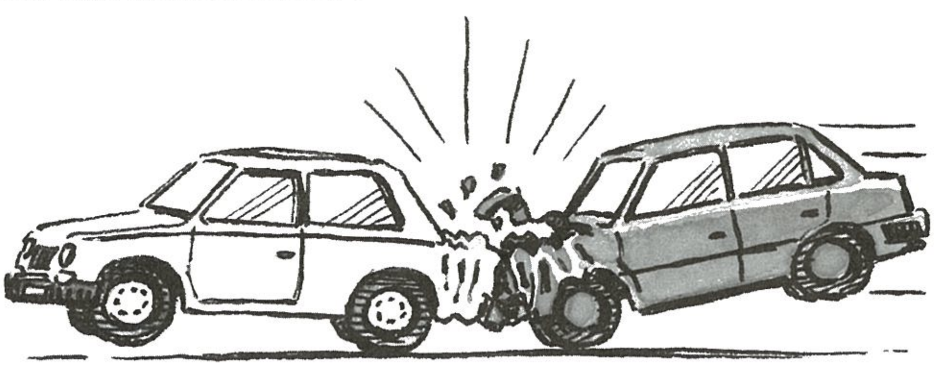
Kinetics and Equilibrium

TOPIC 8

What Scientists Know About Chemical Reactions

What do car accidents and chemical reactions have in common?

Well, they both must involve collisions. Just like all car collisions do not cause damage, not all chemical collisions cause a reaction. Consider that most cars have bumpers that can absorb energy at low speeds and avoid damage. But at higher speeds—CRUNCH! Colliding molecules also need a minimum amount of energy, called the activation energy, to cause changes and start chemical reactions.



TOPIC
8 Kinetics and Equilibrium

Vocabulary

activated complex	entropy	potential energy diagram
activation energy	equilibrium	stress
catalyst	Le Châtelier's principle	

Topic Overview

In this topic you will be introduced to two important ideas in chemistry—the collision theory and equilibrium. The collision theory explores why reactions occur, and the factors that affect those reactions. Equilibrium introduces an important surprise. Not only do reactant particles produce products, but often, these products can react to regenerate the reactants. Many reactions can proceed in two directions. These processes are not only vital in industry, but even more in our own bodies. We have many equilibrium systems that help maintain our health on an even keel.

Kinetics

Kinetics is the branch of chemistry that is concerned with the rates of chemical reactions. Several different factors affect how quickly chemical reactions occur. One of the basic concepts of kinetics is that in order for a reaction to occur, reactant particles must collide. This is called the collision theory. Collisions between particles can produce a reaction if both the spatial orientation and energy of the colliding particles are conducive to a reaction.

Factors Affecting Rates of Reaction

The rate of a chemical reaction is dependent on factors such as the nature of the reactants, concentration, surface area, the presence of a catalyst, and temperature. All these factors affect rate of reaction by changing the number of effective collisions that take place between particles. Pressure can also be a factor that affects the rate of reactions involving gases.

Nature of the Reactants Reactions involve the breaking of existing bonds and the formation of new ones. In general, covalently bonded substances are slower to react than ionic substances due to the greater number of bonds that must be broken before a reaction can occur. Breaking more bonds requires that the particles must have more energy when they collide.

Concentration Most chemical reactions will proceed at a faster rate if the concentration of one or more reactants is increased. An obvious example is the rate of combustion of paper in air, which is 20% oxygen, compared with the much faster rate in pure oxygen. The kinetic molecular theory would predict that because there are more collisions between the paper and oxygen in pure oxygen than in air, the rate in pure oxygen would be faster. Indeed, this is the case.

Surface Area When more surface area of a substance is exposed, there are more chances for reactant particles to collide, thus increasing the reaction rate. A finely divided powder will react more rapidly than a single lump of the same mass.

Pressure While pressure has little or no effect on the rate of reactions between solids or liquids, it has a pronounced effect on gases. An increase in pressure has the effect of increasing the concentration of gaseous particles. Therefore, it increases the rate of a reaction that involves gases.

The Presence of a Catalyst **Catalysts** are substances that increase the rate of a reaction by providing a different and easier pathway for a reaction. Catalysts take part in a reaction, but they are unchanged when the reaction is complete.

Temperature By definition, temperature implies that the greater the temperature of a substance, the faster the molecules move. The kinetic molecular theory states that collisions must occur in order for a reaction to take place. When these two concepts are put together you can see that if the particles are moving faster, there will be more collisions, thus increasing the likelihood that a reaction will occur. At a higher temperature, not only will there be more collisions, but the reacting particles will have more energy, making it more likely that the collisions will be effective.

Table 8-1. Factors that Affect Rate of Reaction

Factor	Increases Rate
Nature of reactants	ionic more than covalent
Concentration	increased concentration
Pressure	increased pressure for gases
Temperature	increased temperature
Surface area	increased surface area
Catalyst	presence of a catalyst

Review Questions — Set 8.1

1. As the number of effective collisions between reacting particles increases, the rate of the reaction

(1) decreases
(2) increases
(3) remains the same

2. Which of the following pairs of reactants will react most quickly?

(1) sodium chloride and silver nitrate
(2) water and hydrogen chloride
(3) hydrogen and propene
(4) oxygen and methane

3. In the reaction $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$, as the surface area of Mg(*s*) increases, the rate of the reaction

(1) decreases
(2) increases
(3) remains the same

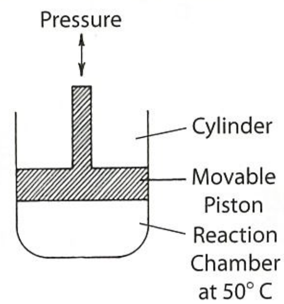
4. Consider the following equation.

$$A(g) + B(g) \rightarrow C(g)$$

As the concentration of A(*g*) increases, the frequency of collisions of A(*g*) with B(*g*)

(1) decreases
(2) increases
(3) remains the same

5. The reaction $A(g) + B(g) \rightarrow C(g)$ is occurring in the apparatus shown below.



The rate of the reaction can be decreased by increasing the

(1) pressure on the reactants
(2) temperature of the reactants
(3) concentration of reactant A(*g*)
(4) volume of the reaction chamber

6. Consider the following equation.

$$Mg(s) + 2H_2O(\ell) \rightarrow Mg(OH)_2(s) + H_2(g)$$

For the reaction to occur at the fastest rate, 1 g of Mg(*s*) should be added in the form of

(1) large chunks
(2) small chunks
(3) a ribbon
(4) a powder

7. Raising the temperature speeds up the rate of chemical reaction by increasing
   (1) the effectiveness of the collisions only
   (2) the frequency of the collisions only
   (3) both the effectiveness and frequency of the collisions
   (4) neither the effectiveness nor frequency of the collisions

8. Consider the following equation.

   $Fe(s) + CuSO_4(aq) \rightarrow Cu(s) + FeSO_4(aq)$

   The Fe reacts more rapidly when it is powdered because the increased surface due to powdering permits
   (1) increased reactant contact
   (2) decreased reactant contact
   (3) pressure to affect reaction rate
   (4) warmer solution to be used

9. If the pressure on gaseous reactants is increased, the rate of reaction is increased because there is an increase in the
   (1) temperature
   (2) volume
   (3) concentration
   (4) heat of reaction

10. Consider the following equation.

    $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

    The reaction can be made to occur more slowly by
    (1) raising the temperature and using a single piece of zinc rather than powdered zinc of the same mass
    (2) lowering the temperature and using a single piece of zinc rather than powdered zinc of the same mass
    (3) raising the temperature and using powdered zinc rather than a single piece of zinc of the same mass
    (4) lowering the temperature and using powdered zinc rather than a single piece of zinc of the same mass

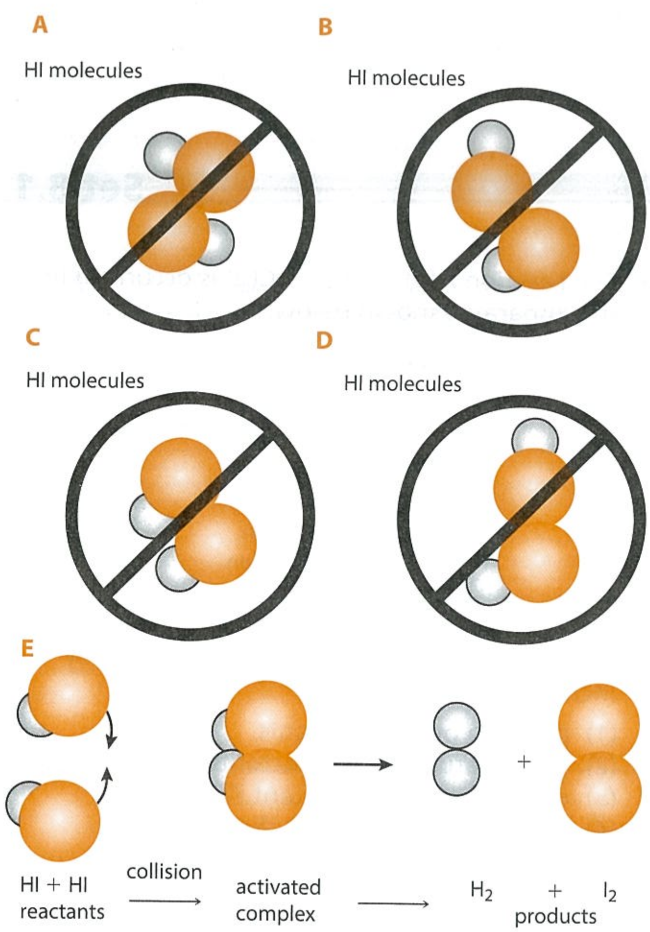


Figure 8-1. Collisions of molecules: If HI molecules collide in any arrangement other than the one shown in part E, the collision is not effective and no products form.

Potential Energy Diagram

As was mentioned when discussing the nature of the reactants, chemical bonds contain energy. Specifically, they contain potential chemical energy. A diagram, called a **potential energy diagram,** illustrates the potential energy change that occurs during a chemical reaction. The vertical axis of this diagram represents the change in potential energy. The horizontal axis is called the reaction coordinate, which represents the progress of the reaction.

In order for a reaction to occur, the reactants must have sufficient energy to collide effectively. As the reactant particles approach each other, kinetic energy is converted into potential energy.

Not only must the particles collide in order for a reaction to occur, they must be properly positioned. Look at Figure 8-1. If the particles collide in the proper orientation, an activated complex is formed. This **activated complex** is a temporary, intermediate product that may either break apart and reform the reactants or rearrange the atoms and form new products.

Figure 8-2 shows a potential energy diagram for the following reaction.

$$A + B \rightarrow C + D + heat$$

Line 1 extends from the origin of the y-axis to the reactants and represents the amount of potential

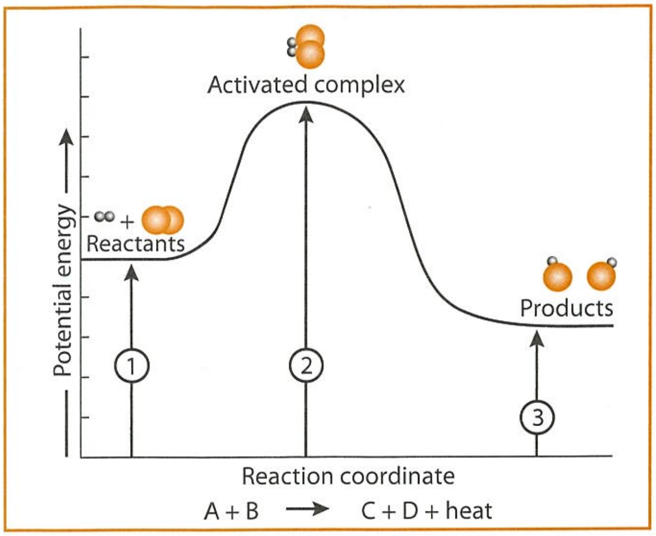


Figure 8-2. Potential energy diagram: This figure shows the potential energy of the reactants, the activated complex, and the products of the reaction.

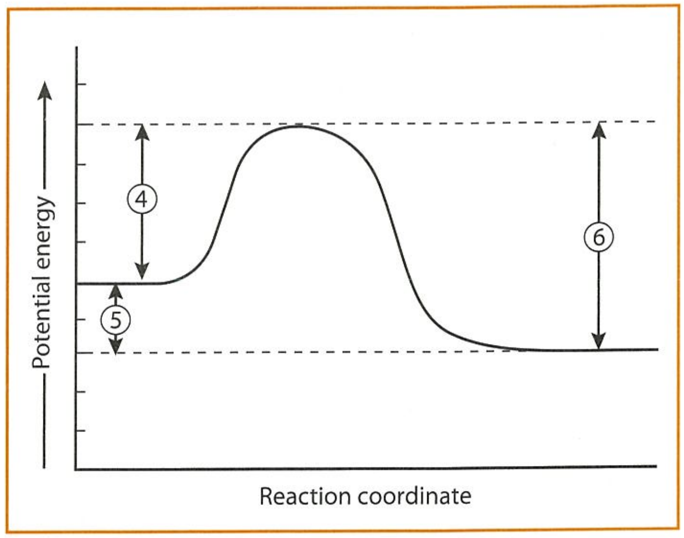


Figure 8-3. Activation energies and heat of reaction

energy of the reactants. Line 2 extends from the origin of the *y*-axis to the activated complex and represents the potential energy of the complex. Line 3 represents the potential energy of the products. Any line that begins at the origin of the *y*-axis of such a graph is a measure of potential energy.

Figure 8-3 shows the same potential energy diagram, but the lines represent the differences between the potential energies of different substances. Line 4 represents the difference in potential energy between the reactants and the activated complex. The amount of energy needed to form the activated complex from the reactants is called the **activation energy.** Because the diagram is read from left to right, it is also called the activation energy of the forward reaction.

Line 5 represents the difference between the potential energy of the reactants and the potential energy of the products. The difference between the potential energy of the reactants and products is called the <u>heat of reaction</u> and is represented by ΔH.

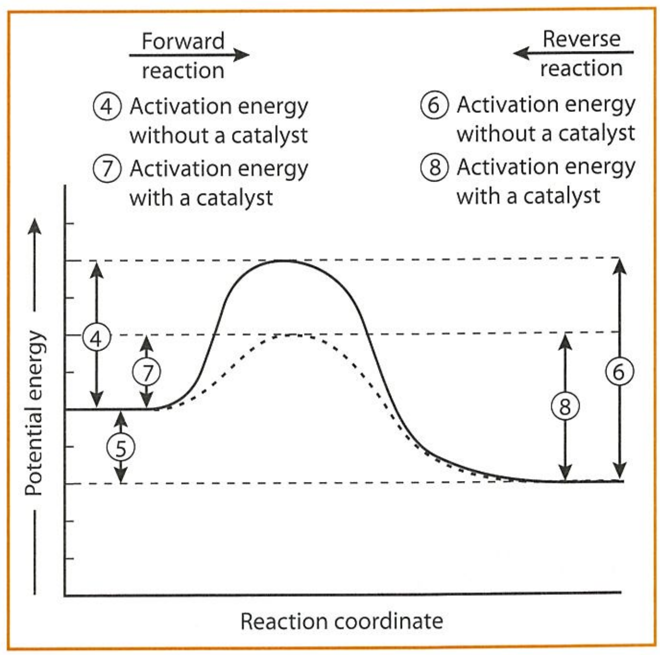


Figure 8-4. Effect of a catalyst on activation energy: Note that the heat of reaction is unchanged with the addition of a catalyst, but the activation energy is decreased.

Line 6 represents the difference between the potential energies of the products and the activated complex. How can this be useful? Some reactions can proceed, not only in the forward direction, but also in the reverse, or right to left on the diagram. In this case, the line represents the activation energy of the reverse reaction.

Figure 8-4 is similar to the previous diagrams, but a new line has been added. This new line represents the effect of a catalyst on the reaction.

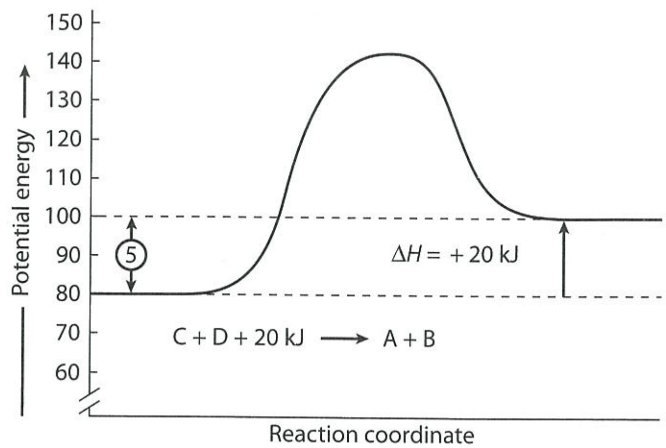


Figure 8-5. Potential energy diagram of an endothermic reaction: Note that there is a gain in potential energy from reactants to products.

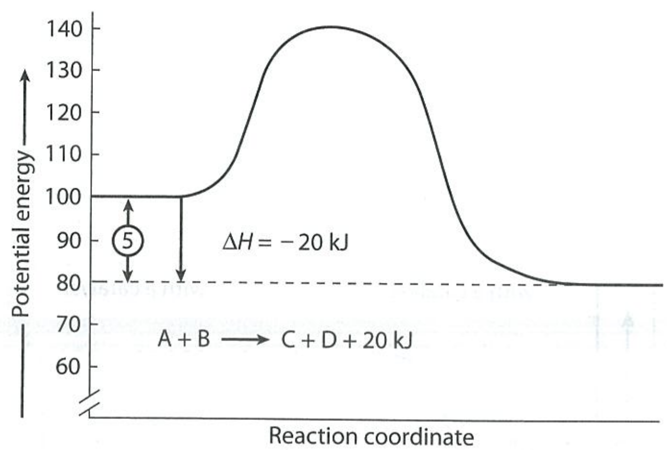


Figure 8-6. Potential energy diagram of an exothermic reaction: Note that there is a loss of potential energy from reactants to products.

Note that the only difference between a reaction with a catalyst and a reaction without a catalyst is the activation energy. Most catalysts speed up a reaction by providing a new pathway with a lower activation energy. The activation energy of the reverse reaction is also lowered. Note that ΔH remains unchanged.

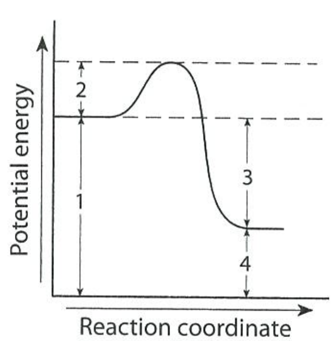
As the reaction proceeds toward the product side, two outcomes are possible.

1. As the activated complex changes to become the product, it will lose energy. If the product has more potential energy than the reactants, the reaction will be endothermic. Because more energy was absorbed to form the activated complex than was released to form the product, there was a net gain of energy. Because there has been a gain in energy, the heat of reaction has a positive value ($\Delta H = +$), as shown in Figure 8-5.
2. If the product is lower on the vertical axis than the reactants, all of the energy that was absorbed to form the activated complex is recovered, plus the difference between the potential energy of the reactants and products. This represents a loss of potential energy compared to the reactants, indicating a release of energy and an exothermic reaction. In this case the heat of reaction has a negative value ($\Delta H = -$), as shown in Figure 8-6.

Review Questions — Set 8.2

Base your answers to Questions 11 and 12 on the diagram below, which represents the reaction:

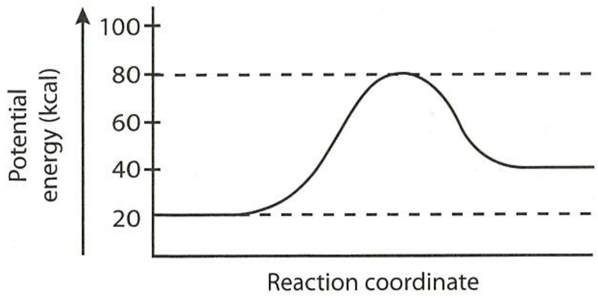
$A + B \rightarrow C + \text{energy}$



11. Which statement correctly describes this reaction?
    (1) It is endothermic and energy is absorbed.
    (2) It is endothermic and energy is released.
    (3) It is exothermic and energy is absorbed.
    (4) It is exothermic and energy is released.

12. Which numbered interval will change with the addition of a catalyst to the system?
    (1) 1
    (2) 2
    (3) 3
    (4) 4

13. A potential energy diagram of a chemical system is shown below.



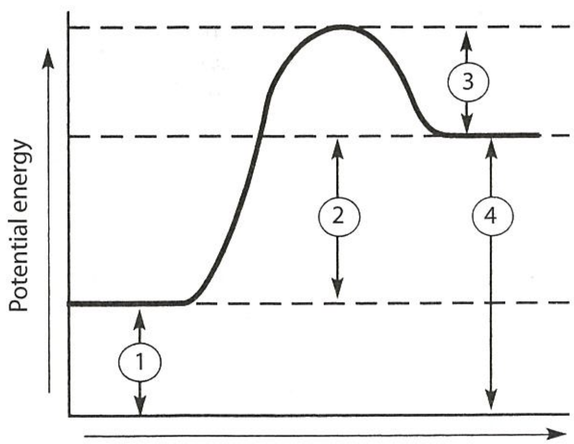
What is the difference between the potential energy of the reactants and the potential energy of the products?

(1) 20. kcal
(2) 40. kcal
(3) 60. kcal
(4) 80. kcal

14. Consider the reaction for which $\Delta H = +$ 33 kJ/mol.

$$N_2(g) + 2O_2(g) \rightleftarrows 2NO_2(g)$$

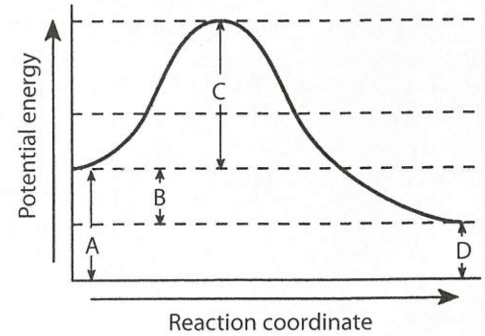
The potential energy diagram of the reaction is shown below.



Which arrow represents the heat of reaction for the reverse reaction?

(1) 1
(2) 2
(3) 3
(4) 4

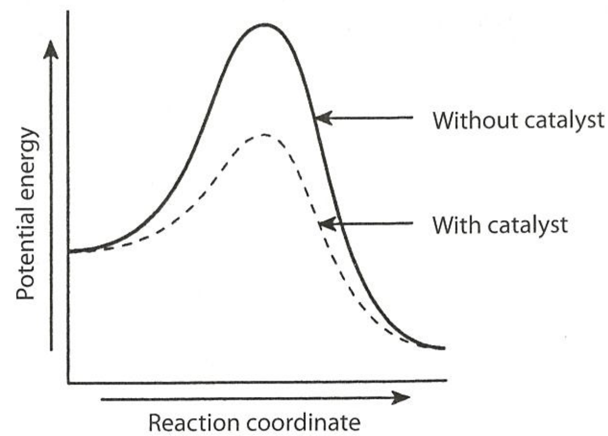
15. The potential energy diagram of a chemical reaction is shown below.



Which letter in the diagram represents the heat of reaction?

(1) A (2) B (3) C (4) D

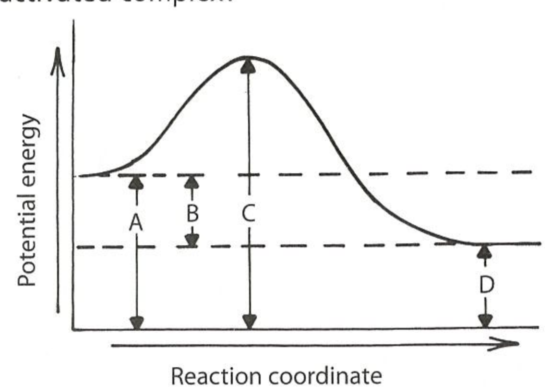
16. A potential energy diagram is shown below.



Which reaction would have the lowest activation energy?

(1) the forward catalyzed reaction
(2) the forward uncatalyzed reaction
(3) the reverse catalyzed reaction
(4) the reverse uncatalyzed reaction

17. In the potential energy diagram below, which arrow represents the potential energy of the activated complex?



(1) A (2) B (3) C (4) D

Figure 8-7. Equilibrium in a closed container: In the open container, the liquid evaporates at a constant rate until it is all evaporated. In the closed container, evaporation continues, but it is balanced by condensation.

Equilibrium

Each of the potential energy diagrams shown depicts a reaction that is proceeding from left to right, that is, in the forward direction. The reactants first collide to form the activated complex, and then they form products. Can the reverse ever happen? Can the products collide to form the activated complex and become reactants? Not only can a reverse reaction occur, but both the forward and reverse reactions can occur at the same time. When both the forward and reverse reactions occur at the same rate, the condition is called **equilibrium.** An equation representing equilibrium uses a double arrow ($\rightleftarrows$) instead of a single arrow ($\rightarrow$) to show that reactions are proceeding in both directions.

Equilibrium is a state of balance between the rates of two opposite processes that are taking place at the same rate. Equilibrium can only occur in a system in which neither reactants nor products can leave the system.

Equilibrium is a dynamic process, that is, it implies motion in which the interactions of reactant particles are balanced by the interactions of product particles. Equilibrium is an important concept because many chemical reactions and physical processes are reversible, that is, they are able to proceed in both directions.

It must be emphasized that the quantities of reactants and products are not necessarily equal at equilibrium. Indeed, it would be unusual if they were equal. It is the rates of the two reactions, forward and reverse, that are equal. As shown in Figure 8-7, in a closed container half-filled with water, there is equilibrium between the evaporating liquid water and the condensing water vapor. Obviously there is far more liquid water than water vapor. At equilibrium, it is the rate of evaporation and condensation that are equal.

Physical Equilibrium

Although many examples of equilibrium involve chemical reactions, equilibrium also occurs during physical processes such as change of state (phase) or dissolving.

Phase Equilibrium Phase equilibrium can exist between the solid and liquid phases of a substance. We define this condition as the melting point of the solid phase or the freezing point of the liquid phase. At 0°C in a closed container, both water and ice exist at the same time. Some of the ice is melting, and some of the water is freezing. An equation can be written to show that both the forward and reverse processes are taking place. The double-pointed arrow shows that both reactions are taking place at the same rate.

$$H_2O(s) \rightleftarrows H_2O(\ell)$$

There may not be the same amounts of solid and liquid present, but the rate of melting will be equal to the rate of freezing.

A similar relationship can exist in a closed container for liquid-gas equilibrium, where the rate of evaporation is equal to the rate of condensation.

$$H_2O(\ell) \rightleftarrows H_2O(g)$$

Solution Equilibrium Solids dissolved in liquids exist in equilibrium in a saturated solution. When solid sugar is first placed into water, the sugar dissolves, but no sugar is recrystallizing. When all of the sugar dissolves that can be dissolved at that temperature, the solution is saturated. If additional solid sugar is placed into the saturated solution, the process of dissolving will continue, but it is exactly balanced by the process of recrystallization. When the rate of dissolving and recrystallizing are equal, equilibrium exists, and the solution is saturated.

$$C_{12}H_{22}O_{11}(s) \rightleftarrows C_{12}H_{22}O_{11}(aq)$$

Equilibrium may also be attained in a closed system between a gas dissolved in a liquid and the undissolved gas. In a closed bottle or can of soda there is equilibrium between the gaseous and dissolved state of carbon dioxide.

$$CO_2(g) \rightleftarrows CO_2(aq)$$

In both of these cases, the equilibrium can be disturbed by a change in temperature. If the temperature is raised, a solid generally becomes more soluble in a liquid. For a short time the rate of dissolving exceeds the rate of recrystallization. As more solid is placed into solution, the rate of recrystallization increases until a new equilibrium is reached.

The opposite is true when the temperature of a solution of a gas in a liquid is raised. As the temperature increases, the rate of the gas escaping from the liquid increases, while the rate at which gas particles dissolve decreases. This decreases the solubility of the gas in the liquid. As the temperature rises, the solubility of all gases decreases in a liquid.

Chemical Equilibrium

When reactants are first mixed and no products are present, only the forward reaction can occur. Examine what happens in the chemical reaction between water vapor and methane.

$$CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$$

As time progresses, the concentrations of $CH_4(g)$ and $H_2O(g)$ decrease, causing the forward reaction to slow, while the concentrations of $H_2(g)$ and $CO(g)$ increase, causing the rate of the reverse reaction to increase.

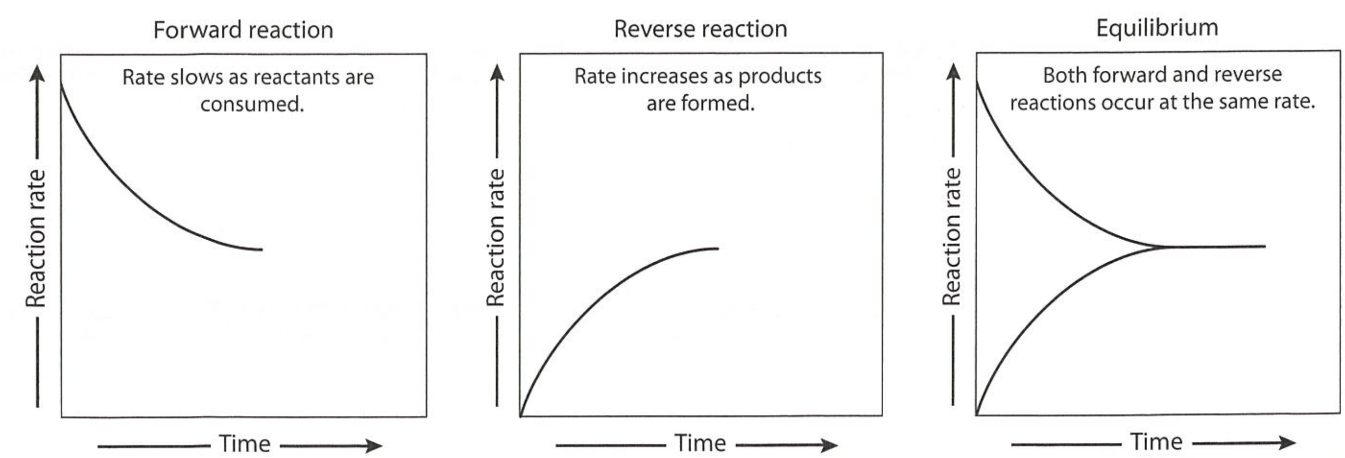


Figure 8-8. Chemical equilibrium: Equilibrium occurs when opposite reactions occur at the same rate.

This slowing of the forward reaction and speeding up of the reverse reaction continues until the rates of the two reactions become the same. At this point, chemical equilibrium exists. Figure 8-8 summarizes this process.

As with physical equilibrium, it is important to remember that no reactant or product can leave the system. If a precipitate is formed or a gas is formed in a system that is not closed, equilibrium will not be reached. The effect of any change in equilibrium is explained by Le Châtelier's principle.

Le Châtelier's Principle

Any change in temperature, concentration or pressure on an equilibrium system is called a **stress. Le Châtelier's principle** explains how a system at equilibrium responds to relieve any stress on the system. Examined below are several types of stress and how equilibrium shifts to relieve them.

Concentration Changes Again consider the reaction represented by the following equation.

$$CH_4(g) + H_2O(g) \rightleftarrows 3H_2(g) + CO(g)$$

If the stress is the addition of more methane (CH_4), the rate of the forward reaction will increase and more products will form. If the concentration of one substance is increased, the reaction that reduces the amount of the added substance is favored. In this example, the system is said to shift to the right as more product is formed. As more product forms, the rate of the reverse reaction also increases until once again the rates of the forward and reverse reactions are equal.

If the concentration of methane is reduced, the rate of the forward reaction decreases. When the concentration of a substance decreases, the reaction that produces that substance is favored. Initially the reverse reaction will take place faster than the forward reaction, and the system is said to be shifting to the left, or toward the reactant side.

Tables 8-2 and 8-3 show how a change in concentration affects equilibrium. A plus sign (+) means the concentration increases, and a minus sign (−) means that the concentration decreases. An increase causes the system to shift away from the stress, causing the stress to be lessened. In this example, the addition of NH_3 causes the system to shift to the right.

Table 8-2. Effect of Increasing the Concentration of NH_3

$4NH_3(g)$	$+ \ 5O_2(g)$	$\rightleftarrows$	$4NO(g)$	$+ \ 6H_2O(g)$	+ heat
Stress	Effect	System shift	Effect	Effect	Effect
$+$**NH_3**	$-O_2$	$\rightarrow$	+NO	$+H_2O$	+ heat
Increase	Decrease	Away from stress	Increase	Increase	Increase

Table 8-3. Effect of Decreasing the Concentration of NH_3

$4NH_3(g)$	$+ \ 5O_2(g)$	$\rightleftarrows$	$4NO(g)$	$+ \ 6H_2O(g)$	+ heat
Stress	Effect	System shift	Effect	Effect	Effect
$-$**NH_3**	$+O_2$	$\leftarrow$	−NO	$-H_2O$	−heat
Decrease	Increase	Toward the stress	Decrease	Decrease	Decrease

A decrease of NH_3 causes the system to move toward the stress, or a shift to the left, replacing some of the lost substance.

Notice that all factors on the same side of the arrow as the stress do the opposite of the stress. For example, as the NH_3 increases, O_2 decreases. All factors on the opposite side of the arrow from the stress increase or decrease in the same way as the stress.

A second consideration about equilibrium is important. While the rates of the forward and reverse reactions are equal, the concentrations of the reactants and products are most likely not equal. Figure 8-9 shows a situation in which carbon dioxide [CO_2(g)] and hydrogen [H_2(g)] are beginning to react to form carbon monoxide [CO(g)] and water [H_2O(g)]. At the beginning of the reaction (t_0) both CO_2 and H_2 are present while there is no CO(g) or H_2O(g). As the reaction proceeds these two reactants [CO_2(g) and H_2(g)] are consumed and their concentrations decrease while the products [CO(g) and H_2O(g)] begin to appear and their concentrations increase (t_1). As time progresses, a point is finally reached (t_2) when the concentrations of both reactants and products no longer change, but remain constant (t_3). This is the second characteristic of a system at equilibrium. The concentrations of reactants and products at equilibrium remain constant.

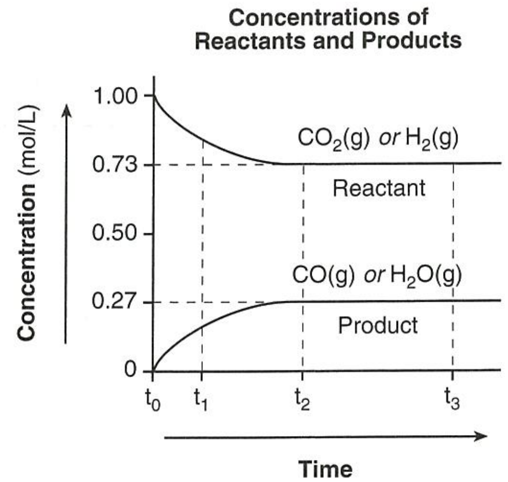


Figure 8-9
$CO_2(g) + H_2(g) \rightleftarrows CO(g) + H_2O(g)$

Important Concepts to Remember:

- The rates of reactions can be changed by changes in concentrations, temperature and the presence of a catalyst.

At Equilibrium:

- The rates of forward and reverse reactions are equal.
- The concentrations of reactants and products are constant, but the amounts of reactant and products are not necessarily equal.

Temperature Changes Consider the production of ammonia:

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g) + \text{heat}$$

Le Châtelier's principle states that a system will undergo changes to reduce a stress. For this reaction, heat can be considered as a product. If the temperature is raised, the rates of both the forward and reverse reactions are increased, but not equally. The reverse reaction is endothermic and will absorb some of the applied heat. The endothermic reverse reaction is favored over the exothermic forward reaction. In other words, more reactants will form when temperature is increased in this reaction. A decrease in temperature will favor the exothermic reaction and, for this reaction, more products will form.

Table 8-4: Effect of Increasing the Heat

$4NH_3(g)$	+ $5O_2(g)$	$\rightleftarrows$	$4NO(g)$	+ $6H_2O(g)$	+ heat
Effect	Effect	System shift	Effect	Effect	Stress
$+NH_3$	$+O_2$	←	−NO	$-H_2O$	+ heat
Increase	Increase	Away from stress	Decrease	Decrease	Increase

Table 8-5: Effect of Decreasing the Heat					
$4NH_3(g)$ +	$5O_2(g)$	$\rightleftarrows$	$4NO(g)$ +	$6H_2O(g)$ +	heat
Effect	Effect	System shift	Effect	Effect	Stress
$-NH_3$	$-O_2$	$\rightarrow$	$+NO$	$+H_2O$	− heat
Decrease	Decrease	Toward the stress	Increase	Increase	Decrease

In the following representation of how a temperature change affects equilibrium, note that the results are seen in a change of concentration of reactants and products, even though the stress is actually a change of energy. Because heat is a product of the reaction, a change in temperature is essentially a change in the concentration of that product.

Pressure Changes Remember that pressure changes do not have an effect on the rate of reaction when only solids and liquids are involved. They do, however, have an effect on gases. An increase in pressure increases the concentration of the gases.

Consider the following system.

$$CO_2(g) \rightleftarrows CO_2(aq)$$

When the pressure increases, the concentration of the gaseous CO_2 increases. Le Châtelier's principle predicts that the system will move away from the added stress—the system will shift to the right, causing more dissolved CO_2. Conversely, when the pressure on this system is reduced, the system shifts to the left, forming more gaseous CO_2. Recall what happens when a soda bottle is opened. The pressure is reduced, and the dissolved gas becomes bubbles of gaseous CO_2.

In the $CO_2(g) \rightleftarrows CO_2(aq)$ reaction, only one side of the equation contains a gaseous molecule. How will a system react when there are gaseous molecules on both sides? An increase in pressure will increase the concentration of gaseous molecules on both reactant and product sides of the equation, but the effects will be unequal. An increase in pressure will favor the reaction toward the side with fewer gas molecules. In the system:

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$$

there are four gaseous molecules on the reactant side and only two on the product side. An increase in pressure will favor the reaction toward the product side, increasing the amount of NH_3 formed.

A decrease in pressure has the opposite effect. A decrease in pressure favors the reaction toward the side with the greater number of gas molecules. Thus, when the pressure is reduced the reaction shifts to the left, forming more $N_2(g)$ and $H_2(g)$ and decreasing the amount of $NH_3(g)$.

One more case remains. What happens if there are the same number of gaseous molecules on both sides? In the equation, $H_2(g) + Cl_2(g) \rightleftarrows 2HCl(g)$, the reactant and product sides each have two gaseous molecules. Where there are the same number of gaseous reactants and product molecules, pressure changes have no effect on the system.

The following points summarize how pressure changes affect the rate of reaction when gases are involved.

- An increase in pressure will favor the reaction toward the side with the fewer number of gas molecules.
- A decrease in pressure will favor the reaction toward the side with the greater number of gas molecules.
- A change in pressure will not affect a system if there are no gas molecules or the same number of gas molecules on both sides.
- A catalyst has no net effect on an equilibrium system.

Effect of a Catalyst The addition of a catalyst changes the rates of both the forward and reverse reactions equally. This is because the catalyst equally lowers the activation energy for both the forward and the reverse reactions. A catalyst may cause equilibrium to be established more quickly but does not change any of the equilibrium concentrations.

Review Questions — Set 8.3

18. Which factors must be equal when a reversible chemical process reaches equilibrium?

(1) mass of the reactants and mass of the products
(2) rate of the forward reaction and rate of the reverse reaction
(3) concentration of the reactants and concentration of the products
(4) activation energy of the forward reaction and activation energy of the reverse reaction

19. A solute is added to water and a portion of the solute remains undissolved. When equilibrium between the dissolved and undissolved solute is reached, the solution must be

(1) dilute
(2) saturated
(3) unsaturated
(4) supersaturated

20. Which description applies to a system in a sealed flask that is half full of water?

(1) Only evaporation occurs, but it eventually stops.
(2) Only condensation occurs, but it eventually stops.
(3) Neither evaporation nor condensation occurs.
(4) Both evaporation and condensation occur.

21. Solution equilibrium always exists in a solution that is

(1) unsaturated
(2) saturated
(3) dilute
(4) concentrated

22. Given the reaction at equilibrium:

$$A(g) + B(g) \rightleftarrows C(g) + D(g)$$

The addition of a catalyst will

(1) shift the equilibrium to the right
(2) shift the equilibrium to the left
(3) increase the rate of forward and reverse reactions equally
(4) have no effect on the forward or reverse reactions

23. If a catalyst is added to a system at equilibrium and the temperature and pressure remain constant, there will be no effect on the

(1) rate of the forward reaction
(2) rate of the reverse reaction
(3) activation energy of the reaction
(4) heat of reaction

24. Consider the equation for the following reaction at equilibrium.

$$X + Y \rightleftarrows 2Z + \text{heat}$$

The concentration of the product could be increased by

(1) adding a catalyst
(2) adding more heat to the system
(3) increasing the concentration of Y
(4) decreasing the concentration of X

25. In a reversible reaction, chemical equilibrium is attained when the
(1) rate of the forward reaction is greater than the rate of the reverse reaction
(2) rate of the reverse reaction is greater than the rate of the forward reaction
(3) concentration of the reactants reaches zero
(4) concentration of the products remains constant

26. Consider the following equation.

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g) + \text{heat}$$

What stress would cause the equilibrium to shift to the left?
(1) increasing the temperature
(2) increasing the pressure
(3) adding $N_2(g)$ to the system
(4) adding $H_2(g)$ to the system

27. Consider the equation for the following reaction at equilibrium.

$$CaSO_4(s) \rightleftarrows Ca^{2+}(aq) + SO_4^{2-}(aq)$$

When Na_2SO_4 is added to the system, how will the equilibrium shift?
(1) The amount of $CaSO_4$ will decrease, and the concentration of $Ca^{2+}(aq)$ will decrease.
(2) The amount of $CaSO_4$ will decrease, and the concentration of $Ca^{2+}(aq)$ will increase.
(3) The amount of $CaSO_4$ will increase, and the concentration of $Ca^{2+}(aq)$ will decrease.
(4) The amount of $CaSO_4$ will increase, and the concentration of $Ca^{2+}(aq)$ will increase.

28. Consider the following equation.

$$Zn(s) + HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

As the concentration of the HCl(aq) decreases at constant temperature, the rate of the forward reaction
(1) decreases
(2) increases
(3) remains the same

29. Consider the following equation.

$$H_2(g) + F_2(g) \rightleftarrows 2HF(g) + \text{heat}$$

Which change will not shift the point of equilibrium?
(1) changing the pressure
(2) changing the temperature
(3) changing the concentration of $H_2(g)$
(4) changing the concentration of HF(g)

30. Consider the following equation.

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

As the pressure increases at constant temperature, the mass of $H_2(g)$
(1) decreases
(2) increases
(3) remains the same

Entropy and Enthalpy

What are the factors that cause chemical and physical changes to occur? There are two fundamental tendencies in nature that help determine whether or not these changes will occur.

Enthalpy

There is a tendency in nature to change to a state of lower energy (enthalpy). Exothermic reactions move toward a lower energy state because some of the energy contained in the reactants is released. The products have less potential energy than do the reactants.

A study of potential energy diagrams for reversible chemical reactions shows that the activation energy for the exothermic direction is less than that for the endothermic direction. Therefore, at any given temperature, the particles in a system are more likely to collide with enough energy to react in the exothermic direction than in the endothermic direction. On the basis of energy change alone, we expect reactions to go in the exothermic direction. This drive toward lower energy is also called a drive toward lower enthalpy.

Entropy

There is a tendency in nature to change to a state of greater randomness or disorder, which refers to the lack of regularity in a system. **Entropy** is a measure of the disorder or randomness of a system. The greater the disorder, the higher the entropy. Figure 8-10 illustrates the concept of increasing entropy as an originally ordered state becomes "messy" or more random.

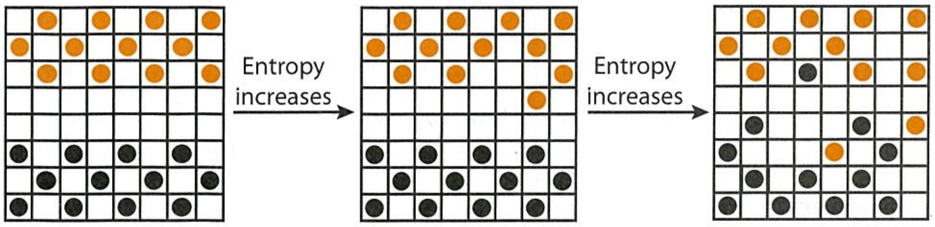


Figure 8-10. Entropy: Entropy is a measure of disorder or randomness.

It is usually necessary for particles to collide in a special way in order to form a more highly organized or regular arrangement. On the other hand, there are many ways in which they can collide to produce more disorder. Therefore, it is to be expected that systems will often go from conditions of greater order (lower entropy) to conditions of greater disorder (higher entropy). On the basis of entropy change alone, we expect reactions to go in the direction of greater entropy.

Examples of entropy change are physical changes from the solid, crystalline phase (great order, low entropy), to the liquid phase (more randomness, higher entropy), to the gaseous phase (maximum randomness, highest entropy). For chemical changes, compounds represent a state of greater order and lower entropy than the free elements of which they are composed.

To identify whether reactants or products have the greater amount of entropy consider:

1. The solid phase has less entropy than the liquid phase, which has less entropy than the gaseous phase.
2. Generally, the side of the equation with the greater number of molecules has the greater amount of entropy.

Review Questions — Set 8.4

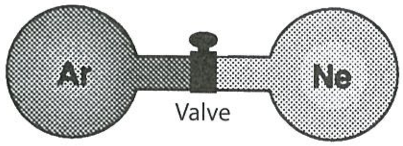
31. Which change in a sample of water is accompanied by the greatest increase in entropy?

(1) $H_2O(\ell)$ at 100°C is changed to $H_2O(g)$ at 200°C
(2) $H_2O(g)$ at 100°C is changed to $H_2O(g)$ at 200°C
(3) $H_2O(s)$ at −100°C is changed to $H_2O(s)$ at 0°C
(4) $H_2O(s)$ at 0°C is changed to $H_2O(\ell)$ at 0°C

32. What occurs when a sample of $CO_2(s)$ changes to $CO_2(g)$?

(1) The gas has greater entropy and less order.
(2) The gas has greater entropy and more order.
(3) The gas has less entropy and less order.
(4) The gas has less entropy and more order.

33. The diagram below shows a system of gases with the valve closed.



As the valve is opened, the entropy of the gaseous system

(1) decreases
(2) increases
(3) remains the same

34. Which series of physical changes represents an entropy increase during each change?

(1) gas → liquid → solid
(2) liquid → gas → solid
(3) solid → gas → solid
(4) solid → liquid → gas

35. Which tendencies favor a spontaneous reaction?

(1) lower energy and decreasing entropy
(2) lower energy and increasing entropy
(3) higher energy and decreasing entropy
(4) higher energy and increasing entropy

36. Consider the following equation.

$$H_2O(\ell) + \text{heat} \rightleftarrows H_2O(g)$$

Which will occur if the temperature of the system is increased?

(1) The average kinetic energy of the system will decrease.
(2) The entropy of the system will increase.
(3) The number of moles of $H_2O(g)$ will decrease.
(4) The number of moles of $H_2O(\ell)$ will increase.

37. As NaCl(*s*) dissolves according to the equation $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$, the entropy of the system

(1) decreases
(2) increases
(3) remains the same

38. Which change results in an increase in entropy?

(1) $H_2O(g) \rightarrow H_2O(\ell)$
(2) $H_2O(s) \rightarrow H_2O(\ell)$
(3) $H_2O(\ell) \rightarrow H_2O(s)$
(4) $H_2O(g) \rightarrow H_2O(s)$

39. A reaction must be spontaneous if its occurrence is

(1) endothermic with an increase in entropy
(2) endothermic with a decrease in entropy
(3) exothermic with an increase in entropy
(4) exothermic with a decrease in entropy

The Equilibrium Expression

The mathematical expression that shows the relationship of reactants and products in a system at equilibrium is called the equilibrium expression. It is a fraction with the concentrations of reactants and products expressed in moles per liter. Each concentration is then raised to the power of its coefficient in a balanced equation. This expression equals a value called the equilibrium constant (K_{eq}), which remains the same for a particular reaction at a specified temperature.

To write an equilibrium expression, follow these steps.

1. Write a balanced equation for the system.
2. Place the products as factors in the numerator of a fraction and the reactants as factors in the denominator.
3. Place a square bracket around each formula. The square bracket means *molar concentration*.
4. Write the coefficient of each substance as the power of its concentration. The resulting expression is the equilibrium expression, which should be set equal to the K_{eq} for that reaction.

SAMPLE PROBLEM

Write the equilibrium expression for the equilibrium system of nitrogen, hydrogen, and ammonia.

SOLUTION: Identify the known and unknown values.

Known	*Unknown*
reactants = N_2, H_2	equilibrium expression = K_{eq}
product = NH_3	

1. Write a balanced equation for the reaction.

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g) + \text{heat}$$

2. Place the products as factors in the numerator of a fraction and the reactants as factors in the denominator.

$$\frac{NH_3}{H_2 \times N_2}$$

3. Place a square bracket around each formula to show the concentration of each.

$$\frac{[NH_3]}{[H_2][N_2]}$$

4. Write the coefficient of each substance as the power of its concentration. This is the equilibrium expression, labeled K_{eq}.

$$K_{eq} = \frac{[NH_3]^2}{[H_2]^3[N_2]}$$

The equilibrium constant is a specific numerical value for a given system at a specified temperature. Changes in concentrations will not cause a change in the value of K_{eq}, nor will the addition of a catalyst. Only a change in temperature will affect the value of K_{eq}.

When the value of K_{eq} is large, the numerator is larger than the denominator, indicating that the products are present in larger concentration than the reactants. Chemists would simply say that the products are favored. If the value is small, the opposite is true, and the reactants are favored.

Practice Questions
for the New York Regents Exam

Directions
Review the Test-Taking Strategies section of this book. Then answer the following questions. Read each question carefully and answer with a correct choice or response.

Part A

1 In order for a chemical reaction to occur, there must always be
(1) an effective collision between reacting particles
(2) a bond that breaks in a reactant particle
(3) reacting particles with a high charge
(4) reacting particles with high kinetic energy

2 As the number of effective collisions between reacting particles increases, the rate of reaction
(1) decreases
(2) increases
(3) remains the same

3 Activation energy is required to initiate
(1) exothermic reactions only
(2) endothermic reactions only
(3) both endothermic and exothermic reactions
(4) neither endothermic nor exothermic reactions

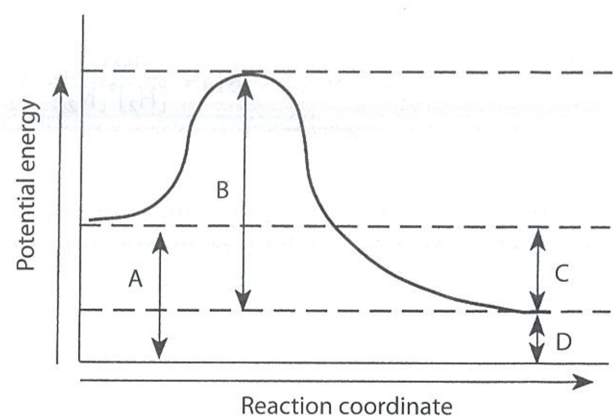
4 For a chemical reaction, the difference between the potential energy of the products and the potential energy of the reactants is equal to the
(1) heat of fusion.
(2) heat of reaction.
(3) activation energy of the forward reaction.
(4) activation energy of the reverse reaction.

5 Which conditions will increase the rate of a chemical reaction?
(1) decreased temperature and decreased concentration of reactants
(2) decreased temperature and increased concentration of reactants
(3) increased temperature and decreased concentration of reactants
(4) increased temperature and increased concentration of reactants

6 What will change when a catalyst is added to a chemical reaction?
(1) activation energy
(2) heat of reaction
(3) potential energy of the reactants
(4) potential energy of the products

7 The energy needed to start a chemical reaction is called
(1) potential energy
(2) kinetic energy
(3) activation energy
(4) ionization energy

Use the potential energy diagram of a chemical reaction shown below to answer questions 8 and 9.

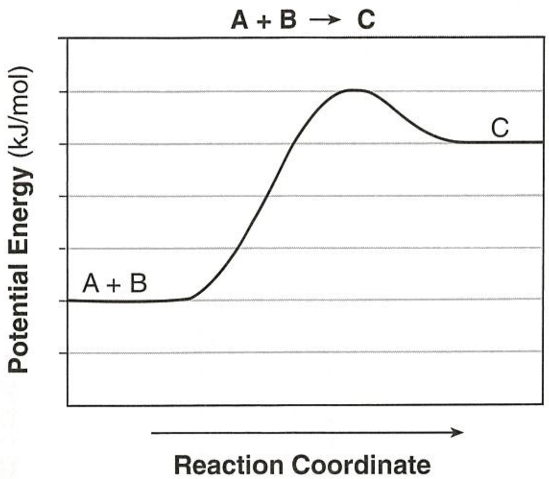


8 Which arrow represents the part of the reaction most likely to be changed by the addition of a catalyst?
(1) A (3) C
(2) B (4) D

9 Which letter represents the activation energy for the reverse reaction?
(1) A (3) C
(2) B (4) D

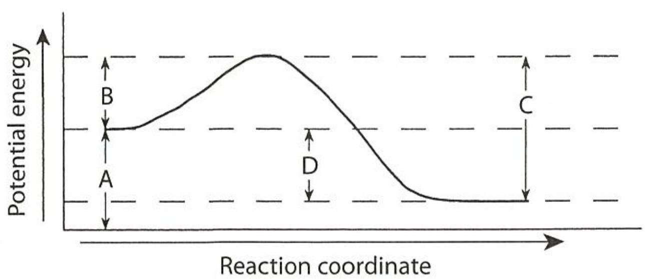
10 Adding a catalyst to a chemical reaction will
(1) lower the activation energy needed
(2) lower the potential energy of the reactants
(3) increase the activation energy
(4) increase the potential energy of the reactants

11 Given the equation and potential energy diagram representing a reaction:



If each interval on the axis labeled "Potential Energy (kJ/mol)" represents 10. kJ/mol, what is the heat of reaction?
(1) +60. kJ/mol
(2) +30. kJ/mol
(3) +20. kJ/mol
(4) +40. kJ/mol

12 The graph below is a potential energy diagram of a compound that is formed from its elements. Which interval represents the heat of reaction?

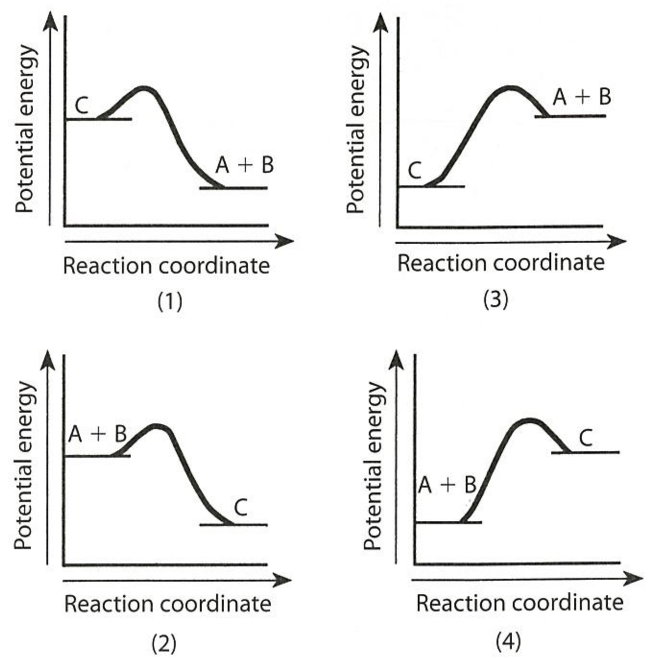


(1) A
(2) B
(3) C
(4) D

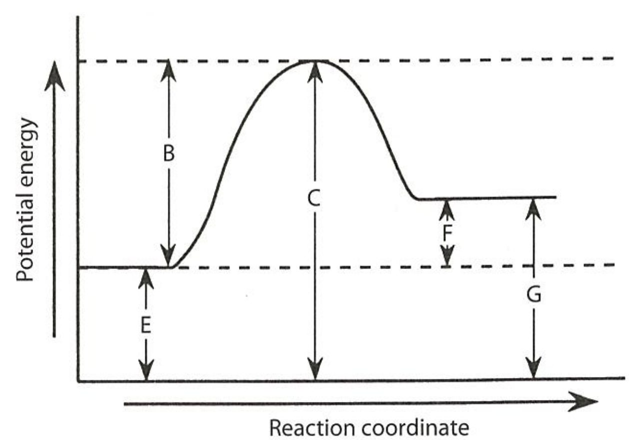
13 For any chemical reaction at equilibrium, the rate of the forward reaction is
(1) less than the rate of the reverse
(2) greater than the rate of the reverse
(3) equal to the rate of the reverse
(4) unrelated to the rate of the reverse

14 Which term is defined as a measure of the disorder of a system?
(1) heat
(2) entropy
(3) kinetic energy
(4) activation energy

15 Which potential energy diagram represents the reaction A + B → C + energy?



16 Given the potential energy diagram below, what does interval B represent?



(1) potential energy of the reactants
(2) potential energy of the products
(3) activation energy
(4) activated complex

17 Solution equilibrium most likely exists in which type of solution?
(1) supersaturated
(2) unsaturated
(3) saturated
(4) dilute

Part B–1

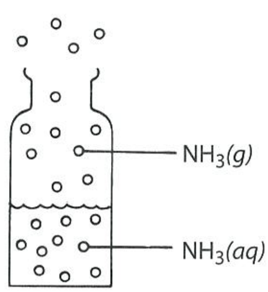
18 A student adds two 50-milligram pieces of Ca(*s*) to water. A reaction takes place according to the following equation.

$$Ca(s) + 2H_2O(\ell) \rightarrow Ca(OH)_2(aq) + H_2(g)$$

Which change could the student have made that would most likely have increased the rate of the reaction?
(1) used 10 10-mg pieces of Ca(*s*)
(2) used one 100-mg piece of Ca(*s*)
(3) decreased the amount of water
(4) decreased the temperature of the water

19 Under which conditions will the forward rate of a chemical reaction most often decrease?
(1) The concentration of the reactants decreases, and the temperature decreases.
(2) The concentration of the reactants decreases, and the temperature increases.
(3) The concentration of the reactants increases, and the temperature decreases.
(4) The concentration of the reactants increases, and the temperature increases.

20 The diagram below shows a bottle containing $NH_3(g)$ dissolved in water. How can the equilibrium $NH_3(g) \rightleftarrows NH_3(aq)$ be reached?



(1) Add more water.
(2) Add more NH_3.
(3) Cool the contents.
(4) Stopper the bottle.

21 A 1-cm^3 cube of sodium reacts more rapidly in water at 25°C than does a 1-cm^3 cube of calcium at 25°C. This difference in rate of reaction is most closely associated with the different
(1) surface area of the metal cubes
(2) nature of the metals
(3) density of the metals
(4) concentration of the metals

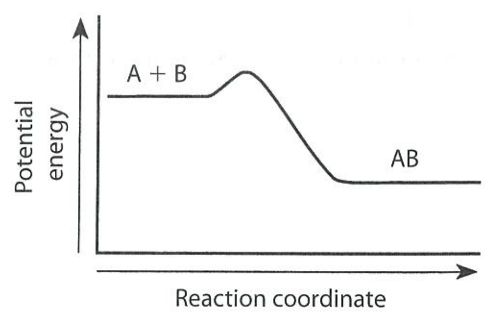
22 At room temperature, which reaction would be expected to have the fastest reaction rate?
(1) $Pb^{2+}(aq) + S^{2-}(aq) \rightarrow PbS(s)$
(2) $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$
(3) $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$
(4) $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

23 Consider the following equation.

$$A(s) + B(aq) \rightarrow C(aq) + D(s)$$

Which change would most likely increase the rate of this reaction?
(1) a decrease in pressure
(2) an increase in pressure
(3) a decrease in temperature
(4) an increase in temperature

24 The potential energy diagram shown below represents the reaction $A + B \rightarrow AB$.



Which statement correctly describes this reaction?
(1) It is endothermic and energy is absorbed.
(2) It is endothermic and energy is released.
(3) It is exothermic and energy is absorbed.
(4) It is exothermic and energy is released.

25 Consider the following equation.

$$AgBr(s) \rightleftarrows Ag^+(aq) + Br^-(aq)$$

Which change occurs when KBr(*s*) is dissolved in the reaction mixture?
(1) The amount of AgBr(*s*) decreases.
(2) The amount of AgBr(*s*) remains the same.
(3) The concentration of $Ag^+(aq)$ decreases.
(4) The concentration of $Ag^+(aq)$ remains the same.

26 Consider the following equation.

$$C(s) + O_2(g) \rightleftarrows CO_2(g) + \text{heat}$$

Which stress on the system will increase the concentration of $CO_2(g)$?
(1) increasing the temperature of the reaction
(2) increasing the concentration of $O_2(g)$
(3) decreasing the pressure on the reaction
(4) decreasing the amount of $C(s)$

27 Which compound is formed from its elements by an exothermic reaction at 298 K and 101.3 kPa?
(1) $C_2H_4(g)$
(2) $HI(g)$
(3) $H_2O(g)$
(4) $NO_2(g)$

28 Which equation represents a change that results in an increase in disorder?
(1) $I_2(s) \rightarrow I_2(g)$
(2) $CO_2(g) \rightarrow CO_2(s)$
(3) $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$
(4) $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$

29 Consider the following change of phase.

$$CO_2(g) \rightarrow CO_2(s)$$

As $CO_2(g)$ changes to $CO_2(s)$, the entropy of the system
(1) decreases
(2) increases
(3) remains the same

30 Which reaction system tends to become less random as reactants form products?
(1) $C(s) + O_2(g) \rightarrow CO_2(g)$
(2) $S(s) + O_2(g) \rightarrow SO_2(g)$
(3) $I_2(s) + Cl_2(g) \rightarrow 2ICl(g)$
(4) $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

31 In which reaction will the point of equilibrium shift to the left when the pressure on the system is increased?
(1) $C(s) + O_2(g) \rightleftarrows CO_2(g)$
(2) $CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$
(3) $2Mg(s) + O_2(g) \rightleftarrows 2MgO(s)$
(4) $2H_2(g) + O_2(g) \rightleftarrows 2H_2O(g)$

32 Consider the following equation.

$$A(g) + B(g) \rightleftarrows C(g) + D(g)$$

Which relationship is an indication that this reaction has reached equilibrium?
(1) The concentration of A equals the concentration of B.
(2) The concentration of C equals the concentration of D.
(3) The concentrations of A, B, C, and D are constant.
(4) The concentrations of A, B, C, and D are equal.

33 Consider the following equation.

$$N_2(g) + O_2(g) \rightleftarrows 2NO(g)$$

If the temperature remains constant and the pressure increases, the number of moles of $NO(g)$ will
(1) decrease
(2) increase
(3) remain the same

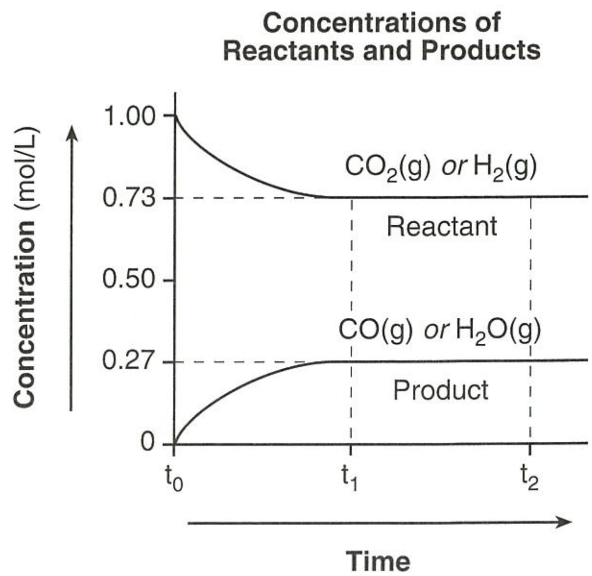
34 Which two fundamental tendencies favor a chemical reaction occurring spontaneously?
(1) toward higher energy and less randomness
(2) toward higher energy and greater randomness
(3) toward lower energy and less randomness
(4) toward lower energy and greater randomness

Parts B–2 and C

Base your answers to questions 35 through 37 on the information below.

At 550°C, 1.00 mole of $CO_2(g)$ and 1.00 mole of $H_2(g)$ are placed in a 1.00-liter reaction vessel. The substances react to form $CO(g)$ and $H_2O(g)$. The balanced equation for this process is shown below along with a graph showing the changes in the concentrations of the reactants and the products.

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$$



35 What effect would increasing the pressure of the system have on the equilibrium concentrations of $CO(g)$ and $H_2O(g)$?

36 Determine the change in concentration of $CO_2(g)$ between time t_0 and time t_1.

37 What can be concluded from the graph about the concentrations of the reactants and the concentrations of the products between time t_1 and t_2?

Base your answers to questions 38 and 39 on the following information.

When soda pop, such as Coke or Pepsi, is manufactured, CO_2 gas is dissolved in it forming a solution.

38 A capped bottle of cola contains $CO_2(g)$ under high pressure. When the cap is removed, how does pressure affect the solubility of the dissolved $CO_2(g)$?

39 A glass of cold cola is left to stand at room temperature for 5 minutes. How does temperature affect the solubility of the $CO_2(g)$?

Base your answers to questions 40 through 43 on the information below.

Several steps are involved in the industrial production of sulfuric acid. One step involves the oxidation of sulfur dioxide gas to form sulfur trioxide gas. In a rigid cylinder with a movable piston, this reaction reaches equilibrium, as represented by the equation below.

$$2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g) + 392 \text{ kJ}$$

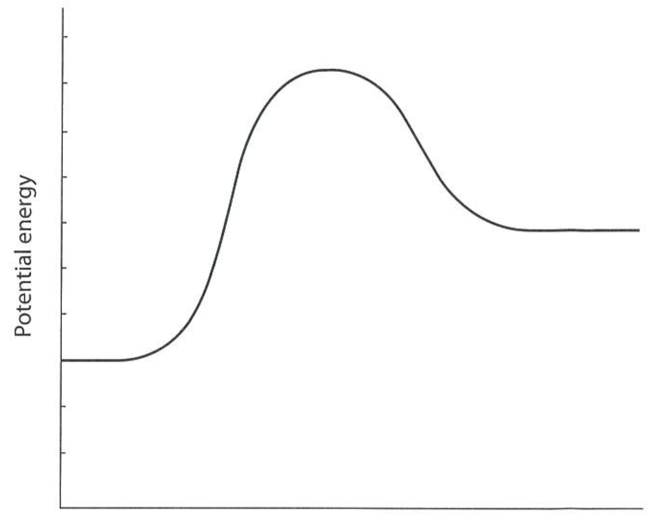
40 Explain, in terms of collision theory, why increasing the pressure of the gases in the cylinder increases the rate of the forward reaction.

41 What happens to the entropy of the system as the reaction progresses in the forward direction.

42 State, in terms of the concentration of $SO_3(g)$, what occurs when more $O_2(g)$ is added to the reaction at equilibrium.

43 State, in terms of concentration of $O_2(g)$, what occurs when the temperature of the system is increased.

Base your answers to questions 44 through 46 on the potential energy diagram shown below.



44 Is the forward reaction endothermic or exothermic?

45 Compare the activation energy of the forward reaction to the activation energy of the reverse reaction.

46 Draw a dotted line on the graph to illustrate the potential energy diagram as it would be altered by the action of a catalyst added to the system.

Base your answers to questions 47 through 49 on the following information.

The Haber process is the main industrial procedure for the production of ammonia today. The process converts atmospheric nitrogen, $N_2(g)$, to ammonia $NH_3(g)$, by a reaction with hydrogen $H_2(g)$. In a closed system, the reaction will reach equilibrium as illustrated in the balanced equation:

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g) + 92.4 \text{ kJ/mol}$$

47 In terms of the concentration of $NH_3(g)$, what would be the effect of increasing the pressure of the system?

48 Describe, in terms of a shift in equilibrium, the effect of an increased temperature on the system.