
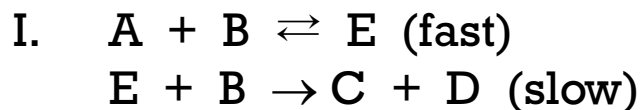
Answer: Both are consistent. In both mechanisms, the molecularity of the slow, rate determining step is consistent with the rate law. Furthermore, the sum of the elementary steps for both mechanisms gives the overall balanced equation for the reaction.

Intermediates in mechanism 1: X, XY<sub>2</sub>. Intermediates in mechanism 2: X, XY, Y, X<sub>2</sub>Y

LO 4.7: Evaluate alternative explanations, as expressed by reaction mechanisms, to determine which are consistent with data regarding the overall rate of a reaction, and data that can be used to infer the presence of a reaction intermediate.

# + Reaction Mechanisms

The rate law for a reaction is found to be  $\text{Rate} = k[\text{A}]^2[\text{B}]$ . What is the intermediate? Which of the following mechanisms gives this rate law?



- A. I  
B. II  
C. III  
D. Two of these

Answer: E is the intermediate. Only Mechanism II is consistent with the rate law. Whenever a fast equilibrium step producing an intermediate precedes the slow rate determining step and we want to remove the intermediate from the rate law, we can solve for the concentration of the intermediate by assuming that an equilibrium is established in the fast step. The concentration of the intermediate in the rate determining slow step can be replaced with an expression derived from the equilibrium constant  $[\text{E}] = K_{\text{eq}}[\text{A}][\text{B}]$ . This substitution gives us the desired rate law:  $\text{rate} = k'[\text{A}]^2[\text{B}]$



# + Reaction Mechanisms and Energy Profiles – Practice Problem

Draw and label axes for the energy profiles below. Match the curves with the appropriate description.

**A. exothermic reaction with a 2 step mechanism where the first step is slow.**

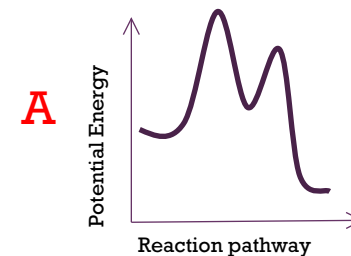
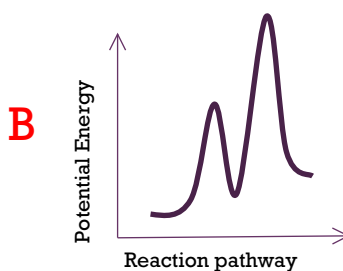
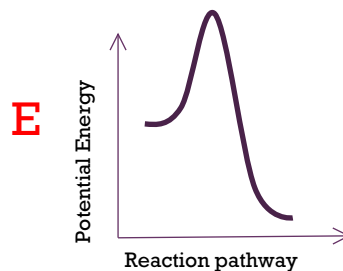
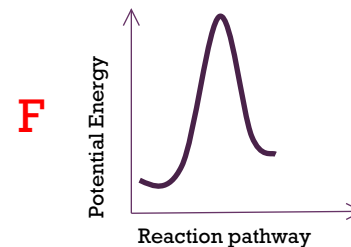
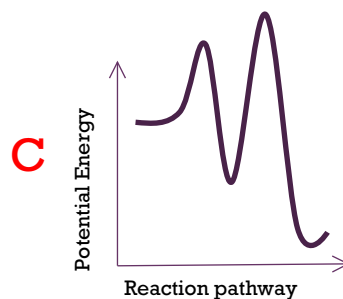
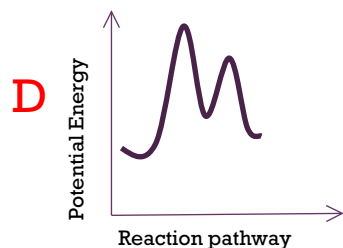
**B. endothermic reaction with a 2 step mechanism where the second step is slow**

**C. exothermic reaction with a 2 step mechanism where the second step is slow.**

**D. endothermic reaction with a 2 step mechanism where the first step is slow.**

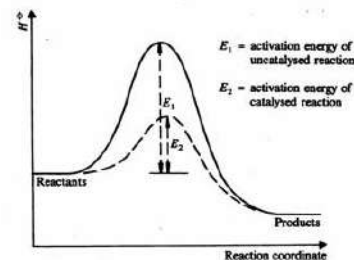
**E. exothermic reaction with a 1 step mechanism.**

**F. endothermic reaction with a 1 step mechanism.**



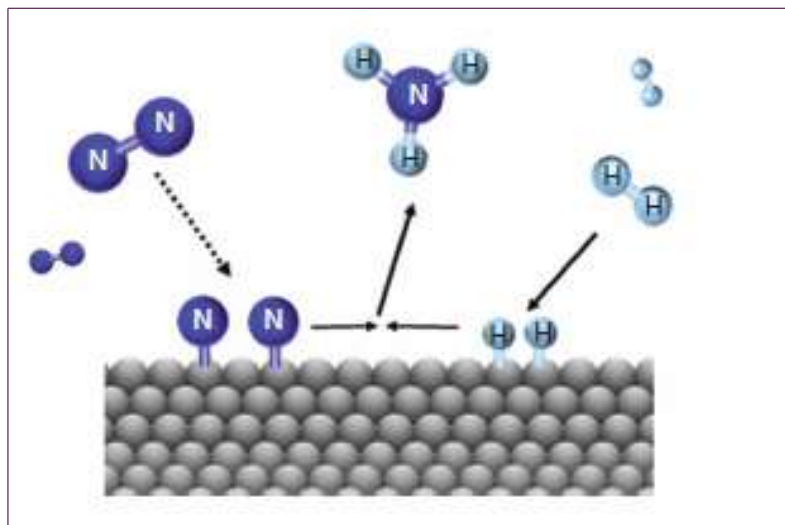
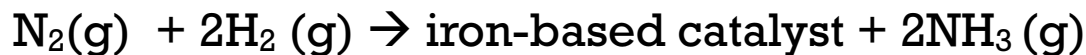
# + Catalysts

- A catalyst can stabilize a transition state, lowering the activation energy.
- A catalyst can participate in the formation of a new reaction intermediate, providing a new reaction pathway.

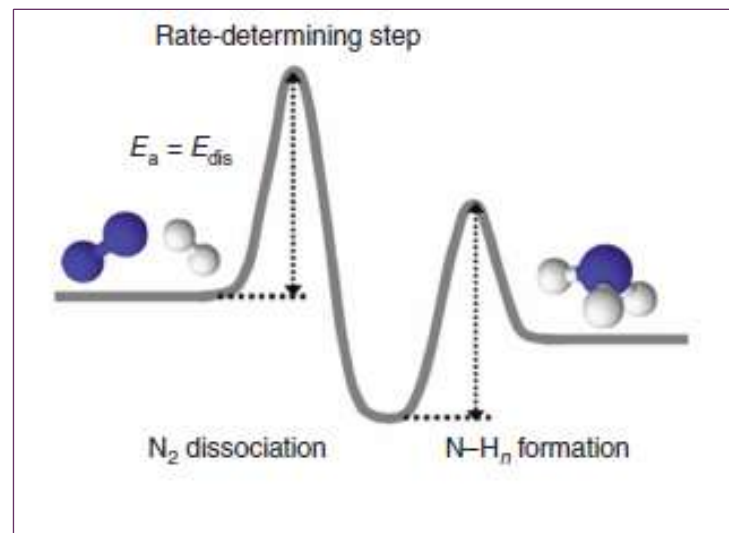


Video

The rate of the Haber process for the synthesis of ammonia is increased by the use of a heterogeneous catalyst which provides a lower energy pathway.



Iron based catalyst



LO 4.8 The student can translate among reaction energy profile representations, particulate representations, and symbolic representations (chemical equations) of a chemical reaction occurring in the presence and absence of a catalyst.

# + Catalysts

catalysts provide alternative mechanisms with lower activation energy

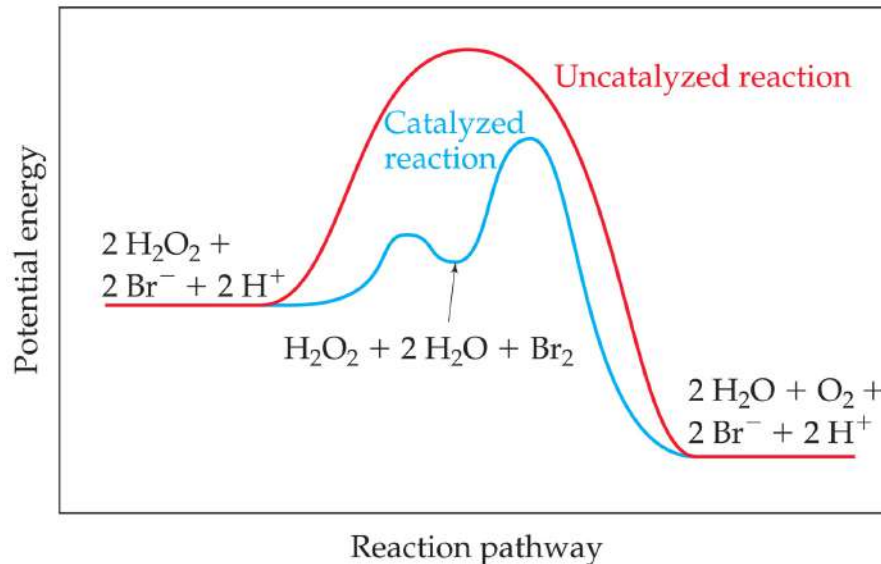
Source



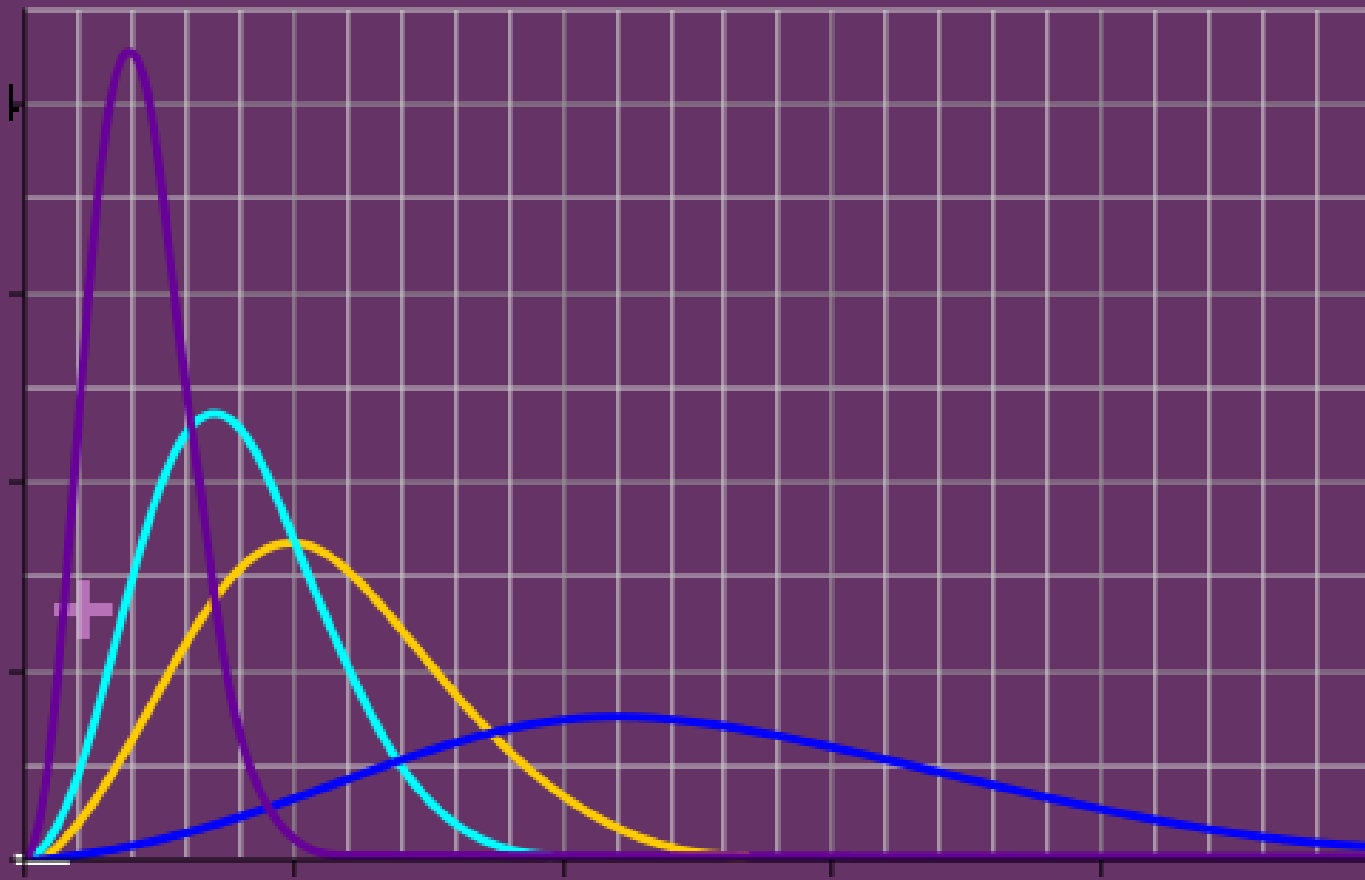
Video

- In acid-base catalysis, a reactant either gains or loses a proton, changing the rate of the reaction.
- In surface catalysis, either a new reaction intermediate is formed or the probability of successful collisions is increased.
- In Enzyme catalysis enzymes bind to reactants in a way that lowers the activation energy. Other enzymes react to form new reaction intermediates.

Homogeneous catalysis  
of the decomposition of  $\text{H}_2\text{O}_2$



LO 4.9 The student is able to explain changes in reaction rates arising from the use of acid-base catalysts, surface catalysts, or enzyme catalysts, including selecting appropriate mechanisms with or without the catalyst present.



Big Idea #5

Thermochemistry

# + Bond Energy, Length & Strength

Source

■ Bond strength is determined by the distance between the atoms in a molecule and bond order. Multiple bonds shorten the distance & increase the force of attraction between atoms in a molecule.

■ Bond Energy is **ENDOTHERMIC** –the energy needed to break the bond.

[Video](#)

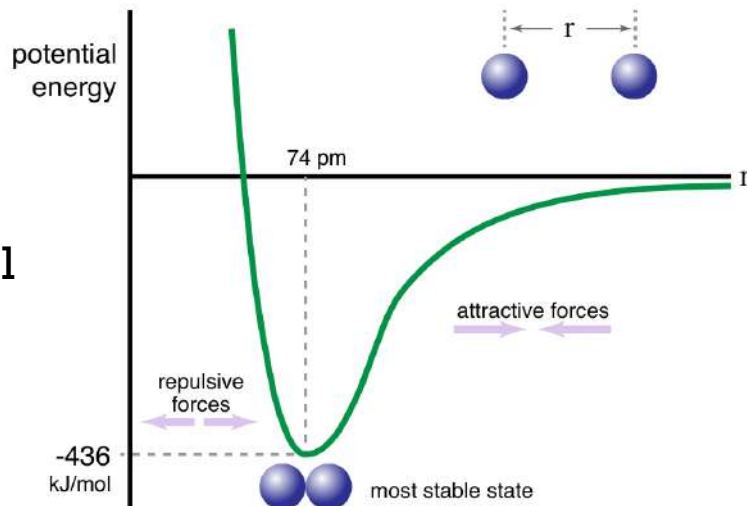
<i>Bond</i>	<i>Length (pm)</i>	<i>Energy (kJ/mol)</i>
C - C	154	346
C=C	134	612
C≡C	120	835
C - N	147	305
C=N	132	615
C≡N	116	887
C - O	143	358
C=O	120	799
C≡O	113	1072
N - N	145	180
N=N	125	418
N≡N	110	942

## 3 Factors

1) Size: H-Cl is smaller than H-Br

2) Polarity: HCl is more polar than H-C

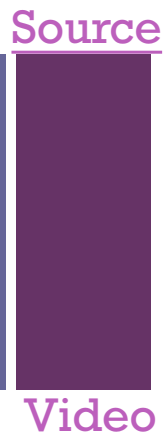
3) Bond order (length) C=C involves more e<sup>-</sup> is shorter than C-C.



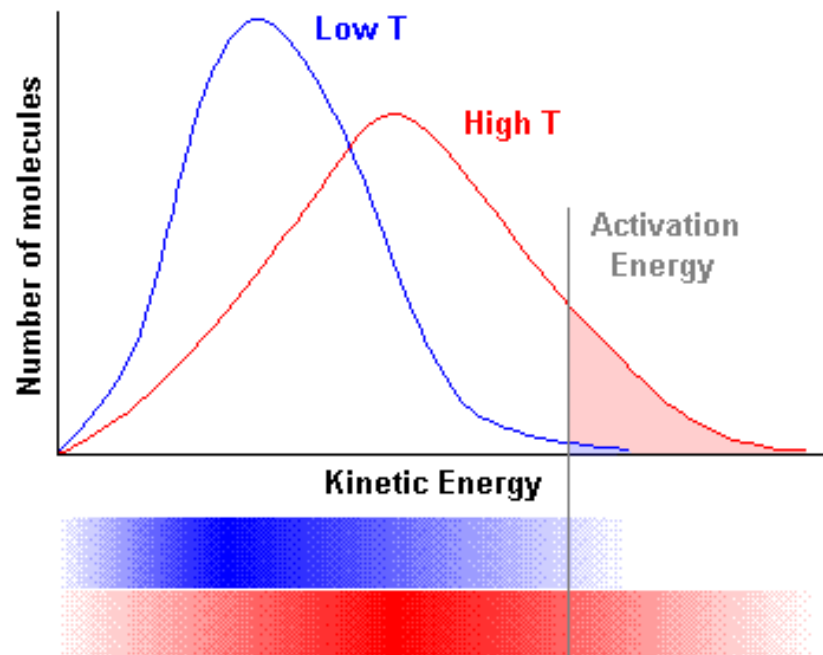
Lowest PE = Bond Energy

LO: 5.1 The student is able to create or use graphical representations in order to connect the dependence of potential energy to the distance between atoms and factors, such as bond order and polarity, which influence the interaction strength.

# + Maxwell –Boltzmann Distributions



- Temperature is a measure of the average Kinetic Energy of a sample of substance.
- Particles with larger mass will have a lower velocity but the same Average KE at the same Temperature.
- Kinetic Energy is directly proportional to the temperature of particles in a substance. (if you double the Kelvin Temp you double the KE)
- The M-B Distribution shows that the distribution of KE becomes greater at higher temperature.
- The areas under the curve are equal and therefore the number of molecules is constant
- Increasing Temperature (KE) increases the number of particles with the Activation Energy necessary to react.
- Activation Energy is not changed with temperature but may be changed with a catalyst.

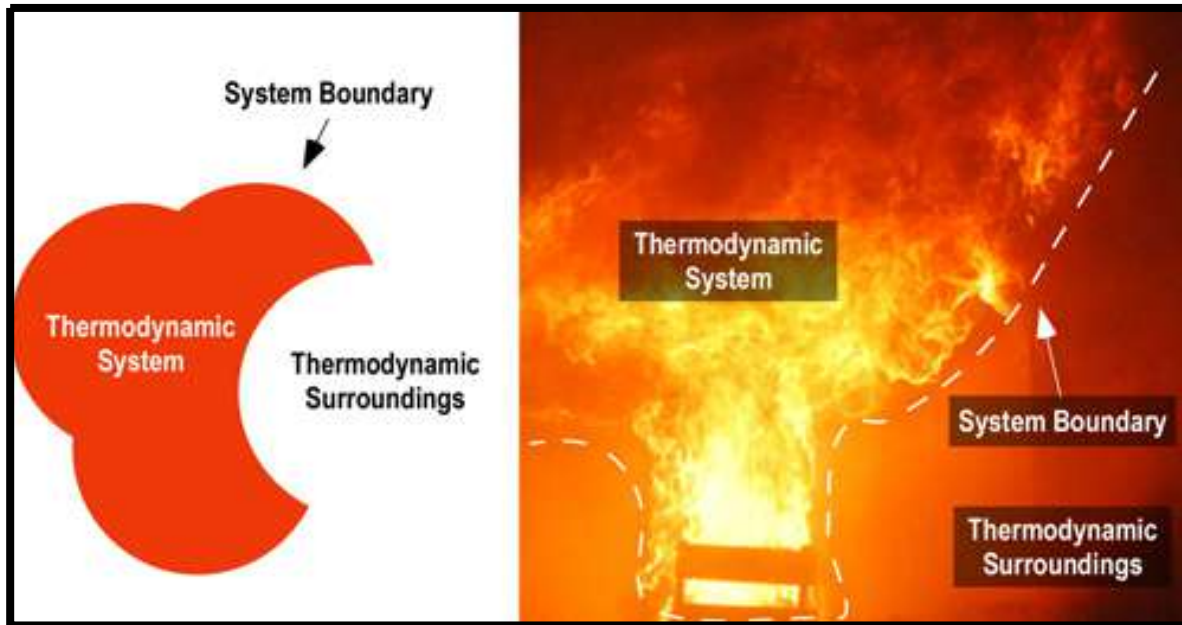


LO 5.2: The student is able to relate Temp to motions of particles in particulate representations including velocity , and/ or via KE and distributions of KE of the particles.

# + Thermodynamic vocabulary

- **Universe:** The sum of the system and surroundings
- **System:** The species we want to study
- **Surroundings:** the environment outside the system
- **Endothermic:** Heat flows to the system from the surroundings (surroundings temperature drops-i.e. beaker feels cold)
- **Exothermic:** Heat flows from the system to the surroundings. (surroundings temperature rises-i.e. beaker feels hot)

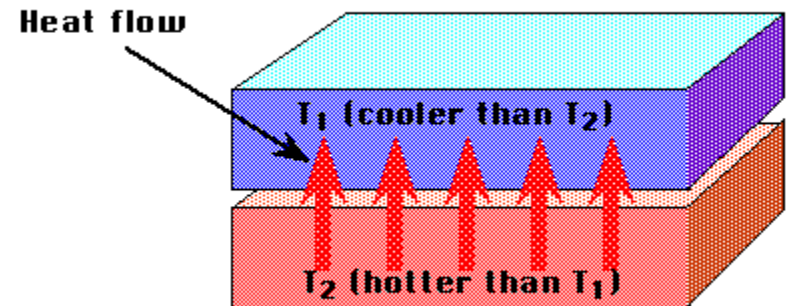
Video



LO 5.3: The student can generate explanations or make predictions about the transfer of thermal energy between systems based on this transfer being due to a kinetic energy transfer between systems arising from molecular collisions.

# + Heat Transfer

- Kinetic energy transferred between particles of varying temperature is heat energy.
- Heat flows from particles of higher energy (hot) to those of lower energy (cold) when particles collide.
- When the temperature of both particles are equal the substances are in thermal equilibrium.
- Not all particles will absorb or release the same amount of heat per gram.
- Specific Heat Capacity is a measure of the amount of heat energy in Joules that is absorbed to raise the temperature of 1 gram of a substance by 1 degree Kelvin.
- Heat transfer can be measured  $q=mc_p\Delta T$

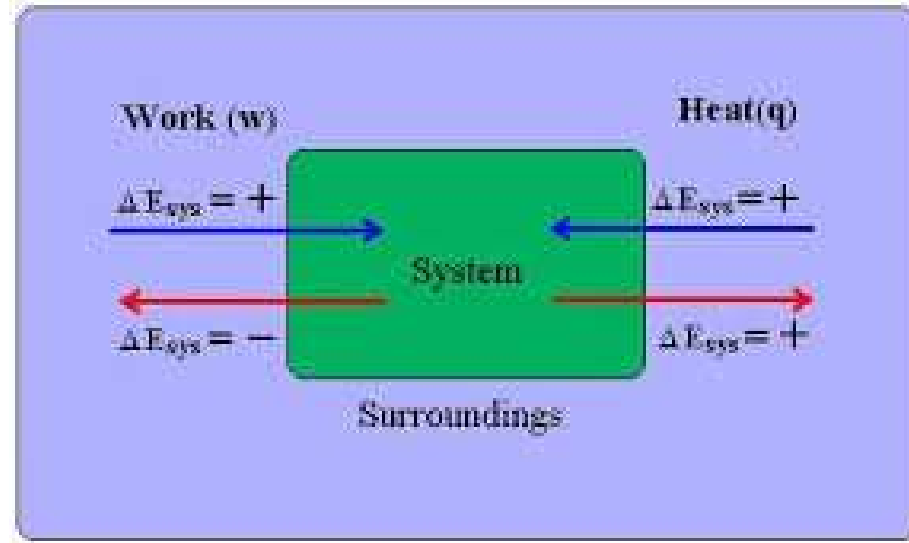


LO 5.3: The student can generate explanations or make predictions about the transfer of thermal energy between systems based on this transfer being due to a kinetic energy transfer between systems arising from molecular collisions.



# + Conservation of Energy

- 1<sup>st</sup> Law of Thermodynamics: Energy is conserved
- Temperature is a measure of the average Kinetic energy of particles in a substance
- Energy can be transferred as Work or Heat
- $\Delta E = q + w$
- Work =  $-P\Delta V$  (this is the work a gas does on the surroundings i:e the volume expanding a piston) a gas does no work in a vacuum.

[Video](#)

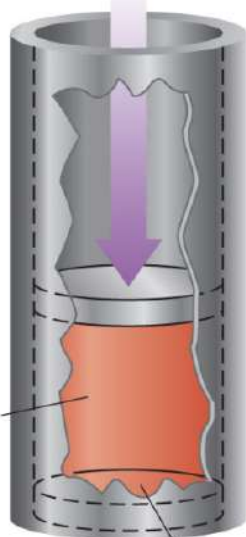
**LO 5.4:** The student is able to use conservation of energy to relate the magnitude of the energy changes occurring in two or more interacting systems, including identification of the systems, the type (heat vs. work), or the direction of the energy flow.

# + Conservation of Energy

System does work  $w = -P\Delta V$  on surroundings as gas expands, pushing piston up distance  $\Delta h$

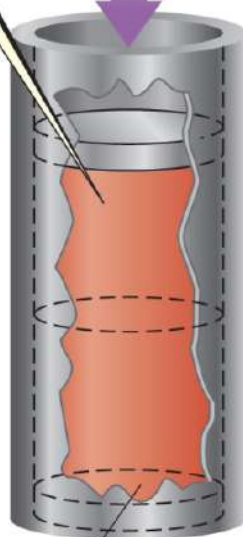
$$P = F/A$$

$$P = F/A$$

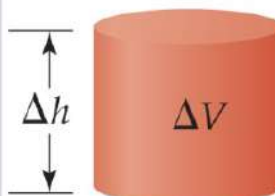


Cross-sectional  
area =  $A$

Initial  
state



Final  
state



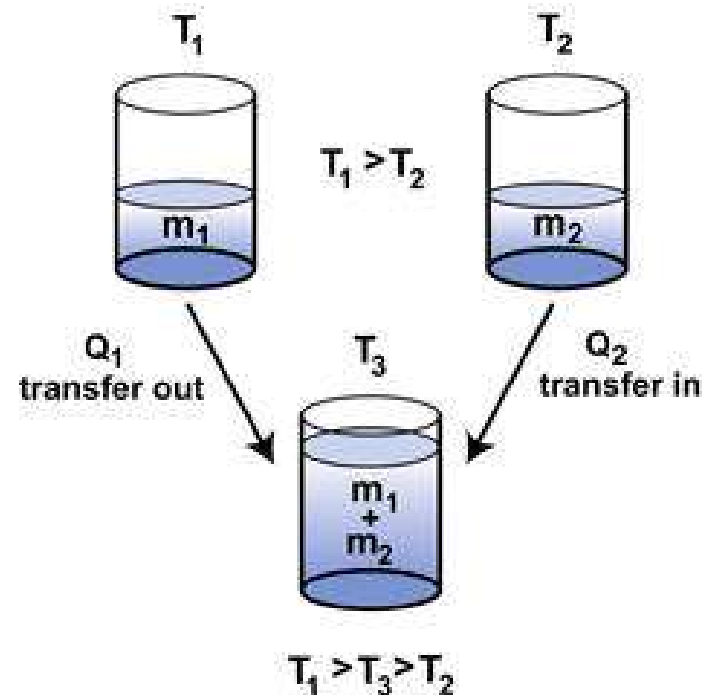
Volume  
change

- Expansion/Compression of a gas
- Volume increases, work is done by the gas
- Volume decreases, work is done on the gas

**LO 5.4: The student is able to use conservation of energy to relate the magnitude of the energy changes occurring in two or more interacting systems, including identification of the systems, the type (heat vs. work), or the direction of the energy flow.**

# + Conservation of Energy when Mixing

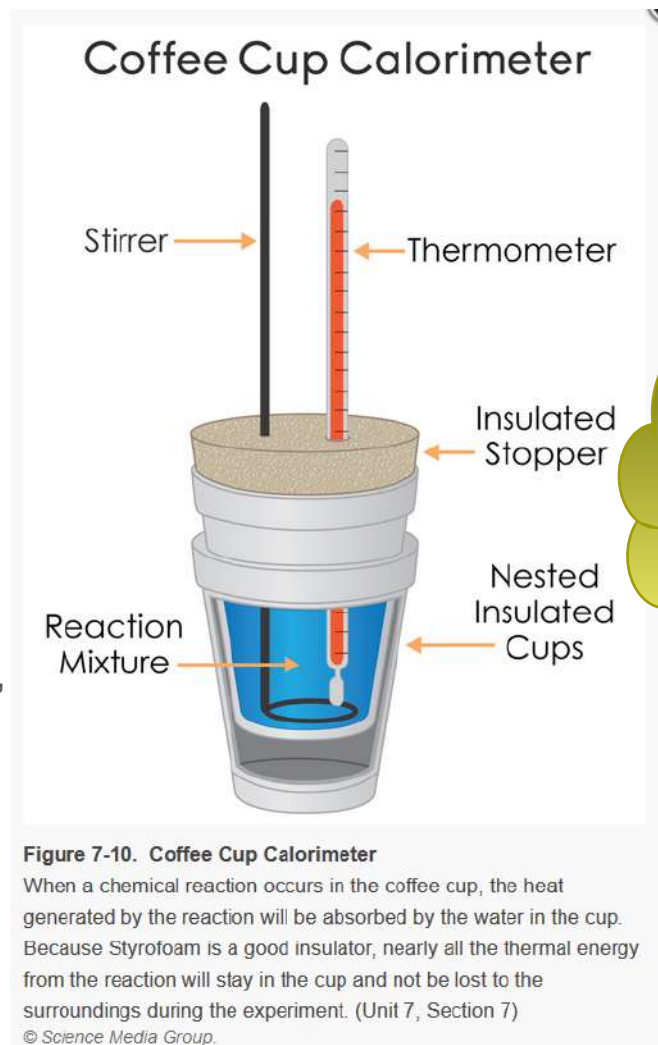
- Energy is transferred between systems in contact with one another
- Energy lost by one system is gained by the other so that total energy is always conserved.
- $-Q$  lost by system =  $+Q$  gained by surroundings
- For example :
  - When room temperature water  $T_1$  (system) is mixed with cold water  $T_2$  (surroundings), the final temperature  $T_3$  will be in-between.
- $Q_1 + Q_2 = 0$  and energy is conserved



LO 5.5: The student is able to use conservation of energy to relate the magnitudes of the energy changes when two non reacting substances are mixed or brought into contact with one another.

+ **Calorimetry:** an experimental technique used to determine the heat transferred in a chemical system. System can be a chemical reaction or physical process.

- Can use Calorimetry to solve for Heat Capacity of a calorimeter ( $C$ ),, specific heat of a substance, ( $c$ ), and  $\Delta H_{\text{vap}}$ ,  $\Delta H_{\text{fus}}$ ,  $\Delta H_{\text{rxn}}$ .
- The data handling and math:
  - Law of Conservation of Energy:  $Q_{\text{system}} + Q_{\text{surroundings}} = 0$
  - $Q_{\text{system}} = - Q_{\text{surroundings}}$  where System = reaction, Surroundings = calorimeter
  - SO:  $Q_{\text{rxn}} = - Q_{\text{calorimeter}}$
  - Heat Transfer due to Temperature Change in the Calorimeter:
    - $Q = C\Delta T$ , or  $Q = mc\Delta T$  where  $Q$  in J,  $C$  in J/K,  $m$  in g,  $c$  in J/g-K,  $\Delta T$  in K
  - **$Q_{\text{rxn}} = - Q_{\text{calorimeter}} = - C\Delta T$**  if the calorimeter Heat Capacity is Known, or can be determined.
  - **$Q_{\text{rxn}} = - Q_{\text{calorimeter}} = - mc\Delta T$**  for reactions in solution.
- **When calculating  $\Delta H$ , must take into account the mass of reactant that caused  $Q_{\text{rxn}}$ .**



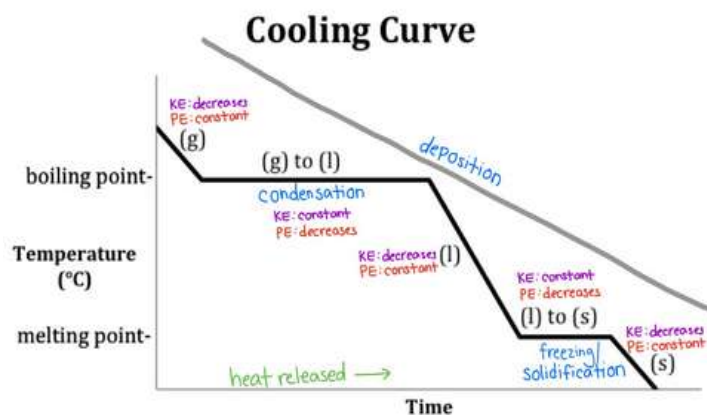
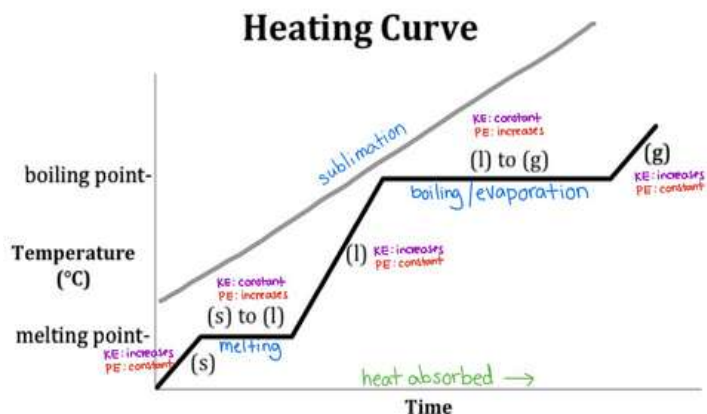
Source

Video

Example problem in video

LO 5.5: The student is able to use conservation of energy to relate the magnitudes of the energy changes when two non-reacting substances are brought into contact with one another.

- + Chemical Systems undergo 3 main processes that change their energy: heating/cooling, phase transitions, and chemical reactions.



#### 1. Heat Transfer due to Temperature Change: (kJ)

$$Q = mc\Delta T$$

$m$  = mass (g),  $c$  = specific heat capacity (J/g-°C),  $\Delta T$  = Temp. change in °C

$Q$  is + for Heating, - for cooling

#### 2. Heat Transfer due to Phase Change: (kJ/mol)

$$Q = \Delta H_{\text{phase change}}$$

$Q_{\text{phase change}}$  = + for  $\Delta H_{\text{fusion}}$ ,  $\Delta H_{\text{vaporizing}}$ ,  $\Delta H_{\text{subliming}}$ , - for  $\Delta H_{\text{freezing}}$ ,  $\Delta H_{\text{condensing}}$ ,  $\Delta H_{\text{deposition}}$

#### 3. $Q$ for a chemical reaction at constant pressure = $\Delta H_{\text{rxn}}$

When calculating  $\Delta H_{\text{rxn}}$  from  $Q$ , remember  $\Delta H_{\text{rxn}}$  must agree with the stoichiometric coefficients in the reaction.

Units of  $\Delta H_{\text{rxn}}$  are **kJ/mol rxn**.

#### 4. When a gas expands or contracts in a chemical reaction, energy is transferred in the form of Pressure-Volume work. $W = -P\Delta V$ (l-atm)

Gas Expands – Does work on surroundings (system loses energy)

Gas Contracts – Work done on the gas (system gains energy) No change in volume, no work done.

Source

Video

LO 5.6: The student is able to use calculations or estimations to relate energy changes associated with heating/cooling a substance to the heat capacity, relate the energy changes associated with a phase transition to the enthalpy of fusion/vaporization, relate energy changes associated with a chemical reaction to the enthalpy of the reaction, and relate the energy changes to  $P\Delta V$  work.

- + **Calorimetry:** an experimental technique used to determine the heat transferred in a chemical system. System can be a chemical reaction or physical process.

**Question:**

A student is using a calorimeter made from a polystyrene cup and a thermometer to determine the specific heat capacity of an unknown solid. The cup was weighed, then filled with 100mL of water. After the water reached equilibrium with the room the temperature was measured at 25.0°C. A piece of the unknown metal was found to weigh 50.0 g, the solid was heated to 100.°C. After the solid was placed in the water the

The correct answer is "b", the calculated value would be too small because of the heat lost to the surroundings. As the temperature of the water increases energy will be lost to the cooler surroundings. Having a top on the cup will minimize that loss, without the top the measured temperature will be lower than it should be, giving a lower value for the specific heat capacity.

surroundings.

- d. The calculated value would be too small because of the heat absorbed from the surroundings.
- e. The calculated value would not be changed.

©2011, Aaron Glimme, LearnAPChemistry.com

LO 5.7 The student is able to design and/or interpret the results of an experiment in which calorimetry is used to determine the change in enthalpy of a chemical process. (heating/cooling, phase transition, or chemical reaction) at constant pressure.

- ✦ The net energy change during a reaction is the sum of the energy required to break the reactant bonds and the energy released in forming the product bonds. The net energy change may be positive for endothermic reactions where energy is required, or negative for exothermic reactions where energy is released.

Any bond that can be formed can be broken. These processes are in opposition. (their enthalpy changes are equal in magnitude, opposite sign)

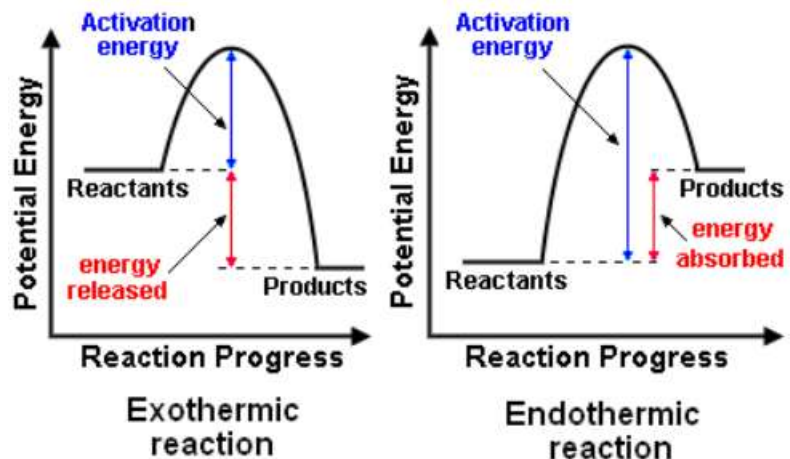
- $\Delta H$  bonds breaking  $\rightarrow$  ENDOTHERMIC (+)
- $\Delta H$  bonds forming  $\rightarrow$  EXOTHERMIC (-)
- To find  $\Delta H_{rxn}$ , apply Hess's Law:
- $\Delta H_{rxn} = \sum \Delta H$  bonds breaking (+) +  $\sum \Delta H$  bonds forming (-)

**To calculate or estimate  $\Delta H_{rxn}$  from Bond Energy:**

1. Draw the Lewis Structure. Don't forget about double and triple bonds!
2. Add up  $\Delta H$  bonds breaking. It's + (kJ)
3. Add up  $\Delta H$  bonds forming. It's - (kJ).
4. Add the two terms. Units are kJ/mol rxn.

**To calculate  $\Delta H^\circ_{rxn}$  from a table of standard enthalpies of formation:**

$$\Delta H^\circ_{rxn} = \sum \Delta H^\circ_f \text{ products} - \sum \Delta H^\circ_f \text{ reactants}$$



If a reaction is EXOTHERMIC, there is a **net release in energy**, since weaker bonds break and stronger bonds form. Product has higher kinetic energy and lower potential energy than reactant.

If a reaction is ENDOTHERMIC, there is a **net absorption of energy**, since stronger bonds break, and weaker bonds form. Product has lower kinetic energy, and higher potential energy than reactant.

**LO 5.8:** The student is able to draw qualitative and quantitative connections between the reaction enthalpy and the energies involved in the breaking and formation of chemical bonds.



Electrostatic forces exist between molecules as well as between atoms or ions, and breaking these intermolecular interactions requires energy.

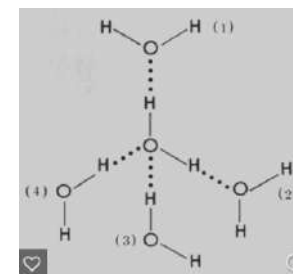
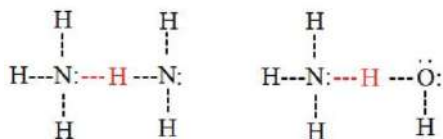
The **Stronger the IMF** the more energy required to break it, the **Higher the Boiling Point**, the **Lower the Vapor Pressure**.

**Intermolecular Forces Listed from weakest to strongest.** Thus the boiling points and vapor pressure of molecular substances can be ordered based on IMF strength:

- 1. Dispersion (Induced Dipole- Induced Dipole):** Caused by distortion of electron cloud. The larger the electron cloud, and the more surface area, the more polarizable the cloud, the stronger the dispersion force. **Thus the boiling point trend in halogens is  $I_2 > Br_2 > Cl_2 > F_2$  and *n*-butane (30.2° C) has a higher boiling point than isobutane (-11 °C). All substances have dispersion forces, as all electron clouds distort.** Nonpolar molecules and atoms have only dispersion forces, as they have no permanent dipoles.
- 2. Dipole- Induced Dipole:** Occurs between a polar molecule (HCl) and a nonpolar molecule. ( $Cl_2$ ) The nonpolar molecule's cloud distorts when affected by a dipole.
- 3. Dipole-Dipole:** Occurs between 2 polar molecules. (HCl-HCl)
- 4. Hydrogen Bond:** An extreme case of Dipole – Dipole. Occurs between molecules containing a H covalently bonded to F, O, or N. The **“bond”** occurs between the lone pair of F, O, or N, and the H which is attached to one of those elements.

Weaker IMF,  
Lower Boiling,  
Higher Vapor  
Pressure

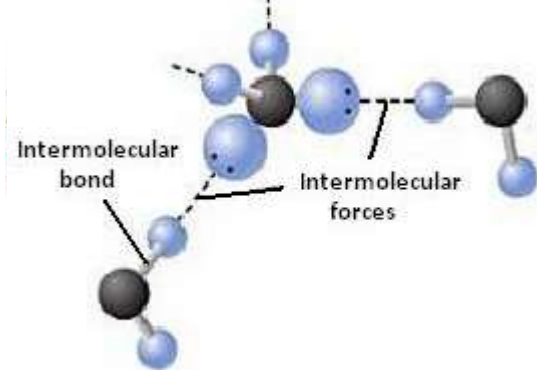
Stronger IMF,  
Higher Boiling,  
Lower Vapor  
Pressure



LO 5.9: Make claims and/or predictions regarding relative magnitudes of the forces acting within collections of interacting molecules based on the distribution of electrons within the molecules and the types of intermolecular forces through which the molecules interact.



# Inter vs Intra Chemical vs. Physical



If you are asked to rank molecules in order of melting point, boiling point, viscosity, surface tension or vapour pressure ... what they are actually asking is for you to rank them by strength of intermolecular forces (either increasing or decreasing).

Here is my strategy for this:

1. Look for molecules with hydrogen bonding capability will have the strongest intermolecular forces.
2. Look for molecules with dipoles. These will have the next strongest intermolecular forces.
3. Larger molecules will have stronger London dispersion forces. These are the weakest intermolecular forces but will often be the deciding factor in multiple choice questions

**Strong IMF= High BP, High MP, High viscosity, high surface tension, low vapor pressure!**

**LO 5.10: The student can support the claim about whether a process is a chemical or physical change (or may be classified as both) based on whether the process involves changes in intramolecular versus intermolecular interactions.**

# +IMF and Biological/Large Molecules

Source  
Source  
Source  
Video

## Intermolecular forces in liquids and solids

Weak intermolecular forces (**non-covalent interactions**) act between molecules, causing them to be attracted to each other in varying degrees. The strength of these forces at a particular temperature determines whether a molecular substance is a gas, a liquid, or a solid at that temperature.

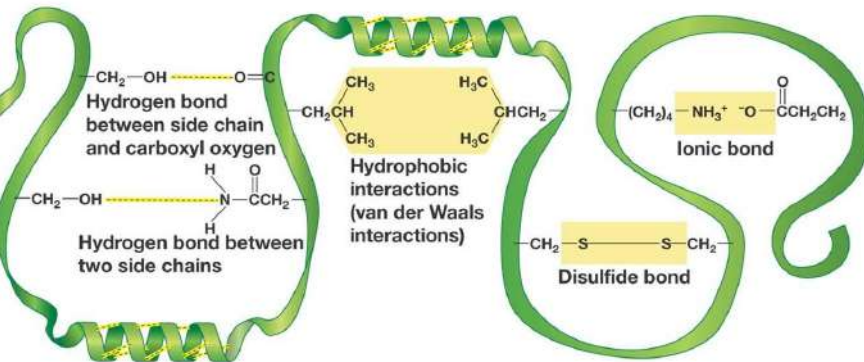
Non-covalent forces also contribute to the secondary, tertiary, or quaternary structures of biopolymers (namely proteins and nucleic acids), maintain the stability of biomembranes, and play important roles in highly specific biological interactions (enzyme – substrate, antigen – antibody, signal molecules – receptor).

### Types of intermolecular forces:

- hydrogen bonds,
- dipole–dipole interactions,
- dispersion forces (London forces).

Dipole–dipole and dispersion forces are sometimes referred collectively to as **van der Waals forces**.

43



This image shows the tertiary structure of a protein segment. Tertiary structure results from different interactions, or forces, between groups. Move the example of each force to the appropriate description on the protein. Then identify the major force controlling tertiary structure.

Diagram illustrating various intermolecular forces in a protein segment, with corresponding chemical structures for identification:

- hydrogen bond
- ionic bond
- hydrophobic interaction
- disulfide bond

Chemical structures for identification:

- $\text{CH}(\text{CH}_3)_2 \cdots \text{H}_3\text{C}-\text{HC}(\text{H}_3\text{C})$
- $\text{CH}_2-\text{C}(\text{OH})=\text{O} \cdots \text{HO}-\text{CH}_2$
- $\text{CH}_2-\text{S}-\text{S}-\text{CH}_2$
- $\text{CH}(\text{CH}_3)_2 \cdots \text{H}_3\text{C}-\text{HC}(\text{H}_3\text{C})$
- $\text{CH}_2-\text{NH}_3^+-\text{O}-\text{C}(=\text{O})-\text{CH}_2$
- $\text{CH}_2-\text{NH}_3^+-\text{O}-\text{C}(=\text{O})-\text{CH}_2$

continued

LO 5.11: The student is able to identify the noncovalent interactions within and between large molecules, and/or connect the shape and function of the large molecule to the presence and magnitude of these interactions.

# + Entropy- Embrace the Chaos!

Entropy Changes that result

in a  $\Delta S$ :

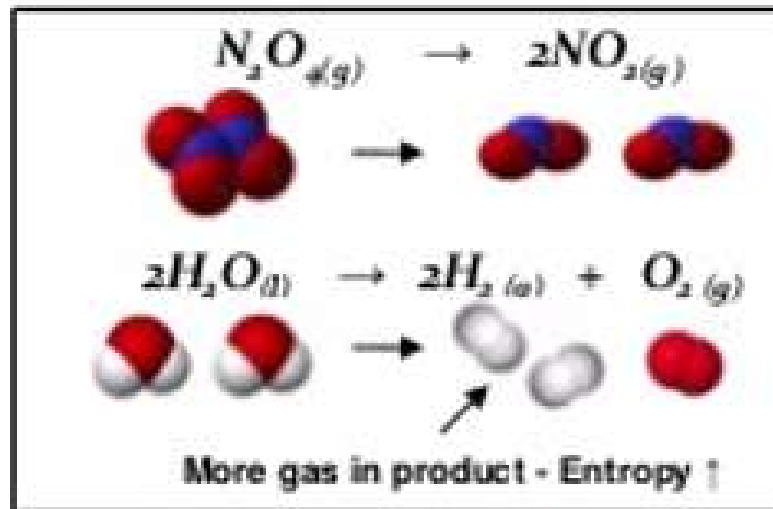
Increasing moles

Increasing temperature

Increasing volume

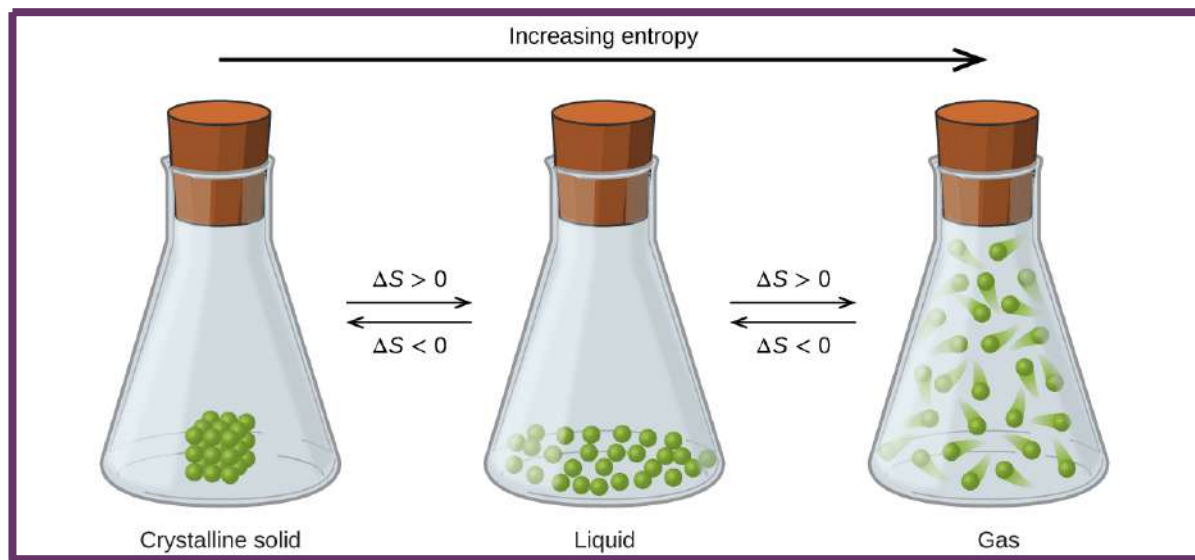
Solid to liquid to gas

Forming more complicated molecules. (More moles of electrons)



Source  
Source

Video



LO 5.12: The student is able to use representations and models to predict the sign and relative magnitude of the entropy change associated with chemical or physical processes.

# Predicting How Reactions Will Go

•  $\Delta G = \Delta H - T\Delta S$  when will delta G < 0

$\Delta H$	$\Delta S$	Thermodynamic Favorability
-	+	spontaneous at all temperatures
+	-	non-spontaneous at all temperatures
-	-	spontaneous at low temperatures non-spontaneous at high temperatures
+	+	spontaneous at high temperatures non-spontaneous at low temperatures

[Video #1](#)  
[Video #2](#)  
[Source](#)

**CAUTION**

Entropy is typically given in J/K so you MUST convert to kJ!

## $\Delta G$ (Gibbs Free Energy)

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

Free Energy Change (kJ) →  $\Delta G = \Delta H - T\Delta S$  ← Entropy Change (kJ/K)

System temperature (K) ↓

Enthalpy change (kJ) ↗

If  $G < 0$ , i.e. negative, the reaction is thermodynamically favored (spontaneous.)

LO 5.13: The student is able to predict whether or not a physical or chemical process is thermodynamically favored by determination of (either quantitatively or qualitatively) the signs of both  $\Delta H^\circ$  and  $\Delta S^\circ$ , and calculation or estimation of  $\Delta G^\circ$  when needed.



# How can I calculate $\Delta G$ ?

$\Delta G^\circ$	$E^\circ_{\text{cell}}$	$K$	Direction of Reaction
$< 0$	$> 0$	$> 1$	spontaneous in forward direction
$> 0$	$< 0$	$< 1$	spontaneous in reverse direction
$0$	$0$	$1$	no net reaction: system at equilibrium

Source  
Source  
Video  
Video  
Video

## $\Delta G$ and $K$

- Standard free energy change is related to the thermodynamic equilibrium constant,  $K$ , at equilibrium.
  - IF a reaction is NOT at equilibrium, it is proceeding in some direction (forward or reverse) depending on  $Q$ , reaction quotient.
  - That means there exists energy to do work (make reaction proceed)
- $\Delta G = \Delta G^\circ + RT \ln Q$
- At equilibrium:
  - $\Delta G = 0$ , because there is no ability to do any more useful work
  - and  $Q = K$
- So we get:
  - $\Delta G^\circ = -RT \ln K$

$$\Delta G^\circ_{\text{rxn}} = \sum \Delta G^\circ_{\text{(products)}} - \sum \Delta G^\circ_{\text{(reactants)}}$$

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

$$\Delta G^\circ = -$$

**LO 5.14:** Determine whether a chemical or physical process is thermodynamically favorable by calculating the change in standard Gibbs free energy

# Coupling Reactions



Endothermic Reaction

Exothermic Reaction

Source  
Video  
#1  
Choo  
Choo

The sum of the free energy for these two reactions gives the overall  $\Delta G$  for this process ( $\Delta G = -16.7 \text{ kJ/mol}$ ), which is very thermodynamically favorable. Another way in which reactions can be coupled is by breaking down a high energy compound with an enzyme, trapping that energy and using it to drive an endergonic reaction. You can think of energy as chemical currency used to conduct business in the cell. Taking this energy-as-money analogy a bit further, the coupling of the reactions is like what Robin Hood did in the Sherwood forest; stole from the rich and gave to the poor. Coupling reactions is a way to take the energy from the "rich" and bring it to the "poor" that really need it.

For  
to c

other

LO  
unf

ple with  
orable.

# + Coupled Reactions and LeChatelier

Source

Video

Reactions can be coupled together if they share a common intermediate. In this example, the two reactions share the component "D".

$$A + B \rightleftharpoons C + D \quad D + E \rightleftharpoons F$$

Let us assume that the first reaction has an  $K_{eq}$  much less than 1, while the  $K_{eq}$  for the second reaction is much greater than 1.

**What will happen?** Most of the D formed by the first reaction (which is not much), will react with E (assuming E is present) and be removed from the system.

This will inhibit the C+D "back reaction", while the A+B "forward reaction" will continue.

More D will be produced, even though the reaction that produces it is unfavorable.

LO: 5.16 The student can use LeChatelier's principle to make qualitative predictions for systems in which coupled reactions that share a common intermediate drive formation of a product.

+

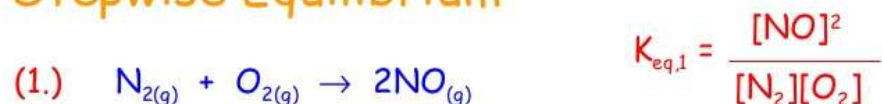
# COUPLING OF REACTIONS

## Coupled Reactions and K

[Video Source](#)  
[Source](#)  
[Source](#)

### Manipulating $K_{eq}$

#### Stepwise Equilibrium



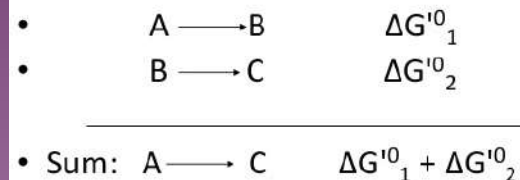
Determine the chemical equation for the overall process

What is the equilibrium constant for the overall process? How does it depend on the value of  $K_{c1}$  and  $K_{c2}$ ?



$$K_{eq} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} = K_{eq,1} \times K_{eq,2}$$

\* UA GenChem



- This principle of bioenergetics explains how a thermodynamically unfavorable (endergonic) reaction can be driven in the forward direction by coupling it to a highly exergonic reaction through a common intermediate



# Is it thermo, kinetics, or K?

Table 20.2 The Relationship Between  $\Delta G^\circ$  and  $K$  at 298 K

Equilibrium constant	Description	Standard Gibbs Free Energy
<b><math>K = 1</math></b>	<b>Neither reactant nor product favored</b>	<b><math>\Delta G^\circ = 0</math></b>
<b><math>K &gt; 1</math></b>	<b>Product favored</b>	<b><math>\Delta G^\circ &lt; 0</math></b> <b>(thermodynamically favorable)</b>

“Thermodynamically UNFAVORABLE” (aka non-spontaneous) reactions will run in reverse when set up with standard conditions (1M/1atm of ALL reactants and products) BUT can be made to proceed forward under different conditions. ”

L 5.18: Explain why a thermodynamically favored chemical reaction may not produce large amounts of product (based on consideration of both initial conditions and kinetic effects), or why a thermodynamically unfavored chemical reaction can produce large amounts of product for certain sets of initial conditions.