Ms. Randall
Regents Chemistry
Unit 9: Kinetics and Equilibrium Notes

Unit Objectives:
- Understand that the collision theory states that a reaction is most likely to occur if reactant particles collide with the proper energy and orientation.
- Define factors affecting rate of a chemical reaction: temperature, concentration, and nature of reactants, surface area, and the presence of a catalyst.
- Describe how some chemical and physical changes can reach equilibrium.
- Define equilibrium as when the rate of the forward reaction equals the rate of the reverse reaction. The measurable quantities of reactants and products remain constant at equilibrium.
- Apply Le Chatelier's principle for predicting the effect of stress (change in pressure, volume, concentration, and temperature) on a system at equilibrium.
- Represent energy released or absorbed by a chemical reaction using a potential energy diagram.
- Explain that the energy released or absorbed during a chemical reaction (heat of reaction) is equal to the difference between the potential energy of the products and the potential energy of the reactants.
- Define a catalyst as providing an alternate reaction pathway, which has lower activation energy than an uncatalyzed reaction.
- Define Entropy as a measure of the randomness or disorder of a system. A system with greater disorder has greater entropy.
- Explain why systems in nature tend to undergo changes toward lower energy and higher entropy.

Focus Questions for the Unit:

- What are the ways chemical reactions can be studied and described?
- How are the conservation of mass, energy, and charge shown or symbolized by chemists?

YOU SHOULD BE ABLE TO ANSWER THESE _IN DETAIL_ BY THE END OF THE UNIT

Define the following vocabulary:
Rate
Surface Area   Entropy
Concentration   Potential Energy
Catalyst   Kinetic Energy
Equilibrium   Spontaneous
Enthalpy   Physical change
Heat of Reaction   Chemical change

Lesson 1: Chapter Diary 14

Objective: To summarize unit concepts

Directions: After reading the Chapter 14 diary answer the following questions in your student workbook.

<u>Lesson 2: Reaction Rates</u>

Objective: To compare and contrast factors that may affect the rate of a chemical reaction

Chemical **kinetics** is a branch of chemistry concerned with **rates and mechanisms of chemical reactions**. In a chemical reaction you have **Reactants** and **Products.**

Review:

Classification (Type) of Reaction	Example: Using Symbols	Example Reactions
Synthesis	A + B → AB	$2H_{2\ (g)} + O_{2\ (g)} \rightarrow 2H_2O_{(l)}$
Decomposition	XY → X + Y	$2H_2O_{\ (l)} \rightarrow 2H_{2\ (g)} + O_{2\ (g)}$
Single Replacement	A + BC → AC + B	$2Al_{(s)} + 3Cu(NO_3)_{2\ (aq)} \rightarrow 2Al(NO_3)_{3(aq)} + 3Cu_{(s)}$
Double Replacement	AC + DE → AE + DC	$Pb(NO_3)_{2\ (aq)} + 2KI_{(aq)} \rightarrow PbI_{2(s)} + 2KNO_{3\ (aq)}$

aq = aqueous, g = gas, s = solid, l = liquid

<u>How is rate defined?</u> Rate can be defined as an increase in concentration of product per unit of time <u>or</u> decrease in concentration of reactant per unit of time.

A **reaction** is the breaking and reforming of BONDS to make entirely new compounds as products

The <u>Reaction Mechanism</u> is the step by step process needed to make a product; how you get from "a" to "b" (like a recipe)

REACTANTS → PRODUCTS

Just like when we bake a cake we must follow directions
- o   CAN'T OMIT any STEPS!
- o   CAN'T CHANGE THE ORDER of the steps!
- o   CAN'T OMIT any REACTANTS
            (ingredients)

Rate Determining Step

A + B + C → ABC   (2 steps)
A + B → AB   (slow)
AB + C → ABC   (fast)

<u>WHAT DETERMINES THE RATE OF A REACTION?</u>
- **NUMBER OF STEPS** = more steps can mean a slower   reactic
- **RATE DETERMINING STEP =** the <u>SLOWEST STEP</u> of the   reactic
  most important factor influencing the reaction rate.

slow

fast

A+B

AB+C

ABC

In order for a reaction to occur, reactant <u>PARTICLES MUST COLLIDE</u> and   have the following when doing so:

(a)
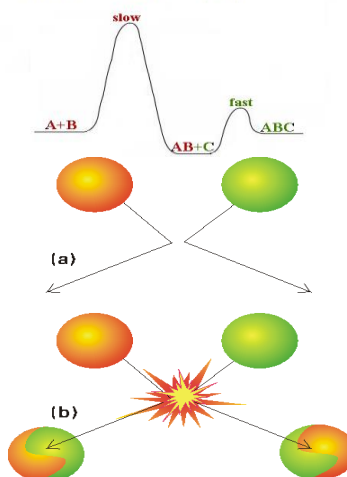
1. Proper amount of <u>ENERGY</u>
2. Proper A<u>LIGNMENT/DIRECTION/ORIENTATION</u>

*Only when particles collide with these two conditions are met will there be   an
        <u>EFFECTIVE COLLISION</u>, resulting in a reaction

(b)

This is known as the <u>Collision Theory</u>

<u>Factors Affecting Rates of Reactions</u>

- Effective collisions have enough energy and proper orientation of colliding particles

Nature of reactants
- Reactions involving ions in aqueous solution are extremely fast(ionic)
- Reactions requiring breaking of bonds are slow(covalent)
- IONIC substances react FASTER
- COVALENT substances react SLOWER

Concentration
- Increased concentration(M) in reactant increases collisions thus increasing reaction rate
- Increased pressure on gases increases concentration thus increasing reaction rate.
- The MORE PARTICLES in a given space, the LESS SPACE between particles → MORE COLLISIONS

Temperature
- Increased temp increases average kinetic energy, increased number and effectiveness of collisions thus increased reaction rate.
- Greater SPEED → MORE total COLLISIONS
- Greater AVERAGE KE → collisions take place with MORE energy

Surface area
- Increased surface area greater opportunity for collisions thus increased rate of reaction.
- Increasing surface area EXPOSES MORE REACTANT PARTICLES to possible collisions

Catalysts
- Substance that increases reaction rate and remains unchanged.
- Decreases activation energy
- Does not change heat of reaction
- Provides a SHORTCUT or ALTERNATIVE PATHWAY for the mechanism

Pressure(only with gases!)
- Increasing pressure DECREASES VOLUME which DECREASES SPACE b/w particles → MORE COLLISIONS

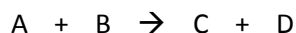Low concentration = Few collisions   High concentration = More collisions
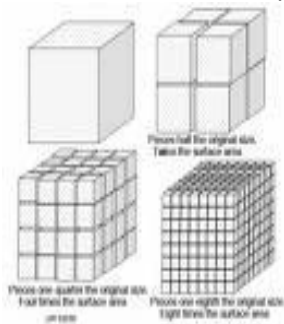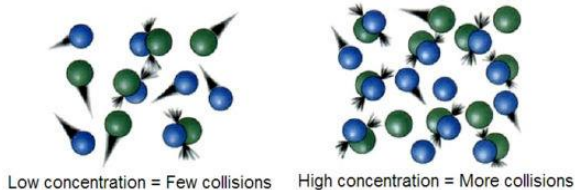
Lesson 3: Energy in reactions

Objective: To apply changes during a reaction in energy to a PE diagram

Recall: A reaction is the breaking and reforming of bonds. Chemical bonds have stored energy (potential energy).

BREAK BONDS → FORM BONDS
$$A + B → C + D$$

Heat of Reaction (ΔH) is the amount of **HEAT** ENERGY LOST or GAINED throughout a REACTION (ΔH = ent**H**alpy). It is the difference in potential energy between the products and reactants.
PE OF THE PRODUCTS - PE OF THE REACTANTS
ΔH=H products –H reactants

Also recall, there are two (2) types of reactions:
1. Reactions that release energy → **EXOTHERMIC**
   - Δ H = negative value (-)
   - A + B → C + D + ENERGY
   - Example: Sodium in water = lots of heat (and fire!) produced as product; heat felt on a test tube during a reaction

2. Reactions that absorb/gain energy → **ENDOTHERMIC**
   - Δ H = positive value (+)
   - A + B + ENERGY → C + D
   - Example: baking (need oven to supply heat)

Table I (of the Reference Tables) tells us if particular reactions are exothermic or endothermic based on sign of the Δ H value. Read the * statement at the bottom of the table. Exothermic reactions are always given a negative value for Δ H. We can read each reaction in the forward or reverse directions. The sign of the reaction is reversed when reading it the opposite way.

Forward Reaction = reading LEFT TO RIGHT in a reaction; reaction moves toward the right
A + B → C + D

**Reverse Reaction =** reading RIGHT TO LEFT in a reaction; reaction moves toward the left
A + B ← C + D
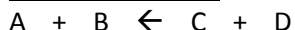
	Δ H (kJ/mol)	Endothermic/Exothermic
1. $N_{2(g)} + 2O_{2(g)} → 2NO_{2(g)}$	**+182.63**	**endothermic**
2. $N_{2(g)} + 3H_{2(g)} → 2NH_{3(g)}$	**-91.8**	**exothermic**
3. $2NH_{3(g)} → N_{2(g)} + 3H_{2(g)}$	**+91.8**	**endothermic**

Notice that number 3 is the reverse reaction of number 2. The quantity for Δ H is the same but the direction of heat flow is reversed. (+ Δ H instead of - Δ H)

Chemists use diagrams called **Potential Energy Diagrams** to illustrate the potential (or stored) energy changes that occur during specific chemical reactions.
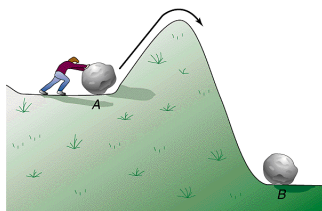

Activation Energy is amount of ENERGY NEEDED TO GET A REACTION STARTED OR FORM THE _ACTIVATED COMPLEX_ of a reaction (you must get over the "bump" in order for a reaction to be successful!)
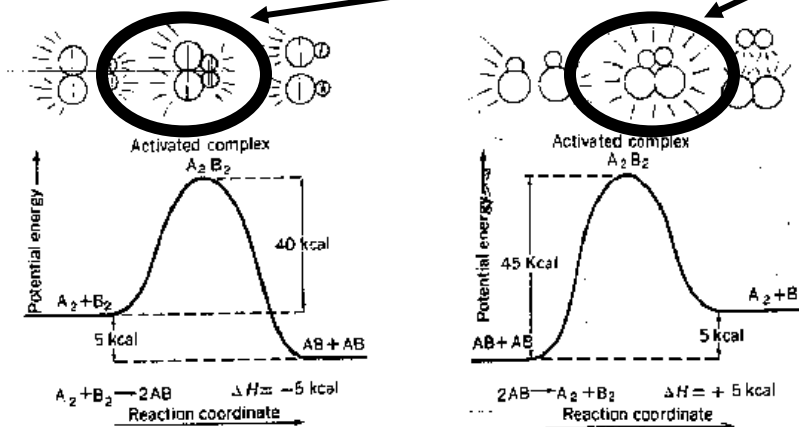
On the left is a potential energy diagram for the changes occurring in a chemical system during an exothermic reaction. On the right is the same type of diagram for an system undergoing an endothermic reaction.

ACTIVATED COMPLEX is the highest energy point of the reaction; this is where full REARRANGEMENT of the reactants occurs. _Remember, this **must** happen for the reaction to be successful._

A **catalyst** can shorten the reaction time needed for a reaction to be completed by changing the reaction pathway. A modified activated complex is formed, lowering the activation energy needed. A catalyst remains unchanged by the reaction and can be used over and over again. Enzymes are considered biological catalysts.
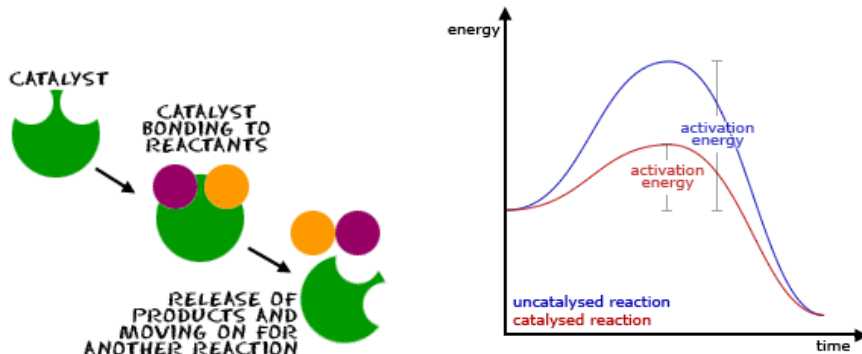
Endothermic Potential Energy Diagrams → POSITIVE ΔH

The potential energy of the product side is always HIGHER than the reactant side meaning that ENERGY is ABSORBED.
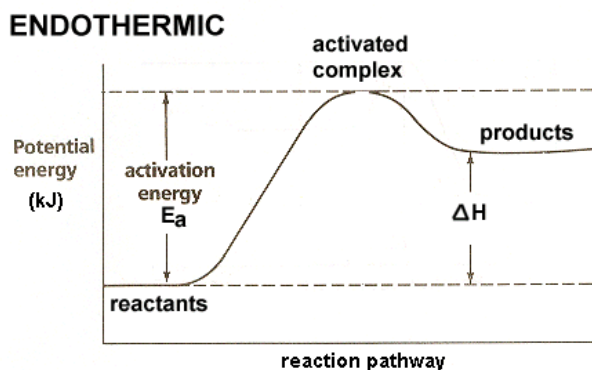
- ΔH=positive
- Energy written the on reactant side of reaction
- A + B + energy→ C+ D

Exothermic Potential Energy Diagrams → NEGATIVE ΔH

The potential energy of the product side is always LOWER than the reactant side meaning that ENERGY is RELEASED
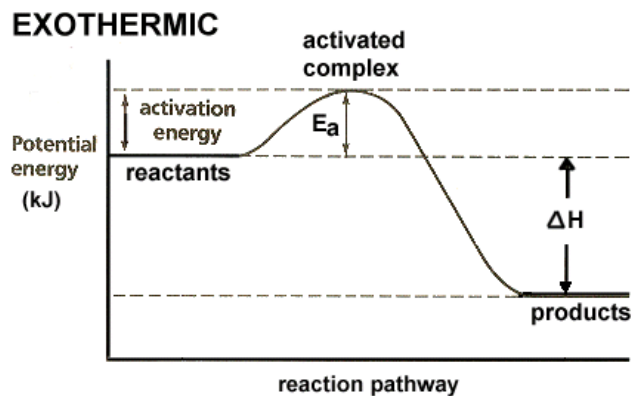
- ΔH=negative
- Energy on product side of reaction
- A + B → C+ D + energy

Watch this PE Diagram Animation

 Objective: To compare and contrast the different types of system equilibriums

Some physical and chemical reactions are capable of reaching equilibrium. Equilibrium occurs WHEN THE **RATE** OF THE FORWARD REACTION EQUALS THE **RATE** OF THE REVERSE REACTION in a closed system. It is a state of balance between products and reactants in a reversible reaction. The overall concentration remains the same for reactants and products even though there is a forward and reverse reaction occurring simultaneously. We call this a **Dynamic Equilibrium.**

When equilibrium is reached, IT DOES NOT MEAN that the reactants and products are of equal QUANTITIES!!!!

- Equilibrium is represented by DOUBLE ARROWS ⇆ instead of a single arrow. This allows us to illustrate that the reactions are proceeding in both directions (forward and reverse).
- Equilibrium is DYNAMIC which means that it is constantly CHANGING or FLUCTUATING
- Equilibrium means that reactant and product CONCENTRATIONS are CONSTANT.
- Equilibrium does NOT mean that reactant and product concentrations are equal.
- Changes of phase of matter are reversible

TYPES OF EQUILIBRIUM (all occur in <u>CLOSED SYSTEMS</u>)

1. **Physical Equilibrium:** Equilibrium that involves physical changes

   Phase Equilibrium

- occurs during a <u>phase change</u>
- Equilibrium between gas dissolved in liquid and gas above liquid
- Affected by temp and pressure by affecting solubility of gas

         Examples: (s) ⇆ (l)   <u>rate</u> of melting = <u>rate</u> of freezing
                               (Sealed container @ 0ºC)
                      (l) ⇆ (g) <u>rate</u> of evaporation =<u>rate</u> of condensation
                               (Sealed container @ 100ºC)

   Solution Equilibrium –

- occurs at a solution's saturation point
- Saturated solution has equilibrium between dissolved and un-dissolved solute
- Dissolving and crystallizing at same rate
- Rate of dissolving =rate of crystallization

         Example: $NaCl_{(s)}$ ⇆ $NaCl_{(aq)}$

2. **Chemical Equilibrium:**

- Recognized by changes in temp, color, pressure no longer occurring
- Forward and reverse reaction rate equal
- <u>Rate</u> of the forward reaction = <u>rate</u> of the reverse reaction
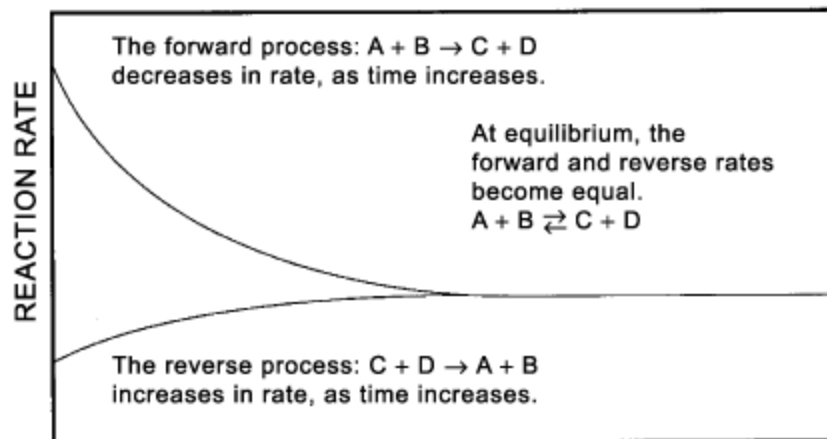- <u>Rate </u>of breaking bonds= <u>rate </u>of bond formation

REACTION RATE

The forward process: A + B → C + D decreases in rate, as time increases.

At equilibrium, the forward and reverse rates become equal.
A + B ⇌ C + D

The reverse process: C + D → A + B increases in rate, as time increases.

Fig. 2   TIME ⟶

Lesson 5: Le Chatelier's Principle

Objective: To apply Le Chatelier's principle to a system at equilibrium and predict the changes on the system

Le Chatelier's principle explains how a system at **Equilibrium** will respond to **Stress**. **Stress** is any change in <u>temperature, concentration or pressurez(gases only)</u> put upon an system at equilibrium . When a stress is added to a system at equilibrium, the system will <u>**SHIFT**</u> in order to relieve that stress and reach a new equilibrium. A shift is an **increase** in the **rate** of either the forward <u>**OR**</u> the reverse reaction.

- **SHIFT TO RIGHT (TOWARD PRODUCTS):**
    - Rate of <u>FORWARD</u> reaction <u>INCREASES</u> ($\rightarrow$)
    - Reactants   Products
    - Favors <u>PRODUCTS</u>

- **SHIFT TO LEFT (TOWARD REACTANTS):**
    - Rate of <u>REVERSE</u> reaction <u>INCREASES</u> ($\leftarrow$)
   - Reactants   Products
    - Favors <u>REACTANTS</u>

Stress	Change	Shift
Concentration	Increase a reactant (something on the left.)	Right (Opposite Side)
	Increase a product (something on the right)	Left (Opposite Side)
	Decrease a reactant (something on the left.)	Left (Same Side)
	Decrease a product (something on the right.)	Right (Same Side)
Temperature	Increase heat/Temperature	Opposite side of energy
	Decrease heat/temperature	Same side as energy
Pressure	Increase Pressure	Side with fewer gas molecules
	Decrease Pressure	Side with greater gas molecules
Catalyst	Increases rate equilibrium is reached. Increase both the right and left equally.	No Shift

Watch this: <u>Le Chatelier's Animation</u>

Types of stresses:

1. Concentration The equilibrium changes (or shifts) when a reactant or product is added (introduced) or decreased (taken away) in a reaction that is at equilibrium.

- When the concentration of a reactant or product is **increased:** the reaction will
  **SHIFT AWAY** from the increase (use up the excess)

Example 1: $4NH_3(g) + 5O_2(g) \leftrightarrows 4NO(g) + 6H_2O(g) + HEAT$
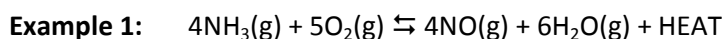
If we add $H_2O(g)$, the system would shift to the LEFT and the $[NH_3]$ would INCREASE.
If we add $O_2(g)$, the system would shift to the RIGHT and the $[NO]$ would INCREASE.
If we add $H_2O(g)$, the system would shift to the LEFT and the $[NO]$ would DECREASE
If we added $NO(g)$, which concentration(s) would decrease?

Answer: $[NO]$, $[H_2O]$

- When the concentration of a reactant or product is **decreased:** the reaction will _**SHIFT TOWARD**_ the side that has experienced the decrease in concentration (replaces what was taken)

Example 2: $2804\ kJ + 6CO_2(g) + 6H_2O(l) \leftrightarrows C_6H_{12}O_6(s) + 6O_2(g)$
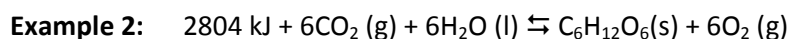
If we remove water, the system will shift to the LEFT and the $[C_6H_{12}O_6]$ will DECREASE.
If we remove $O_2(g)$, the system will shift to the RIGHT and the $[C_6H_{12}O_6]$ will INCREASE.
If we remove glucose, which concentrations will decrease?
Answer: $[CO_2]$, $[H_2O]$
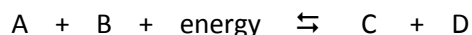
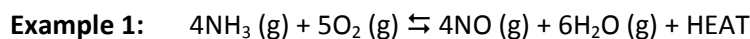If we remove CO_2, which concentration(s) would increase?
Answer: $[CO_2]$, $[H_2O]$

TRICK → AA – what YOU ADD, the SYSTEM shifts AWAY from
TT – what YOU TAKE, the SYSTEM shifts TOWARDS

2. Temperature as initial stress: (involves increasing or decreasing the "HEAT" component of a reaction)

NOTE: HEAT/ENERGY/J/KJ will either be a reactant or a product

$A + B \leftrightarrows C + D + HEAT$

$A + B + energy \leftrightarrows C + D$

- When temperature (or HEAT) is **increased**: the reaction will SHIFT AWAY from the reaction
  side containing "HEAT" (in the ENDOTHERMIC direction)

  - When temperature (or HEAT) is **decreased:** the reaction will SHIFT TOWARD the reaction side containing "HEAT" (in the EXOTHERMIC direction)

Example 1: $4NH_3(g) + 5O_2(g) \leftrightarrows 4NO(g) + 6H_2O(g) + HEAT$

If we added heat, which concentration(s) will decrease?

Answer: $[NO]$, $[H_2O]$

If we added heat, which concentration(s) will increase?   Answer: $[NH_3]$, $[O_2]$

11

Example 2: CO_2 (g) + H_2O (l) + 890.4 kJ $\leftrightarrows$ CH_4 (g) + $2O_2$ (g)
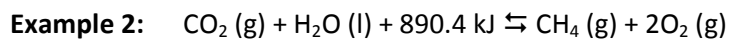
If we remove heat, which concentration(s) will decrease?

Answer: [CH_4], [O_2]

If we remove heat, which concentration(s) will increase?

Answer: [CO_2], [H_2O]

3. Pressure as initial stress: Recall, pressure affects GASES ONLY! So every other state (s, l, aq) in the reaction is UNAFFECTED for this type of stress

Increase pressure: reaction shifts to side with LEAST # GAS MOLECULES (or least # moles of gas)

Decrease pressure: reaction shifts to side with GREATEST # GAS   MOLECULES (or greatest # moles of gas)

NOTE: If the reaction contains NO GAS MOLECULES or if the reaction has the SAME number of
 GAS MOLECULES on each side, there is NO EFFECT and NO SHIFT results from an increase or decrease in pressure.

Example 1: $CO_2(g) \leftrightarrows CO_2(aq)$

If we increase the pressure, the concentrations of which species will increase?

Answer: $CO_2(aq)$

If we increase the pressure, the concentrations of which species will decrease?

Answer: $CO_2(g)$

If we decrease the pressure, the concentrations of which species will increase?

Answer: $CO_2(g)$

If we decrease the pressure, the concentrations of which species will decrease?

Answer: $CO_2(aq)$

Haber process

$$N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{\qquad\qquad} 2NH_{3(g)} \qquad \Delta H = -92\,kJ\,mol^{-1}$$

- Exothermic
- Subject to both temp and pressure changes
- Both reactants and products are gases

4. Catalysts will shorten time to reaching equilibrium effecting forward and reverse reactions equally.

Lesson 6: Entropy/Enthalpy

Objective: To define the conditions necessary for a spontaneous reaction to occur

Spontaneous Reactions: Spontaneous reactions depend on the balance between two fundamental tendencies in nature: (1) toward a lower energy state; and (2) toward randomness.
At constant temperature and pressure, a system tends to undergo a reaction so that, in its final state, it has lower energy than in its initial state. A system tends to change from a state of higher energy to one of low energy. For chemical systems, this energy is called **Enthalpy** represented mathematically as **ΔH.** This tendency in nature favors the exothermic reaction in which ΔH is negative. **Entropy** is the measure of disorder, randomness, or lack of organization of a system. The solid phase, in regular crystalline arrangement, is more organized than the liquid phase the liquid phase is more organized than the gaseous phase. Entropy is so defined that the more random a system is, the higher the entropy. An increase in entropy during a change in the state of a system means that in its final state, the system is more disordered (random) than in its initial state. High entropy (randomness) is favored by high temperatures. A high temperature increases the rate of motion of the particles, and thus, tend to increase randomness. At constant temperature, a system tends to undergo a reaction so that in its final state it has higher entropy (greater randomness) than in its initial state. A system tends to change from state of great order to a state of less order.

ENTROPY (ΔS): degree of RANDOMNESS or CHAOS or DISORDER or
"MESSINESS" in a system; nature tends to proceed to a state of GREATER entropy, or disorder.
The MORE ORDER you have, the LESS ENTROPY in your system.
The LESS ORDER you have, the MORE ENTROPY in your system.

What physical state of matter has the highest entropy? *GAS*

So, going from **(s) → (l) → (aq) → (g)** you will experience INCREASED DISORDER
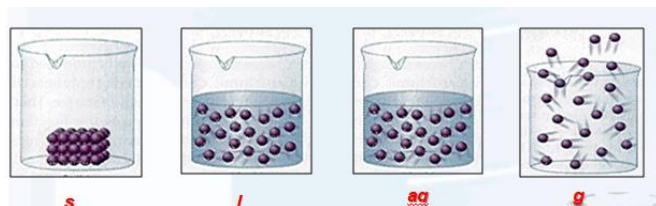
- Entropy INCREASES when a compound is <u>broken down</u>.
- Entropy DECREASES when a compound is <u>created and bonds are formed</u>.

Example: For the following determine if there is an **increase, decrease, or no change in entropy:**

1. $2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$ increase

2. $H_2O_{(l)} \rightarrow H_2O_{(s)}$ decrease

3. $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$ decrease

4. $NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$ increase

5. $KCl_{(s)} \rightarrow KCl_{(l)}$ increase

6. $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$ no change

NOTE: If all states are the same in reaction, count up the # molecules on each side
        (rule: more → less molecules = decrease in entropy, less → more = increase in entropy)

ENTHALPY (ΔH) = the ENERGY in a system; nature tends to proceed to a state of

LOWER enthalpy, or energy

Exothermic reactions → *RELEASE energy & move to LOWER energy state*

> ** Most common types of reactions because less energy has to be put in to get the reaction started (LOWER activation energy)
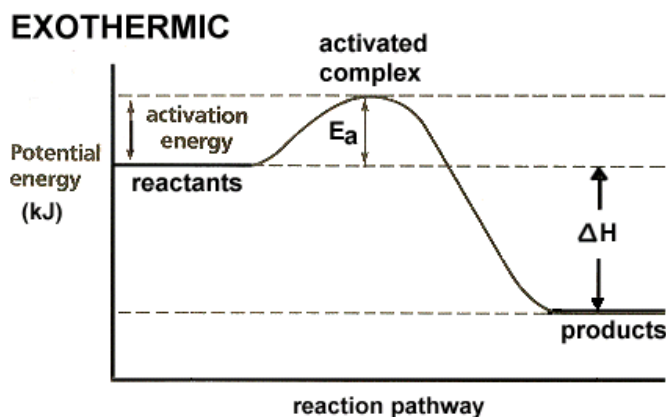
Endothermic reactions → ABSORB energy & move to a HIGHER energy state
(HIGHER ACTIVATION ENERGY NEEDED)

> ** Not as common because more energy must be put in to get the reaction started (HIGHER activation energy)
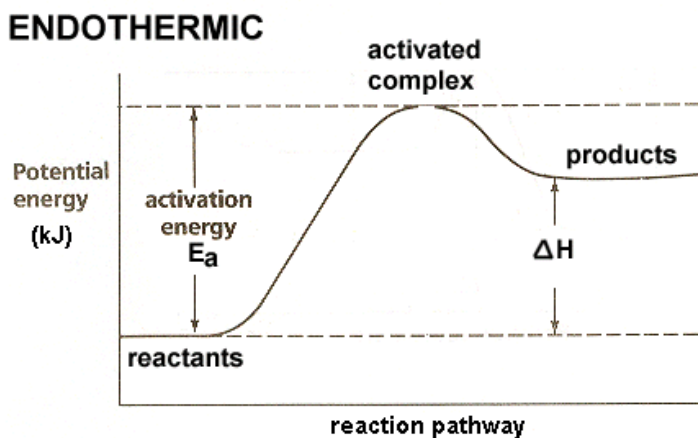
Summary:
- Systems change from high to low energy
- Favors negative ΔH, exothermic reactions
- System changes from great order to low order, high entropy to low entropy
- ΔS positive preferred
- More random system, more entropy
- Gas more entropy than liquid than solid.
- Solid⟶ liquid ⟶ gas   Δ S=pos