# REVIEW: TOPIC 6

NAME: ____________

DUE: ____________

# KINETICS + EQUILIBRIUM

### UNIT 6 – MAJOR UNDERSTANDINGS

- ☆ 3.4d Collision Theory states that a reaction is most likely to occur if reactant particles collide with the proper energy and orientation.
- ☆ 3.4f The rate of a chemical reaction depends on several factors: temperature, concentration,nature of the reactants, surface area, and the presence of a catalyst.
- ☆ 3.4h Some chemical and physical changes can reach equilibrium.
- ☆ 3.4i At equilibrium the rate of the forward reaction equals the rate of the reverse reaction. The measurable quantities of reactants and products remain constant at equilibrium.
- ☆ 3.4j LeChatelier's principle can be used to predict the effect of stress (change in pressure, volume, concentration, and temperature) on a system at equilibrium.
- ☆ 4.1c Energy released or absorbed during a chemical reaction can be represented by a potential energy diagram.

### UNIT 6 – MAJOR UNDERSTANDINGS (CONTINUED)

- ☆ 4.1d Energy released or absorbed during a chemical reaction (heat of reaction) is equal to the difference between the potential energy of the products and potential energy of the reactants.
- ☆ 3.4g A catalyst provides an alternate reaction pathway, which has a lower activation energy than an un-catalyzed reaction.
- ☆ 3.1ll Entropy is a measure of the randomness or disorder of a system. A system with greater disorder has greater entropy.
- ☆ 3.1mm Systems in nature tend to undergo changes toward lower energy and higher entropy.

## A – KINETICS

Chemical kinetics is the branch of chemistry concerned with the rate of chemical reactions and the mechanisms by which chemical reactions occur. The **rate** of a chemical reaction is measured in terms of the number of moles of reactant consumed (or moles of product formed) per unit volume in a unit of time.

The **mechanism** of a chemical reaction is a sequence of stepwise reactions by which the overall change occurs. Though many reactions take place because of a series of steps, only the net reaction is often observable. The net reaction represents a summation of all the changes that occur.

### BONDING & STABILITY

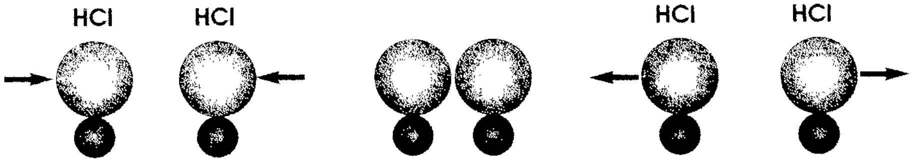
Because there is a release of energy when bonds are formed, systems at lower energy levels are more stable than systems at higher energy levels. So, it follows that bonding will more often occur among atoms if the changes lead to a lower energy condition and, therefore, a more stable structure. The more energy given off when a bond is formed, the stronger and more stable the bond will be. Also, the less energy given off in the formation of a bond, the weaker and less stable it will be.

## COLLISION THEORY

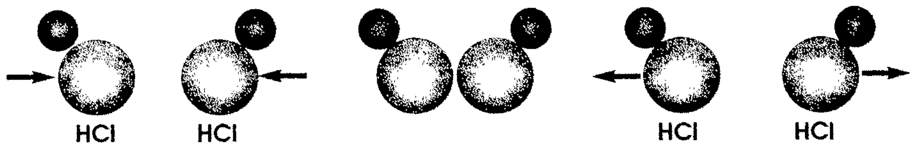
Experiments and observation show that in order for chemical reactions to occur, reacting particles must collide with enough energy and proper orientation so that old bonds are broken and new bonds are formed. This is called an **effective collision**.

### SKILLS 3.4VI *USE COLLISION THEORY TO EXPLAIN HOW VARIOUS FACTORS SUCH AS TEMPERATURE, SURFACE AREA, AND CONCENTRATION, INFLUENCE THE RATE OF REACTION.*

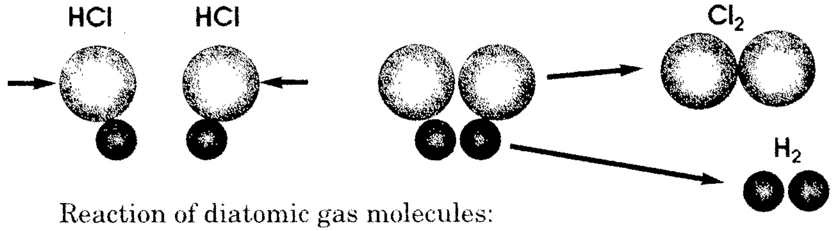
Hydrogen Chloride molecules showing insufficient activation energy. (below)



Hydrogen Chloride molecules showing "improper" activation. (below)



Hydrogen Chloride molecules showing the "right" amount of activation energy and orientation. (below)



Reaction of diatomic gas molecules:

$$2HCl(g) \rightarrow H_2(g) + Cl_2(g)$$

In order for the above reaction to take place, two conditions must be present:

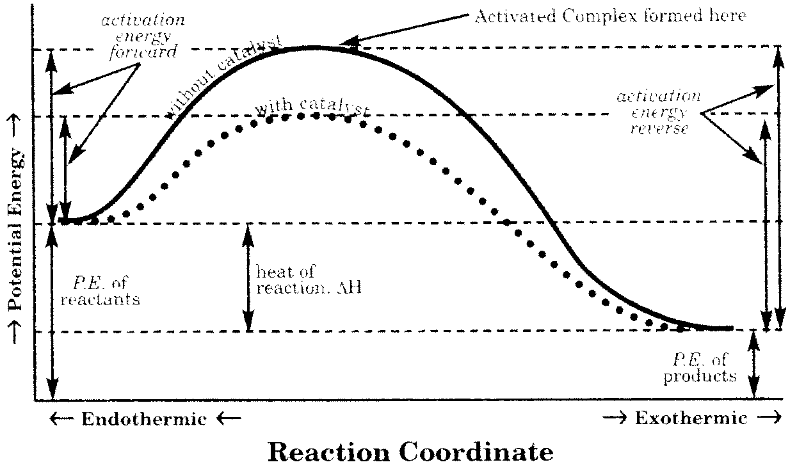
- Particles must collide with enough **activating energy** to form an **activated complex**.
- Particles must collide with the proper geometric orientation so that when the activated complex is formed it can break up to form the new products.

## ROLE OF ENERGY IN REACTIONS

To initiate a chemical reaction, energy is required. Once a chemical reaction begins, energy may be released or absorbed.

### POTENTIAL ENERGY DIAGRAM

For a given reaction, the activation energy and heat of reaction can be shown graphically in a potential energy diagram by plotting potential energy against a reaction coordinate representing the process of the reaction.



- If the potential energy of the products is higher than the potential energy of the reactants, energy has been absorbed (endothermic reaction).
- If the potential energy of the products is lower than the potential energy of the reactants, energy has been liberated (exothermic reaction).

The graph above, when read from left to right, represents an exothermic reaction with the products at a lower potential energy than the reactants. If the graph is reversed, or read from right to left, it would represent an endothermic reaction. The highest point in the curve represents the potential energy of the activated complex. The difference between this point and the initial potential energy of the reactants represents the activation energy of the reaction. **Note**: A catalyst provides an alternative reaction mechanism which has a lower activation energy than the un-catalyzed reaction.

## ENERGY OF CHEMICAL REACTION

By graphing the potential energy of the reactants, the activation energy, and the potential energy of the products against a time sequence, one may describe the energies involved in a chemical reaction.

### ACTIVATION ENERGY

Activation energy is the minimum energy required to initiate a reaction by forming an activated complex.

### HEAT (ENTHALPY) OF REACTION

Heat (enthalpy) of reaction (**ΔH**) is the heat energy released or absorbed in the formation of the products. It represents the difference in heat content between the products and reactants.

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

In an exothermic reaction, energy is released. The products have a lower potential energy than the reactants, and the sign of **ΔH** is negative. The sign that may be used when energy is included in a chemical equation should not be confused with the sign for **ΔH**. For example, the equation for the reaction of hydrogen and oxygen to form water may be written:

$$H_2(g) + {}^1/_2O_2(g) \rightarrow H_2O(l) + 285.8\ kJ$$

Since this is an exothermic reaction (because energy is being produced and is written with the products), the sign of **ΔH** is negative (value: -285.5 J.) In equations that include heat, the phase of each species should be specified, such as (***g***) for gas, (***l***) for liquid, and (***s***) for solid.

When water is formed from gaseous hydrogen and oxygen, the first product that is formed is water vapor [$H_2O(g)$], which condenses into liquid water [$H_2O(l)$]. One possible mechanism for the reaction is:

$$H_2(g) + O_2(g) \rightarrow HOH(g) + O(g) + 241.8\ kJ$$

$$O(g) + H_2(g) \rightarrow HOH(g) + 241.8\ kJ$$

$$2H_2O(g) \rightarrow 2H_2O(l) + 87.78\ kJ$$

**Summarizing**:

$$2\ H_2(g) + O_2(g) \rightarrow 2H_2O(l) + 571.6\ kJ$$

The above reaction shows that when two moles of $H_2O(l)$ are formed, the heat energy produced is 571.6 kJ. *Reference Table I* lists the standard heats of reaction of one mole of various compounds under "standard condition" (1 atm pressure and 298 K) as:

- energy of formation for one mole of $H_2O(g)$ is 241.8 kJ
- energy of formation for one mole of $H_2O(l)$ is 285.8 kJ

In an endothermic reaction, energy is absorbed, the products have a higher potential energy than the reactants, and the sign of **ΔH** is positive.

A good example of this type of reaction is the reverse of the above reaction. If 285.8 kJ is released when one mole of water molecules is formed, when a mole of water molecules is broken down so as to form 1 mole of hydrogen gas and $^1/_2$ mole of oxygen gas, the reaction requires 285.8 kJ of energy. For an endothermic reaction, the energy is written with the reactant. For example:

$$H_2O(l) + 285.8\ kJ \rightarrow H_2(g) + {}^1/_2O_2(g)$$

## FACTORS AFFECTING RATE OF REACTION

Chemical reactions depend on collisions between the reacting particles, atoms, molecules, or ions. It is these collisions that will produce an activated complex so the reaction will take place. The rate of reaction is affected by the number of collisions occurring and the fraction of these collisions that are effective. These effective collisions depend on factors such as the nature of the reactants, concentration, temperature, surface area, and any catalysts involved.

### NATURE OF THE REACTANTS

Since bonds may be broken or formed in a reaction, the nature of the bond is an important fact for affecting reaction rates. Reactions that involve **negligible bond re-arrangements** are usually rapid at room temperature, such as the reactions of ionic substances in aqueous solutions. Reactions that involve the breaking of bonds tend to be slow at room temperature, such as the reaction between hydrogen and oxygen.

### CONCENTRATION AFFECTS THE RATES OF REACTION

- An increase in the concentration of one or more reactants generally increases the rate of reaction.
- An increase in the concentration of a reactant increases the frequency of collisions by increasing the number of collisions per unit time.
- In a gaseous system, an increase in pressure will result in an increase in concentration and thus an increase in the rate of reaction.

## TEMPERATURE AFFECTS THE RATES OF REACTION

An increase in temperature increases the rate of all chemical reactions. An increase in temperature increases the speed (and thus the kinetic energy) of the particles and increases not only the number of collisions per unit time, but also of greater importance, the effectiveness of the collisions.

## SURFACE AREA

Increasing the **surface area of reactants** increases their rate of reaction. By increasing the concentration of the reactants, the number of collisions increases. In heterogeneous reactions, surface area plays an important role. For example, a given amount of zinc will react more readily with dilute hydrochloric acid if the surface area of zinc is increased by using smaller pieces.

## CATALYSTS

**Catalysts** change the activation energy required and thus change the rate of reaction. Also, a catalyst changes the mechanism of a reaction to one involving less activation energy, but does not change the overall process. A catalyst does not initiate a chemical reaction.

# B – EQUILIBRIUM

When a quantity of water is placed in a closed container, it is not long before evaporation begins. The result is small beads of water collecting on the bottom of the cap of the container, and eventually dropping back down to the bottom of the container. This indicates that some of the water vaporized, and because of its added translational movement, hit the bottom of the cap, lost some of its kinetic energy, and condensed.

When the condensed water droplet becomes heavy enough, it drops back into the bottom of the container, where it will start once again on the odyssey of evaporation and condensation. This change of phase from liquid to vapor to liquid is called **phase equilibrium**. If the temperature remains constant, it will continue indefinitely as long as the container is closed.

**Equilibrium** is a state of balance between two opposing reactions (physical or chemical) occurring at the same rate. Most reactions in closed systems are reversible. Equilibrium is dynamic and only describes the overall appearance of the system. It does not describe the activity of individual particles.

The word dynamic implies motion, and **dynamic equilibrium** is that condition where the interaction of the particles of the reactants in one direction, is balanced by the interaction of the particles of the products in the opposite direction. Although the reaction rates for the opposing reactions are equal, a state of equilibrium may exist where the quantities of reactants and products are not equal. Thus equilibrium may be reached when only a small quantity of the products has been formed or when only a small quantity of reactant remains.

**Note**: The quantity of water on the bottom of the cap may not be as great as the quantity of water in the bottom container. However, the rates of evaporation and condensation will be equal.

**Note**: At equilibrium the quantity of water on the bottom of the cap may not be as great as the quantity of water in the bottom container. However, the rates of evaporation and condensation will be equal.

For a system in equilibrium, a change in conditions (such as temperature, concentration, or pressure) may result in a change in the equilibrium point. Because the reactions in an equilibrium are reversible, it follows that equilibrium may be attained either from the forward or the reverse reaction.

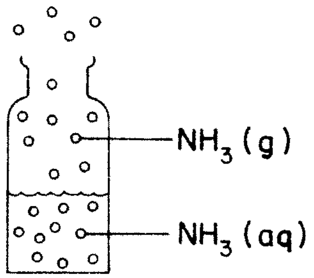
## PHASE EQUILIBRIUM

In general, phase changes (solid to liquid or liquid to gas) are reversible, and, in a closed system, equilibrium may be attained.

Normally, if a solid or a liquid is confined in a closed container, eventually there will be enough particles in the vapor phase so that rate of return is equal to the rate of escape. Therefore, a dynamic equilibrium results where there is an equilibrium vapor pressure, characteristic of the solid or the liquid. The word dynamic refers to the fact that every molecule in the system is participating in a phase change. The basic example is the one stated above, as water changes to a vapor and then returns to its liquid form.

**11** Solution equilibrium always exists in a solution that is
(1) unsaturated
(2) saturated
(3) dilute
(4) concentrated

**12** The diagram at the right shows a bottle containing $NH_3(g)$ dissolved in water. How can the equilibrium $NH_3(g) \leftrightarrow NH_3(aq)$ be reached?
(1) Add more water.
(2) Add more $NH_3(g)$.
(3) Cool the contents.
(4) Stopper the bottle.



## SOLUTION EQUILIBRIUM

### GASES IN LIQUIDS

In a closed system, equilibrium may exist between a gas dissolved in a liquid and the undissolved gas above the liquid. The equilibrium between dissolved and undissolved gas is affected by temperature and pressure in the following ways:

- increased temperature decreases the solubility of gases in liquids
- increased pressure increases the solubility of gases in liquids

An example that points out this type of equilibrium is a bottle of soda. As you decrease the pressure on the top of the soda, by removing the cap, the gas becomes less soluble. You hear the resulting "swoosh..." as the gas escapes.

### SOLIDS IN LIQUIDS

A solution equilibrium exists when the opposing processes of dissolving and crystallizing a solute occur at equal rates. Such a solution exhibiting equilibrium between the dissolved and recrystallized solute must be a saturated solution.

For example, if salt is added to water in a beaker, the salt would dissolve. If more salt is added, the solution will become so saturated with the compound that for every sodium chloride particle going into solution, one would recrystallize out of solution. At this point, solution equilibrium exists, and a **saturated solution** results.

### SOLUBILITY

Solubility is an expression of concentration of a solute in a solvent and can be given under two conditions. The solubility of a solute is defined as the maximum mass of the solute dissolved in a given volume of solvent under specified conditions, not necessarily a saturated solution. And, solubility may also be defined as the concentration of solute in a saturated solution.

## REACTIONS WHICH GO TO COMPLETION

Continuous removal of the product in a closed system may destroy the equilibrium system by removing all of that substance necessary for the reverse reaction. Removal of a product usually causes the reactants to exhaust themselves and the forward reaction to go nearer to completion or to an end.

In an open system, products may be removed from a reaction, wholly or in part by the formation of a gas, formation of an insoluble product (precipitate), or by the formation of an essentially un-ionized product, such as water in an ionic reaction. Such reactions are said to go to "completion."

## CHEMICAL EQUILIBRIUM

Chemical equilibrium is attained when the concentration of the reactants and products remains constant. When observable changes (such as color, pressure, and temperature) no longer occur in a reacting chemical system, the system has reached a state of equilibrium. At this point the forward reaction and the reverse reaction are occurring at equal rates.

## REAL WORLD CONNECTIONS

### HABER PROCESS (ALSO CALLED HABER-BOSCH PROCESS)

In the Haber process, $N_2(g) + 3H_2(g) \leftrightarrow 2\ NH_3(g)$, four moles (volume) of reactants form two moles (volume) of product. The forward reaction thus results in a decrease in the total number of moles (lower volume). Therefore, an increase in pressure will result in an increased production of ammonia, which relieves the effect of increased pressure.

However, in the reaction: $H_2(g) + Cl_2(g) \leftrightarrow 2HCl(g)$ a change in pressure does not affect the equilibrium, since there is an equal volume of gases on either side. **Note**: Solids and liquids are not affected by a pressure change to any appreciable amount.

## LE CHATELIER'S PRINCIPLE

If a stress, such as a change in concentration, pressure, or temperature, is applied to a system at equilibrium, the equilibrium is shifted in a way that usually relieves the effects of the stress. When a chemical system at equilibrium is disturbed, chemical reaction occurs and equilibrium is re-established at a different point (such as with new concentrations of reactants and products).

- **Effect of Concentration** – Increasing the concentration of one substance in a reaction at equilibrium will cause the reaction to go in such a direction as to consume the increase. Eventually, a new equilibrium will be established. For example, in the equilibrium reaction, $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$, increasing the concentration of either nitrogen or hydrogen will increase the rate of ammonia formation. If the system remains closed, the increased concentration of ammonia that results will increase the rate of decomposition of ammonia, and a new equilibrium point will be established.

  Removal of one product of a reaction results in a decrease in its concentration. This will cause the reaction to go in such a direction as to increase the concentration of the products.

- **Effect of Pressure** – A change in pressure affects chemical equilibria in which gases are involved. An increase in pressure will displace the point of equilibrium in the direction that favors the formation of a lesser number of moles (lower volume). If no change in the number of moles is involved (equal volumes of reactants and products), a change in pressure has no effect on the equilibrium.

- **Effect of Temperature** – When the temperature of a system in an equilibrium is raised, the equilibrium is displaced in such a way that heat is absorbed. Chemical changes involve either the evolution or the absorption of energy. In every system in equilibrium, an endothermic and exothermic reaction are taking place simultaneously. The endothermic reaction is favored by an increase in temperature, the exothermic reaction by a decrease in temperature. Keep in mind that the rates of all reactions, both endothermic and exothermic, are increased by a rise in temperature.

  However, the opposing reactions are increased unequally, resulting in a displacement of the equilibrium. For example, in the Haber process, $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g) + 91.8\ kJ$, raising the temperature favors the decomposition of ammonia.

- **Effect of Catalyst** – In a system in equilibrium, a catalyst increases the rate of both the forward and reverse reactions equally, and produces no net change in the equilibrium concentrations. A catalyst may cause equilibrium to be reached more quickly, but does not affect the point of equilibrium.

## COMMON ION EFFECT

The addition of a common ion to the solution of a slightly soluble salt results in a decrease in the solubility of the salt. Consider the equilibrium:

$$AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$$

Addition of NaCl, or any other soluble chloride salt, to this equilibrium system increases the $Cl^-(aq)$ concentration and, according to LeChatelier's Principle shifts the equilibrium to the left. This results in a decrease in the solubility of AgCl.

## ENTROPY CHANGES

Entropy is a measure of the disorder, randomness, or lack of organization of a system. The solid phase is in regular crystalline arrangement and 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. High temperatures increase the rate of motion of the particles and, therefore, increases 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. Therefore, **note**: A system tends to change from a state of great order to a state of less order. For chemical systems, this change in entropy is represented mathematically as $\Delta \mathbf{S}$.

Substances that are solids have ridged bonds with just vibrational movement. As energy is applied, the atoms acquire vibrational and rotational motion which increases the randomness (entropy) of the atoms in the substance, causing it to become a liquid. Finally, as more energy is applied to the substance, the atoms along with the vibrational and rotational motion that they already possess, acquire translational motion. This motion causes the rigid bonds between the atoms to break and it becomes a gas in this phase, and is at its highest state of randomness (or entropy).

## ENERGY CHANGES

As learned earlier, the activation energy required for an exothermic reaction is less than that required for an endothermic reaction. That difference is the energy of the reaction ($\Delta \mathbf{H}$). Therefore, when particles collide, they require less energy to go in the exothermic direction than in the endothermic direction.

This tendency in nature favors the exothermic reaction, in which $\Delta \mathbf{H}$ is negative. Generally, at constant temperature and pressure, a system tends to change from one of high energy to one of low energy.

## REAL WORLD CONNECTIONS

**Exothermic reaction (burning of fossil fuels)** – The burning of wood and carbon-based substances occurs when ignition of the reactants takes place in the presence of oxygen. Once ignition occurs, the reaction proceeds and the potential energy in the fuels is transferred into kinetic energy with the production of light and heat. The reaction for the complete combustion of fossil fuels is:

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l) + \text{energy}$$

# Unit VI KINETICS AND EQUILIBRIUM

Key Concepts

- Collision Theory
- Rate
- Activation Energy
- Factors that effect rate
- Equilibrium
- LeChatelier's Principle: P,[ ], T
- Potential Energy Diagrams
- Catalyst
- Entropy
- Temperature

## I Kinetics

Studies the ***rate*** or speed at which chemical reactions occur. The overall theory that explains reaction rate is called the ***collision theory***. This theory says that in order to react particles must hit each other with enough energy (***activation energy***) and in the right spot. When reactants hit in this way there is an effective collision. The more effective collision you have the faster the rate of the reaction.

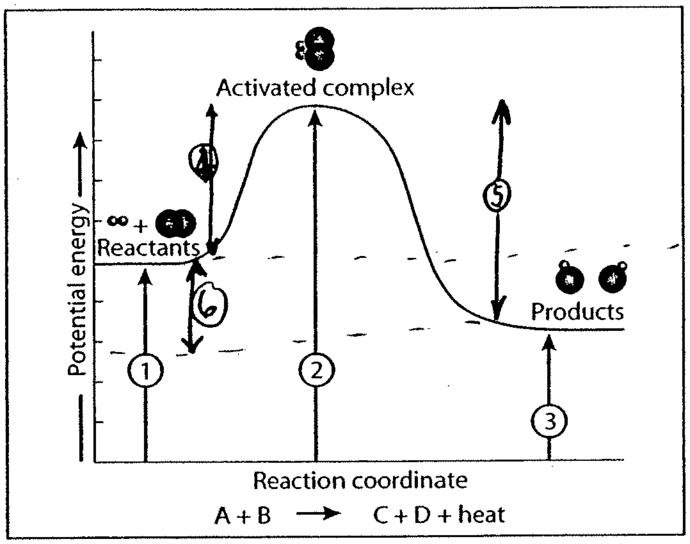
There are five ***factors that affect the rate*** of a reaction.

1. Nature of reactants: since bonds are broken and formed during reactions, the types and number of bonds involved effects the rate. The more complicated a reaction is the longer the reaction will take. Aqueous ionic solutions react the fastest.
2. Concentration of reactants: as the concentration increases, so does the likelihood of collisions. In the case of gases increasing the pressure concentrates the gas particles which increases the likelihood of collisions
3. Temperature: ***temperature*** is the measure of the average kinetic energy of a system. As the temperature increases more particles have enough energy to react and there are more collisions. The rate speeds up as the temperature increases because there are more collisions as well as more effective collisions..
4. Surface area: increasing the surface area of a reactant exposes more particles so there can be more collisions.

5. Catalysts: ***catalysts*** lower the activation energy required for a reaction to occur which speeds up the reaction. by making more collisions effective.

## II *Potential Energy Diagrams*

A potential energy diagram can represent energy released or absorbed during a chemical reaction



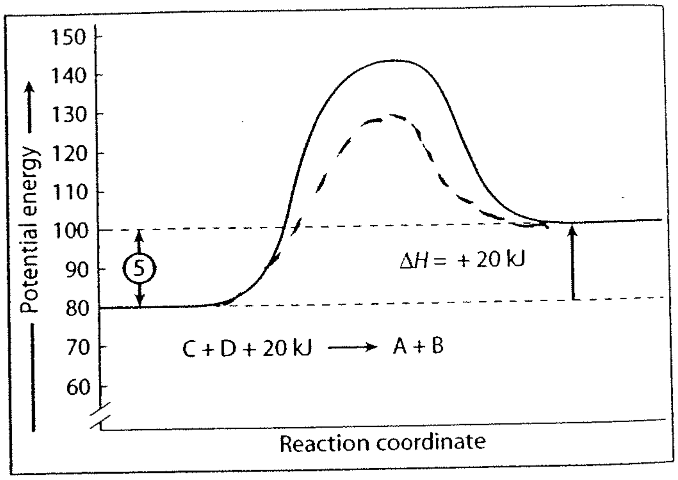
1 is the energy of the reactants.
2 is the energy of the activated complex
3 is the energy of the products
4 is the activation energy of the forward reaction
5 is the activation energy of the reverse reaction
6 is the energy of the reaction, energy products - energy of the reactants

If the potential energy of the products is higher than the potential energy of the reactants, energy has been absorbed (endothermic reaction)

If the potential energy of the products is lower than the potential energy of the reactants, energy has been liberated (exothermic reaction)

## III *Catalyst*

Remember a catalyst lowers the activation energy by providing a different way for the reaction to occur. It speeds up both the forward and reverse reactions so the reaction can happen faster.



The --- line represents the catalyst. It lowers the activation energies of both he forward and the reverse reactions but does not have any effect on the energy of the reaction.

## IV Energy of the Reaction and Entropy

In general systems in nature want low energy (exothermic) and high disorder (large entropy).

### A. Energy of Reactions

$\Delta H$ = Potential energy of products - Potential energy of reactants

$\Delta H$ = Hproducts-H reactants

If $\Delta H$ is a negative number the reaction is exothermic and if $\Delta H$ is positive it is an endothermic reaction.

On Reference Table I use the value of $\Delta H$ to determine if heat is given off, exothermic, or absorbed, endothermic, during a reaction.

Examples:

a.) Dissolving of $NH_4NO_3$ is endothermic, which means heat will be absorbed from the surroundings lower the temperature. Good cold pack.

b.) Dissolving of NaOH is exothermic, which means heat is given off to the surroundings, raises the temperature. Good hot pack.

### B. Entropy

The disorder of a system is the measure of the entropy; the greater the disorder the greater the ***entropy***.

s→l→aq→g increasing disorder, higher entropy

g→aq→l→s increasing order, lower entropy

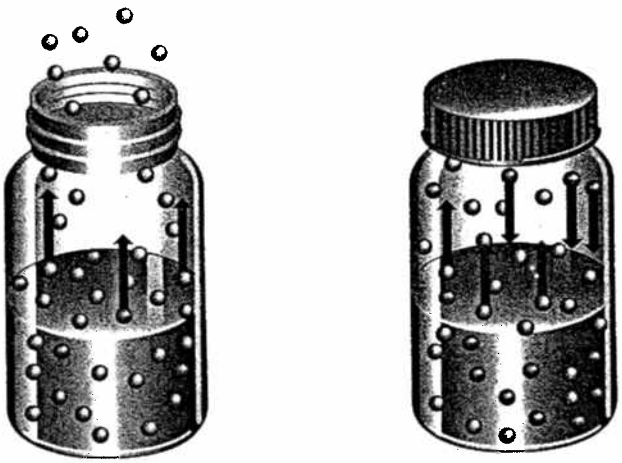
## V Equilibrium

***Equilibrium*** is a state of balance between two opposing reactions (physical or chemical ). The rate of the forward reaction equals the rate of the reverse reaction. Equilibrium has been reached when the amount of products and reactants becomes constant. Equilibrium can only occur in a closed system.

Examples:

a.) phase changes, i.e. one particle evaporates as another condenses

b.) saturated solutions, i.e. as one particle dissolves another comes out of solution.



## VI LeChatelier's Principle

This is the overriding rule used to determine how equilibrium will change when the conditions change. ***LeChatelier's*** can be used to predict the effect of a change in concentration, temperature ,and pressure. In general when the equilibrium moves to the right more products are produced and reactants are used up. When the equilibrium moves to the left more reactants are produced and products are used up.

a.) Increasing the concentration will cause the equilibrium to shift away from what is added.

b.) Increasing the temperature will cause the equilibrium to shift away from the heat. Favor the endothermic reaction.

c.) Increasing the pressure will cause the equilibrium to shift to the side with less moles of gas. As volume changes so does pressure. Increasing volume decreases the pressure.

d.) Adding a catalyst does not effect equilibrium it makes the reaction proceed faster in both directions.

Example: $N_{2(g)} + 3\,H_{2(g)} \rightarrow 2\,NH_{3(g)}$ + heat

For the above reaction adding $N_{2(g)}$ or $H_{2(g)}$, decreasing temperature, increasing pressure will make the reaction move to the right producing more $NH_{3(g)}$ and using up more of the $N_{2(g)}$ and $H_2$.