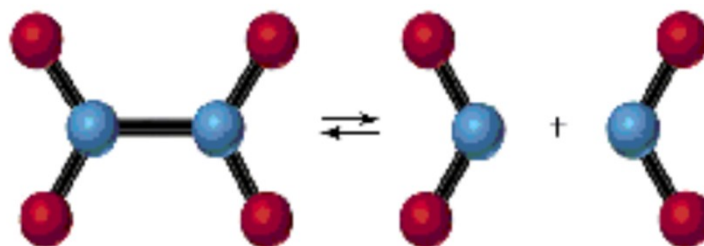


Note Packet Unit 8: Kinetics, Thermodynamics, & Equilibrium



Kinetics:

- Reaction Rate
- Collision Theory
- Reaction Mechanism
- Factors Affecting Rate of Reaction:
 - Nature of Reactants
 - Concentration
 - Surface Area
 - Pressure
 - Catalyst
 - Temperature

Thermodynamics:

- Potential Energy Diagrams
- Heat of Reactions
- Endothermic Reactions
- Exothermic Reactions
- Activated Complex
- Activation Energy
- Effect of Catalyst on Reaction
- Stability (Table I)

Equilibrium:

- Physical Equilibrium
- Phase Equilibrium
- Solution Equilibrium
- Chemical Equilibrium
- Le Chatelier's Principle
 - Temperature Changes
 - Pressure Changes
 - Effect of a Catalyst
- Enthalpy
- Entropy

Kinetics = study of the **RATE** or **SPEED** at which **REACTIONS** occur

A **REACTION** is the **BREAKING** and **REFORMING** of **BONDS** to make entirely new compounds as products

Reaction Mechanism = **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
 - CAN'T OMIT any STEPS!
 - CAN'T CHANGE THE ORDER of the steps!
 - CAN'T OMIT any REACTANTS (ingredients)

Determine whether each of the following chemical reactions is an example of a slow or fast reaction. Explain why knowing this relative rate of rxn is significant.

Rusting slow

alka seltzer in water fast

styrofoam decomposing very slow

weathering of rocks slow

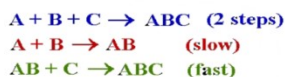
bleach removing color fast

WHAT DETERMINES THE RATE OF A REACTION?

15 steps vs 2 steps

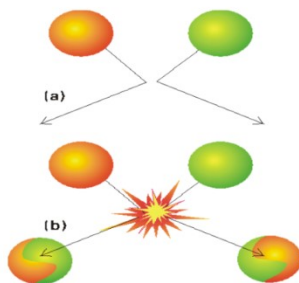
1. **NUMBER OF STEPS** = more steps can mean a slower reaction
2. **RATE DETERMINING STEP** = the **SLOWEST STEP** of the reaction; most important factor influencing reaction rate

Rate Determining Step



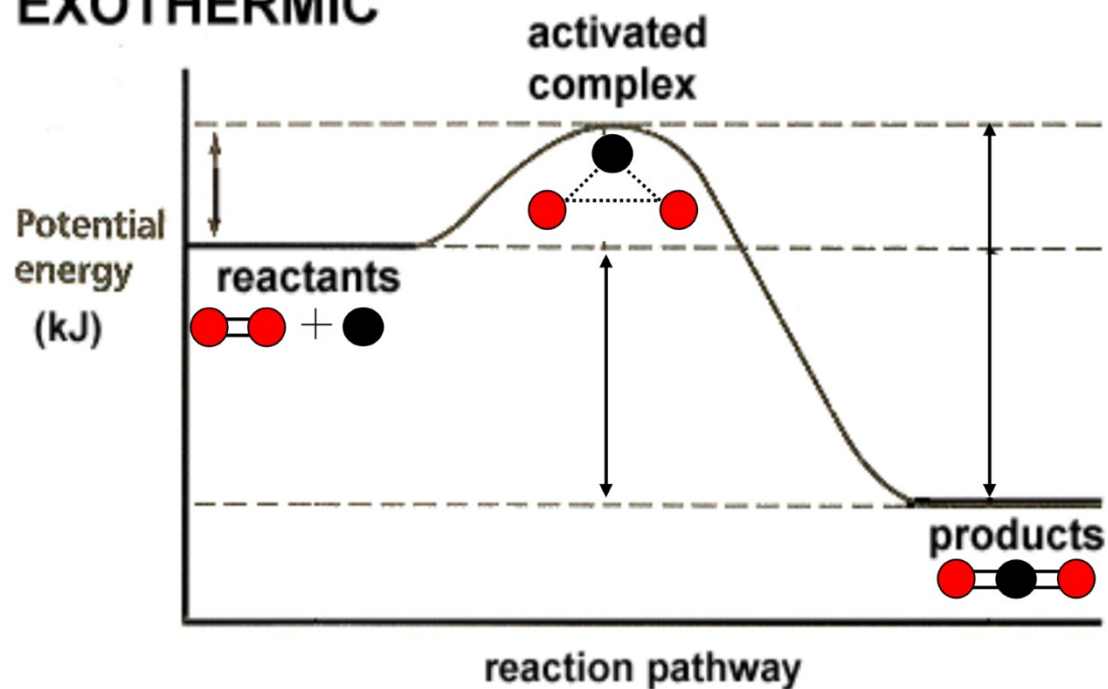
Collision Theory: In order for a reaction to occur, reactant PARTICLES MUST COLLIDE and have the following when doing so:

1. Proper amount of ENERGY
2. Proper ALIGNMENT/DIRECTION/ORIENTATION



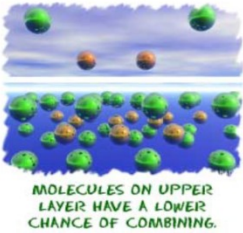
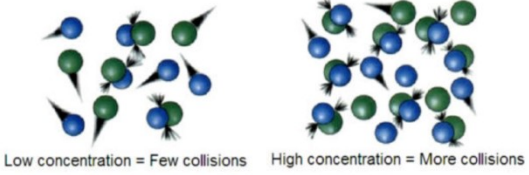
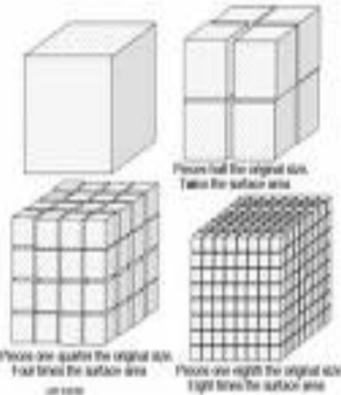
*Only when particles collide with these two conditions are met will there be an EFFECTIVE COLLISION, resulting in a reaction

EXOTHERMIC



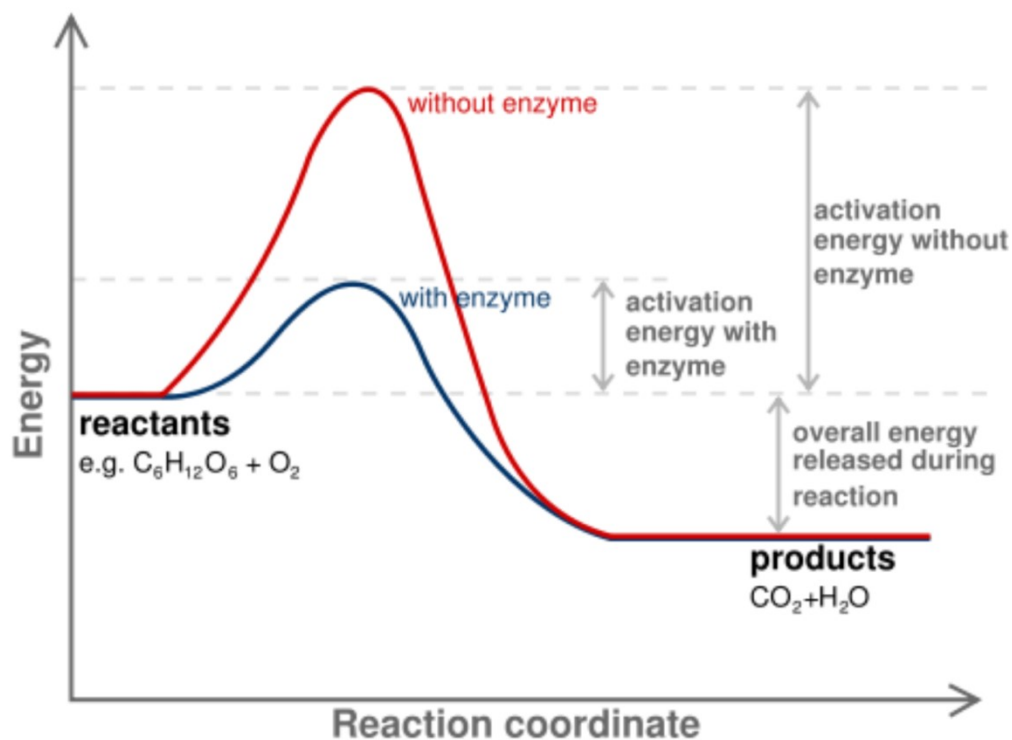
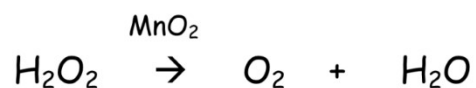
THE 6 Factors Affecting Rate of Reaction:

Factor	How Rate is Affected	Why Rate is Affected
1. Nature of Reactants	PHASE/STATE of matter	<ul style="list-style-type: none"> • GASES = FASTER than solids or liquids • AQUEOUS = FASTER than solids or liquids <p style="text-align: center;"><i>Combustion</i></p> $\text{CH}_4(g) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$ <p style="text-align: center;"><i>Methane</i></p> <ul style="list-style-type: none"> • *SOLIDS = SLOWEST $\text{C}_{25}\text{H}_{52}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$
	<p style="text-align: center;">BOND TYPE</p> <p><i>*This should have an asterisk, and the Regents overgeneralizes in this case. However, it may end up on the June exam...</i></p>	<ul style="list-style-type: none"> • IONIC = FAST (at 25°C) $\text{NaCl}(aq) + \text{AgNO}_3(aq) \rightarrow \text{NaNO}_3(aq) + \text{AgCl}(s)$ <ul style="list-style-type: none"> • COVALENT = SLOW (at 25°C) $2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)$

<p>2. Concentration</p> 	<p>INCREASE concentration, INCREASE rxn rate</p>	<p>The MORE PARTICLES in a given space, the LESS SPACE b/w particles → MORE COLLISIONS</p> 
<p>3. Pressure</p>	<p>INCREASE pressure, INCREASE rxn rate (affects GASES ONLY!)</p>	<p>Increasing pressure DECREASES VOLUME which DECREASES SPACE b/w particles → MORE COLLISIONS</p>
<p>4. Temperature</p>	<p>INCREASE temperature, INCREASE rxn rate</p>	<p>Greater SPEED → MORE total COLLISIONS Greater AVERAGE KE → collisions take place with MORE energy</p>
<p>5. Surface Area</p>	<p>INCREASE the surface area (by making PIECES SMALLER) INCREASES the rxn rate</p> <p>(How many surfaces are there?)</p>	<p>Increasing surface area EXPOSES MORE REACTANT PARTICLES to possible collisions</p> 

<p>6. Catalyst</p>	<p>SPEEDS UP THE RXN WITHOUT CHANGING THE NATURE OF THE REACTANTS/PRODUCTS</p>	<p>Provides a SHORTCUT or ALTERNATIVE PATHWAY for the mechanism Lowers the ACTIVATION ENERGY for the reaction</p>
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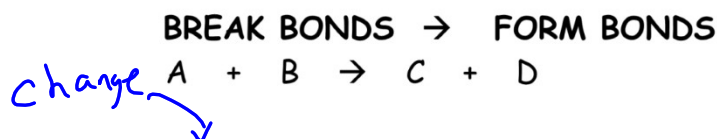
How to speed up chemical reactions,



Potential Energy Diagrams

Recall, we have talked about chemical bonds having stored energy (AKA potential energy). For that reason, chemists use diagrams called Potential Energy Diagrams to illustrate the potential (or stored) energy changes that occur during specific chemical reactions.

Recall: A reaction is the breaking and reforming of bonds



Heat of Reaction (ΔH) = the amount of **HEAT** ENERGY LOST or GAINED throughout a REACTION ($\Delta H = \text{enthalpy}$)
PE OF THE PRODUCTS - PE OF THE REACTANTS

$$\Delta H = H_p - H_R$$

$$\frac{\text{PE products} - \text{PE reactants}}{\Delta H_{\text{rxn}}}$$

Also recall, there are two (2) types of reactions:

1. Reactions that release energy \rightarrow **EXOTHERMIC**

- ΔH is **NEGATIVE** (-)



Ex: Sodium in water \rightarrow heat (and fire!) as product

$$\begin{array}{l} 10 \text{ KJ} \\ \Delta H = -10 \text{ KJ} \end{array}$$

2. Reactions that absorb/gain energy \rightarrow **ENDOTHERMIC**

- ΔH is **POSITIVE** (+)



Ex: baking (need oven to supply heat)

$$\begin{array}{l} 2 \text{ KJ} \\ \Delta H = 2 \text{ KJ} \end{array}$$

Whatever you do to a chemical equation, you also must do to the ΔH .

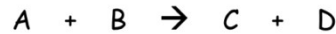
Ex 1: If you REVERSE a reaction (flip the products and reactants), then you must reverse/flip the sign for ΔH .

Ex 2: If you double the equation (or the coefficients), then you must double the ΔH .

Table I (of the Reference Tables) tells us if particular reactions are exothermic or endothermic based on sign of the ΔH value.

	ΔH (kJ/mol)	Endothermic/Exothermic
1. $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$	+66.4	Endothermic
2. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	-91.8	Exothermic
3. $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$	+91.8	Endothermic
4. $2C(s) + 2O_2(g) \rightarrow 2CO_2(g)$	-787.0	Exothermic
5. $CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)$	+283.0	Endothermic

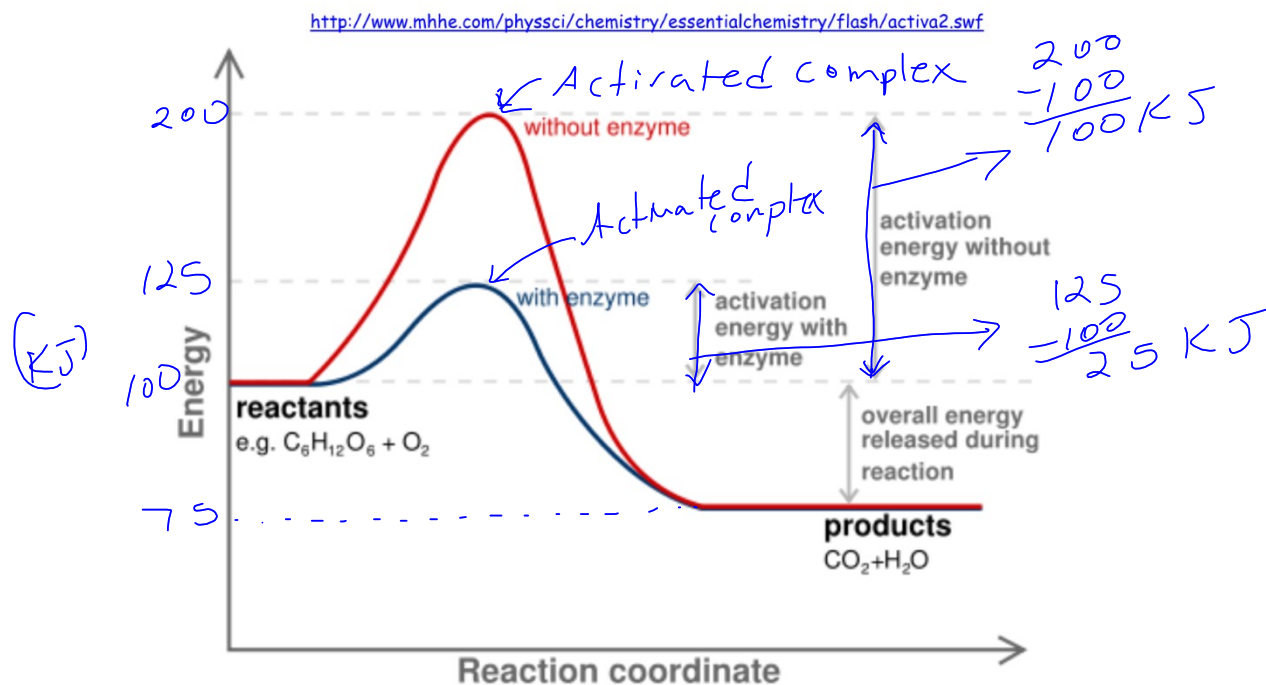
Forward Reaction = reading LEFT TO RIGHT in a reaction; reaction moves toward the right



Reverse Reaction = reading RIGHT TO LEFT in a reaction; reaction moves toward the left



Activation Energy = amount of ENERGY NEEDED TO GET A REACTION STARTED or to FORM THE ACTIVATED COMPLEX of a reaction (you must get "over the hump" in order for a reaction to occur)



HOW EXACTLY DOES A **CATALYST** SHORTEN THE REACTION TIME NEEDED FOR A REACTION TO COMPLETE?

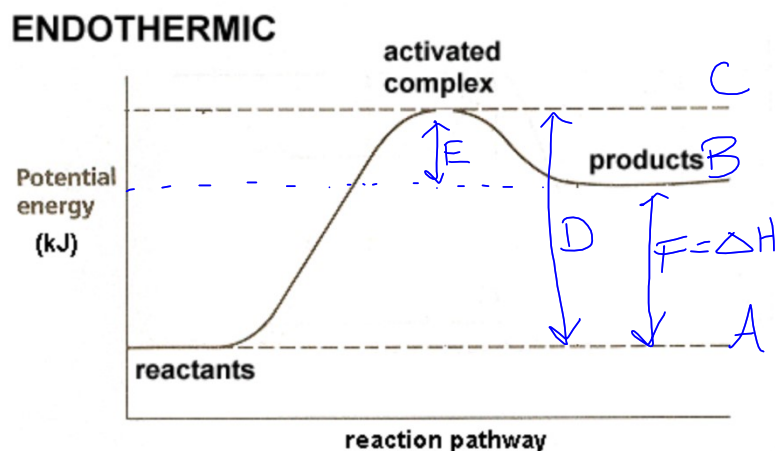
The **ACTIVATED COMPLEX** is lowered ... OR

The **ACTIVATION ENERGY** is decreased ... OR

The **REACTION PATHWAY** is shortened

ENDOTHERMIC Potential Energy Diagrams → POSITIVE ΔH

* Product side (to the R) always **HIGHER** than the reactant side (to the L) meaning that **ENERGY** is **ABSORBED**



Label the following: A = Potential Energy of the Reactants

B = Potential Energy of the Products

C = Potential Energy of the Activated Complex

D = Activation energy of the Forward rxn

E = Activation Energy of the Reverse rxn

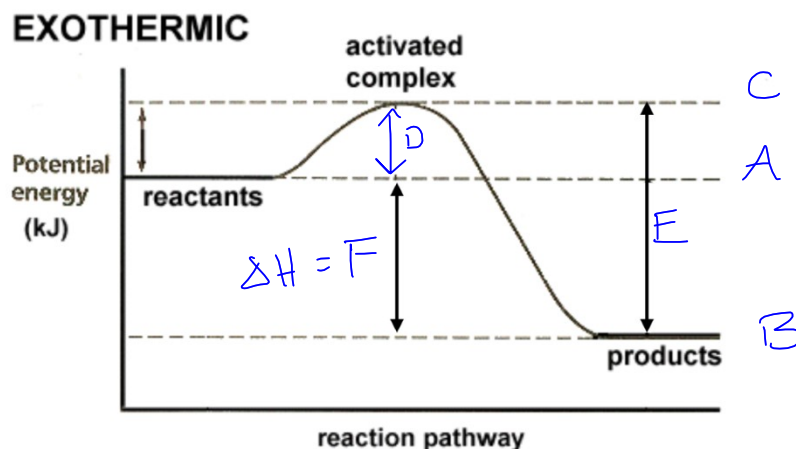
F = Heat of the Reaction ($\Delta H = H_p - H_r$)

ACTIVATED COMPLEX = **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.*

EXOTHERMIC Potential Energy Diagrams → **NEGATIVE ΔH**

* Product side (to the R) always **LOWER** than the reactant side (to the L) meaning that **ENERGY** is **RELEASED**



Label the following: A = Potential Energy of the Reactants

B = Potential Energy of the Products

C = Potential Energy of the Activated Complex

D = Activation energy of the Forward rxn

E = Activation Energy of the Reverse rxn

F = Heat of the Reaction ($\Delta H = H_p - H_r$)

Question: If a catalyst were added to the above diagram, which letter quantities would change within the diagram?

Answer: C, D, E

Question: How does the addition of a catalyst change the heat of reaction (ΔH)? (Increase, decrease, or remains the same)

Answer: ΔH remains the same

Question: What are the benefits to adding a catalyst?

Answer: speeds up rxn, less energy to start

EQUILIBRIUM

A
T
E
S

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.

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

- Equilibrium is represented by DOUBLE ARROWS \rightleftharpoons 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.*

Define *equilibrium* in terms of reactant and product concentrations:

@ equilibrium, concentrations are constant

Define *equilibrium* in terms of forward and reverse reaction rates:

@ equilibrium, forward rate = reverse rate

TYPES OF EQUILIBRIUM

(all occur in CLOSED SYSTEMS)

***IT'S ALL ABOUT THE EQUAL RATES!**

1. Physical Equilibrium: Equilibrium that involves physical changes

a) Phase Equilibrium - occurs during a PHASE CHANGE

Examples:

$(s) \rightleftharpoons (l)$ RATE of MELTING = RATE of FREEZING
(sealed container @ 0°C)

$(l) \rightleftharpoons (g)$ RATE of EVAPORATION = RATE of
CONDENSATION
(sealed container @ 100°C)

b) Solution Equilibrium - occurs at a solution's SATURATION POINT

RATE of DISSOLVING = RATE of CRYSTALLIZATION

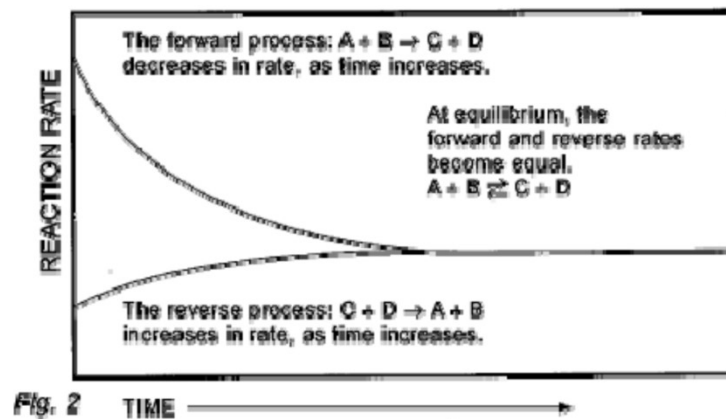
example: $\text{NaCl}_{(s)} \rightleftharpoons \text{NaCl}_{(aq)}$

2. Chemical Equilibrium:

RATE of the FORWARD RXN = RATE of the REVERSE RXN

OR

RATE of BREAKING BONDS = RATE of FORMING BONDS



LE CHATELIER'S PRINCIPLE

Le Chatelier's principle explains HOW A SYSTEM AT EQUILIBRIUM WILL RESPOND TO STRESS.

STRESS = Any change in TEMPERATURE, CONCENTRATION, or PRESSURE put upon an system at equilibrium

When a STRESS is added to a system at equilibrium, the system will SHIFT in order to relieve that stress and reach a new equilibrium.

SHIFT = an increase in the RATE of EITHER the forward OR the reverse rxn

SHIFT TO RIGHT (TOWARD PRODUCTS):

Rate of FORWARD reaction INCREASES (→)

Reactants \rightleftharpoons Products

*Favors PRODUCTS

SHIFT TO LEFT (TOWARD REACTANTS):

Rate of REVERSE reaction INCREASES (←)

Reactants \rightleftharpoons Products

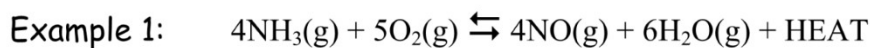
*Favors REACTANTS

DIFFERENT TYPES OF STRESSES:

- 1) **Concentration** as initial stress: Equilibrium changes (or shifts) when a reactant or product is added (introduced) or decreased (taken away) in a reaction that is at equilibrium

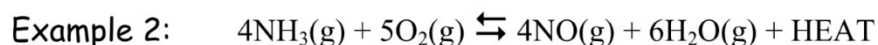
When the concentration of a reactant or product is INCREASED:
the reaction will SHIFT **AWAY** from the increase (use up the excess)

EXO



1. If we add $\text{H}_2\text{O}(\text{g})$, the system would shift to the left and the $[\text{NH}_3]$ would increase.
2. If we add $\text{O}_2(\text{g})$, the system would shift to the right and the $[\text{NO}]$ would increase.
3. If we add $\text{H}_2\text{O}(\text{g})$, the system would shift to the left and the $[\text{NO}]$ would decrease.
4. If we added $\text{NO}(\text{g})$, which concentration(s) would decrease? H_2O , heat

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)



1. If we remove oxygen, the system will shift to the left and the $[\text{NH}_3]$ will increase.
2. If we remove water, the system will shift to the right and the $[\text{NO}]$ will increase.
3. If we remove ammonia, which concentration(s) will decrease?
 NO , H_2O , Heat
4. If we remove $\text{NO}(\text{g})$, which concentration(s) would increase?
 H_2O , Heat

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

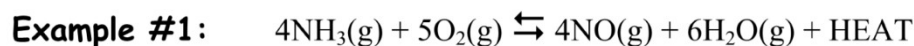
2) **Temperature** as initial stress: (involves increasing or decreasing the "HEAT" component of a reaction)

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

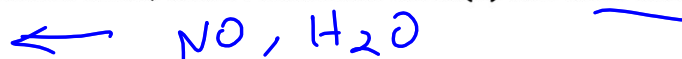


When temperature (or HEAT) is increased: the reaction will SHIFT **AWAY** from the rxn side containing "HEAT" (in the **ENDOTHERMIC** direction)

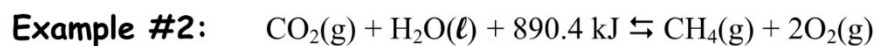
When temperature (or HEAT) is decreased: the reaction will SHIFT **TOWARD** the rxn side containing "HEAT" (in the **EXOTHERMIC** direction)



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



2. If we added heat, which concentration(s) will increase?



Endo

3. If we remove heat, which concentration(s) will decrease?



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



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

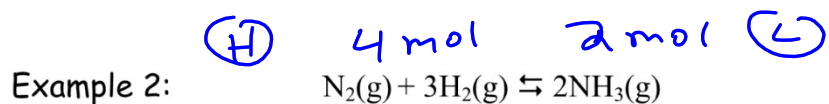
INCREASE PRESSURE: rxn shifts to side with **LEAST # GAS MOLECULES** (or least # moles of gas)

DECREASE PRESSURE: rxn shifts to side with **GREATEST # GAS MOLECULES** (or greatest # moles of gas)

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



1. If we increase the pressure, the concentrations of which species will increase? $\text{CO}_2(\text{aq})$
2. If we increase the pressure, the concentrations of which species will decrease? $\text{CO}_2(\text{g})$
3. If we decrease the pressure, the concentrations of which species will increase? $\text{CO}_2(\text{g})$
4. If we decrease the pressure, the concentrations of which species will decrease? $\text{CO}_2(\text{aq})$



1. If we increase the pressure, in which direction will the equilibrium shift? (Count moles of gases on each side 1st) Right
→
2. If we increase the pressure, the concentration of which species will increase initially? NH₃
3. If we decrease the pressure, the concentration of which species will decrease initially? ← Left
NH₃
4. If we decrease the pressure, the concentration of which species will increase initially? N₂, H₂

AND LASTLY...

WHY DO CHEMICAL AND PHYSICAL CHANGES OCCUR?

Turn the page please...

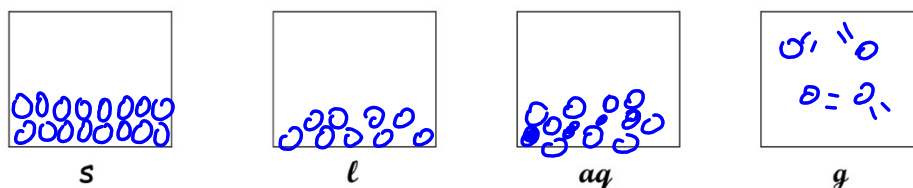
ENTROPY (ΔS): degree of **RANDOMNESS** or **CHAOS** or **DISORDER** or "MESSINESS" in a system; nature tends to proceed to a state of **GREATER** entropy, or disorder.

The **MORE ORDER** you have, the **LESS ENTROPY** in your system.
The **LESS ORDER** you have, the **MORE ENTROPY** in your system.

PHASE CHANGE is the most significant factor in determining ΔS :

Changing from (s) \rightarrow (l) \rightarrow (aq) \rightarrow (g) = **INCREASED** ENTROPY

Draw particle diagrams to illustrate each of the following phases:



*Entropy **INCREASES** when a compound is broken down.

*Entropy **DECREASES** when a compound is created and bonds are formed.

NOTE: If there is no phase change, count up the # molecules on each side

(RULE: # moles \downarrow = **ENTROPY \downarrow = $-\Delta S$** , # moles \uparrow = **ENTROPY \uparrow = $+\Delta S$**)

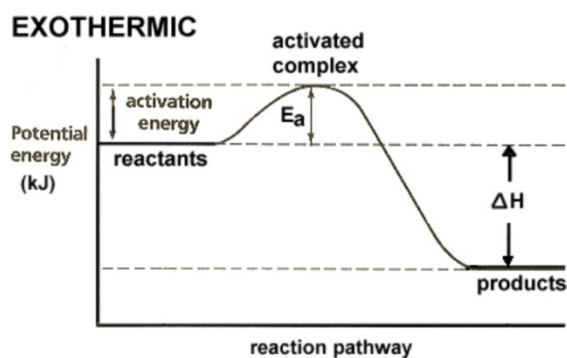
For the following determine if there is an **increase, decrease, or no change in entropy**:

- $2\text{KClO}_{3(s)} \rightarrow 2\text{KCl}_{(s)} + 3\text{O}_{2(g)}$
inc (s) \rightarrow (g)
- $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(s)}$
dec (l) \rightarrow (s)
- $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightarrow 2\text{NH}_{3(g)}$
dec 4 mol \rightarrow 2 mol
- $\text{NaCl}_{(s)} \rightarrow \text{Na}^+_{(aq)} + \text{Cl}^-_{(aq)}$
inc (s) \rightarrow (aq)
- $\text{KCl}_{(s)} \rightarrow \text{KCl}_{(l)}$
inc (s) \rightarrow (l)
- $\text{CO}_{2(s)} \rightarrow \text{CO}_{2(g)}$
inc (s) \rightarrow (g)
- $\text{H}^+_{(aq)} + \text{C}_2\text{H}_3\text{O}_2^-_{(aq)} \rightarrow \text{HC}_2\text{H}_3\text{O}_2_{(l)}$
dec (aq) \rightarrow (l)
- $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$
inc (s) \rightarrow (g)
- $\text{H}_{2(g)} + \text{Cl}_{2(g)} \rightarrow 2\text{HCl}_{(g)}$
2 mol + 2 mol \rightarrow 2 mol
No change equal moles
- $\text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)} \rightarrow \text{AgCl}_{(s)}$
dec (aq) \rightarrow (s)
- $2\text{N}_2\text{O}_5_{(g)} \rightarrow 2\text{NO}_2_{(g)} + \text{O}_2_{(g)}$
2 mol \rightarrow 3 mol
inc 2 mol \rightarrow 3 mol
- $2\text{Al}_{(s)} + 3\text{I}_2_{(s)} \rightarrow 2\text{AlI}_3_{(s)}$
4 mol + 6 mol \rightarrow 2 mol
dec 4 mol \rightarrow 2 mol
- $\text{H}^+_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)}$
dec (aq) \rightarrow (l)
- $2\text{NO}_{(g)} \rightarrow \text{N}_2_{(g)} + \text{O}_2_{(g)}$
2 mol \rightarrow 2 mol
No change
- $\text{H}_2\text{O}_{(g)} \rightarrow \text{H}_2\text{O}_{(s)}$
dec (g) \rightarrow (s)

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 rxns because less energy has to be put in to get the rxn 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 rxn started (**HIGHER** activation energy)

