

CHAPTER 10

Principles of Chemical Thermodynamics and Kinetics



Read This Chapter to Learn About

- Enzymes
- Principles of Bioenergetics
- Thermodynamics: Energy Changes in Chemical Reactions
- Kinetics and Equilibrium: Rate Processes in Chemical Reactions

ENZYMES

The **cell**, the basic unit of life, acts as a biochemical factory, using food to produce energy for all the functions of life, including growth, repair, and reproduction. This work of the cell involves many complex chemical processes, including respiration and energy transfer, in which specific enzymes are used to facilitate the reactions.

Classification of Enzymes

Enzymes are a special category of proteins that serve as biological **catalysts**, speeding up chemical reactions. The enzymes, with names often ending in the suffix *-ase*, are essential to the maintenance of **homeostasis**, or a stable internal environment, within a cell. The maintenance of a stable cellular environment and the functioning of the cell are essential to life.

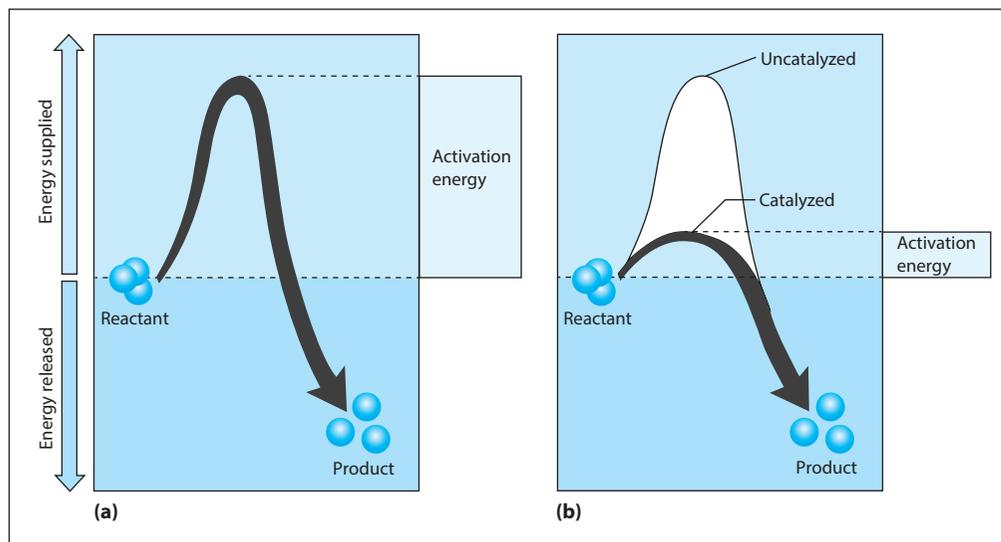


FIGURE 10-1 Lowering activation energy. (a) Activation energy is the amount of energy needed to destabilize chemical bonds. (b) Enzymes serve as catalysts to lower the amount of activation needed to initiate a chemical reaction. *Source:* From George B. Johnson, *The Living World*, 3rd ed., McGraw-Hill, 2003; reproduced with permission of The McGraw-Hill Companies.

Enzymes function by lowering the **activation energy** (see Figure 10-1) required to initiate a chemical reaction, thereby increasing the rate at which the reaction occurs. Enzymes are involved in **catabolic reactions** that break down molecules, as well as in **anabolic reactions** that are involved in biosynthesis. Most enzymatic reactions are reversible. Enzymes are unchanged during a reaction and are recycled and reused.

Enzyme Structure

As stated earlier, enzymes are proteins and, like all proteins, are made up of **amino acids**. Interactions between the component amino acids determine the overall shape of an enzyme, and it is this shape that is critical to an enzyme's ability to catalyze a reaction.

The area on an enzyme where it interacts with another substance, called a **substrate**, is the enzyme's **active site**. Based on its shape, a single enzyme typically only interacts with a single substrate (or single class of substrates); this is known as the enzyme's **specificity**. Any changes to the shape of the active site render the enzyme unable to function. Enzyme kinetics or the rate of biochemical reactions is described by the **Michaelis–Menten mechanism**:



where k_1 , k_{-1} , and k_2 are reaction rate constants.

Enzyme Function

The **induced fit model** is used to explain the mechanism of action for enzyme function seen in Figure 10-2. Once a substrate binds loosely to the active site of an enzyme, a conformational change in shape occurs to cause tight binding between the enzyme and the substrate. This tight binding allows the enzyme to facilitate the reaction. A substrate with the wrong shape cannot initiate the conformational change in the enzyme necessary to catalyze the reaction.

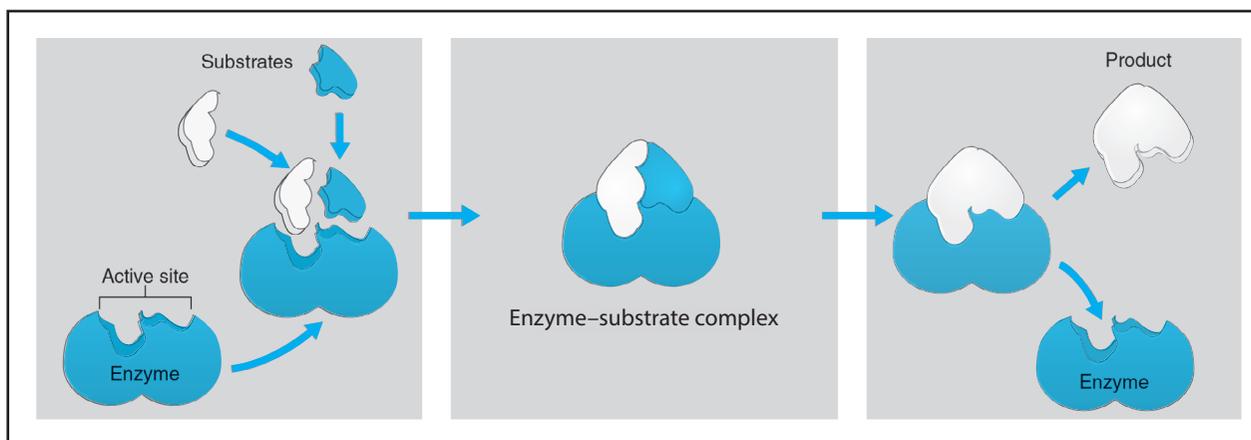


FIGURE 10-2 The induced fit model. Enzymes interact with their substrates to form an enzyme-substrate complex. This complex allows the chemical reaction to occur. *Source:* From George B. Johnson, *The Living World*, 3rd ed., McGraw-Hill, 2003; reproduced with permission of The McGraw-Hill Companies.

Some enzymes require assistance from other substances to work properly. If assistance is needed, the enzyme has binding sites for cofactors or coenzymes. **Cofactors** are various types of ions such as iron and zinc (Fe^{2+} and Zn^{2+}). **Coenzymes** are organic molecules usually derived from vitamins obtained in the diet. For this reason, mineral and vitamin deficiencies can have serious consequences on enzymatic functions.

Factors That Affect Enzyme Function

There are several factors that can influence the activity of a particular enzyme. The first is the **concentration of the substrate** and the **concentration of the enzyme**. Reaction rates stay low when the concentration of the substrate is low, whereas the rates increase when the concentration of the substrate increases. **Temperature** is also a factor that can alter enzyme activity. Each enzyme has an optimal temperature for functioning. In humans, this is typically body temperature (37°C). At lower temperatures, the enzyme is less efficient. Increasing the temperature beyond the optimal point can lead to enzyme **denaturation**, which renders the enzyme useless. Enzymes

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also have an **optimal pH** in which they function best, typically around 7 in humans, although there are exceptions. Extreme changes in pH can also lead to enzyme denaturation. The denaturation of an enzyme is not always reversible.

Control of Enzyme Activity

It is critical to be able to regulate the activity of enzymes in cells to maintain efficiency. This regulation can be carried out in several ways. Feedback, or **allosteric inhibition**, illustrated in Figure 10-3, acts somewhat like a thermostat to regulate enzyme activity. Many enzymes contain allosteric binding sites and require **signal molecules** such as **repressors** and **activators** to function. As the product of a reaction builds up, repressor molecules can bind to the **allosteric site** of the enzyme, causing a change in the shape of the active site. The consequence of this binding is that the substrate can no longer interact with the active site of the enzyme and the activity of the enzyme is temporarily slowed or halted. When the product of the reaction declines, the repressor molecule dissociates from the allosteric site. This allows the active site of the enzyme to resume its normal shape and normal activity. Some allosteric enzymes stay inactive unless activator molecules are present to allow the active site to function.

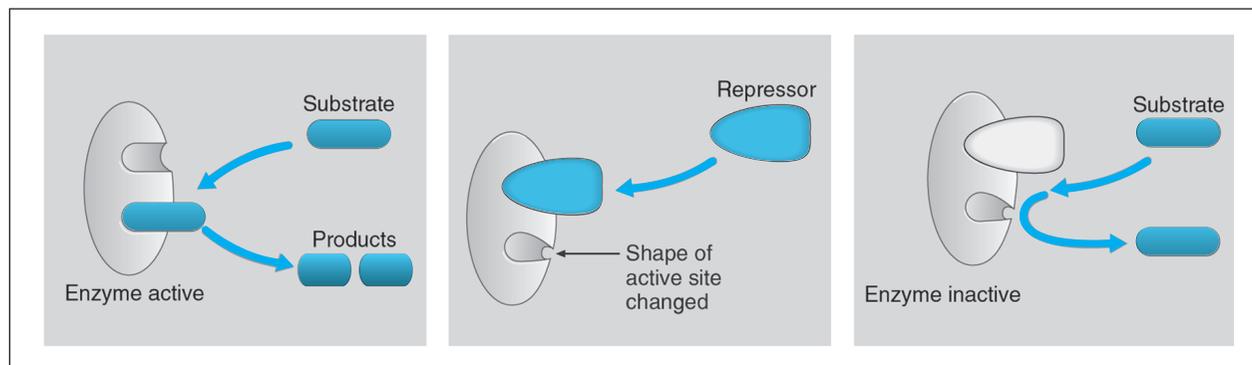


FIGURE 10-3 Allosteric inhibition of an enzyme. Repressors can be used to regulate the activity of an enzyme. *Source:* From George B. Johnson, *The Living World*, 3rd ed., McGraw-Hill, 2003; reproduced with permission of The McGraw-Hill Companies.

Inhibitor molecules also regulate enzyme action. A **competitive inhibitor** is a molecule that resembles the substrate in shape so much that it binds to the active site of the enzyme, thus preventing the substrate from binding. This halts the activity of the enzyme until the competitive inhibitor is removed or is outcompeted by an increasing amount of substrate. **Noncompetitive inhibitors** bind to allosteric sites and change the shape of the active site, thereby decreasing the functioning of the enzyme. Increasing levels of substrate have no effect on noncompetitive inhibitors, but the activity of the enzyme can be restored when the noncompetitive inhibitor is removed.

PRINCIPLES OF BIOENERGETICS

Overview of Metabolism

Living organisms maintain their systems in a dynamic steady state by taking in food. Energy is extracted from food to build complex molecules from simpler ones, and for storage. Collectively, these processes are called **metabolism**, the enzyme-catalyzed transformation of energy and matter.

The metabolic pathways are a sequence of enzymatic reactions that serves to transform energy and matter. In these sequences, the product of one reaction is the substrate for the next. Intermediates are called **metabolites**. There are two aspects of metabolism: catabolism and anabolism. **Catabolism** involves the breakdown of complex molecules into simpler ones. Food molecules are broken down to building block molecules and energy. Some of this energy is stored as **ATP** (adenosine triphosphate). **Anabolism** involves the biosynthesis of complex molecules from the building blocks. The energy needed for this comes from stored ATP, from high-energy hydrogen in the form of **NADPH** (nicotinamide adenine dinucleotide phosphate).

Bioenergetics/Thermodynamics

Metabolism is quantified using principles of thermodynamics: enthalpy, entropy, and free energy. It is the ΔH , ΔS , and ΔG that is considered. **Enthalpy** is the heat content. The ΔH of a reaction can be determined from the sum of the ΔH_f of the products minus the ΔH_f of the reactants. The **entropy** of a system is the degree of randomness. The more random the system, the higher the S . S cannot be measured, but can be obtained from $\Delta G = \Delta H - T\Delta S$ where ΔG , ΔH , and T can be measured. The **free energy** is the amount of useful work that can be obtained from a system at constant temperature, pressure, and volume. The change in free energy ΔG° can be derived from the equilibrium constant K of a reaction, where $\Delta G^\circ = -RT \ln K$. R is the gas constant 8.314 J/mol K and T is temperature in Kelvin. ΔG is a measure of the spontaneity of a reaction. If it is a negative value, the reaction is spontaneous (exothermic), and if it is a positive value, the reaction is endothermic.

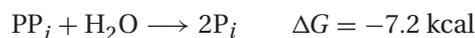
Phosphorylation/ATP

An unfavorable reaction ($+\Delta G$) can be driven forward by coupling it to a favorable one, so that the net ΔG is negative. For instance, the formation of glucose-6-phosphate from glucose and phosphate (P_i) is unfavorable, with a ΔG of +3.3 kcal. If this reaction is coupled to the hydrolysis of ATP to ADP and P_i , which has a $\Delta G = -7.3$ kcal, then glucose can be phosphorylated with a net $\Delta G = -4.0$ kcal.

Phosphorylation Reaction		ΔG
$\text{ATP} + \text{H}_2\text{O}$	$\longrightarrow \text{ADP} + \text{P}_i$	-7.3 kcal
$\text{Glucose} + \text{P}_i$	$\longrightarrow \text{Glucose-6-phosphate}$	$+3.3 \text{ kcal}$
$\text{Glucose} + \text{ATP} + \text{H}_2\text{O}$		$\longrightarrow \text{Glucose-6-phosphate} + \text{ADP}$
		-4.0 kcal

ATP is a high-energy phosphate compound. As such, it has a highly negative ΔG for the hydrolysis of phosphate. All high-energy phosphate compounds have excellent phosphate group transfer potential. ATP transfers phosphate to many sugars and glycerol. The enzymes that catalyze this process are called **hexokinases** and **glycerol kinases**. Kinases are **transfer enzymes**. All high-energy phosphate compounds pass P_i to lower energy acceptors via ATP. The ΔG of ATP hydrolysis, at -7.3 kcal , is intermediate between compounds of high phosphate transfer potential and those with lower phosphate transfer potential. ATP functions as the carrier of phosphate between the catabolic pathways and the anabolic pathways.

Sometimes two terminal phosphates of ATP are removed as pyrophosphate, PP_i , leaving AMP. Energy is obtained by the hydrolysis of pyrophosphate to two phosphates by the enzyme pyrophosphatase as shown:



The AMP reacts with an ATP to form two ADPs by the enzyme adenylate kinase in the reaction:



Other nucleoside triphosphates are used as well. GTP is used in protein synthesis, CTP is used in lipid synthesis, and UTP is used in polysaccharide synthesis. The NDP or NMP formed is re-phosphorylated by ATP in the reaction:



High-energy phosphate compounds act as storage forms of energy. The turnover of ATP is very high. One's body weight in ATP is formed and broken down every 24 hours. Therefore, ATP is not the greatest for energy storage. Creatine phosphate is the storage form of phosphate in humans. During rest, creatine is re-phosphorylated by ATP.

Oxidation–Reduction in Biological Systems

Redox reactions are electron-transfer reactions. **Oxidation** is the loss of electrons while **reduction** is the gain of electrons. The compounds NAD and NADPH are the common reducing agents in metabolic pathways.



The electrons given off are ultimately used to reduce oxygen to water. The ultimate acceptor of electrons derived from food molecules is oxygen. Food molecules transfer electrons to electron carriers such as NAD^+ or FAD. The electrons from the carriers reach oxygen via the electron transport system. Both NAD^+ and FAD are the cofactors for the dehydrogenase enzymes involved in oxidation of food molecules. The breakdown pathways are oxidative, while the anabolic pathways are reductive and use NADPH as the electron donor.

THERMODYNAMICS: ENERGY CHANGES IN CHEMICAL REACTIONS

Thermodynamics is the study of the relationships of enthalpy, entropy (disorder of a system), and free energy. The laws of thermodynamics and certain formulas explain the relationships between free energy, entropy, work, temperature, and equilibrium.

Thermodynamic System and State Functions

A **state function** is a property of a system that depends upon its current condition only. It will not matter how one arrives at that condition. These functions could include ΔE (energy change), ΔU (internal energy change), ΔH (enthalpy change), ΔS (entropy change), or ΔG (Gibbs free energy change). Examples that are not state functions are work (W) and heat (Q).

Zeroth Law of Thermodynamics

The **zeroth law of thermodynamics** explains what happens when three systems are in thermal equilibrium with each other. To summarize, should two systems be separate from each other but both be in thermal equilibrium with a third, then the first two are also in thermal equilibrium with each other. For example, if in a closed system you have three solid metal cubes all at different temperatures and in contact with each other, the heat will flow from the high temperatures to the low temperatures until a thermal equilibrium is reached.

First Law of Thermodynamics

The **first law of thermodynamics** states that the change in the internal energy of a system is given by $\Delta U = Q + W$, where Q = heat and W = work. U is the sum of the kinetic and potential energies. It is a state function; that is, it depends only on the initial and final states, and not on the path between. The **heat Q** is the energy into or out of a

system because of a temperature difference between the system and its surroundings.

Work W is the energy that results when a force moves an object some distance, d .

The enthalpy H is equal to the quantity $U + PV$, where H is also a state function. ΔH is the difference between the initial and final states; at atmospheric pressure, $\Delta H = Q$.

Second Law of Thermodynamics

The **second law of thermodynamics** states that the **total entropy** of a system and its surroundings always increases for a spontaneous process. This law relates spontaneity to entropy. The effect on the surroundings must be taken into account.

For a spontaneous process, ΔS must be $> Q/T$, and at equilibrium, $\Delta S = Q/T = \Delta H/T$.

ENTROPY: A MEASURE OF SYSTEM DISORDER

Entropy, represented by the symbol S , is a measure of the **disorder of a system**. S is also a state function, and ΔS is the difference between the initial and final states.

If ΔS is positive, the process results in more disorder. If ΔS is negative, the process results in more order.

If disorder is increasing, ΔS_{rxn} is positive. Some examples of processes with increasing disorder include more gas produced than used up; a solid converted to a liquid; and a solid dissolved in a solvent.

If order is increasing, ΔS_{rxn} is negative. Some examples of processes that have increasing order include less gas produced than used up; a liquid converted to a solid; and a solid precipitated from a solution.

RELATIVE ENTROPY FOR GAS, LIQUID, AND SOLID STATES

Different phases of matter will have different degrees of freedom and randomness. The more disorder present in a system, the more entropy that system will have. The letter symbol for entropy is S , and because it is a state function, you look at only the final and initial entropy of a system, ΔS .

Because gas molecules are spread out and have a continuous random, straight-line motion with (ideally) no forces of attraction between them, the entropy of gases is far greater than that of liquids. Liquids and solids both have their molecules touching, but the molecules in liquids have more freedom than those of solids. To summarize ΔS for the phases: gas \gg liquid $>$ solid.

Examples of processes in which ΔS is negative might be raking up leaves and placing them in a bag or condensing steam into a liquid. Examples of processes in which ΔS is positive might be the wind blowing those same leaves all over or you spilling a glass of water. One important concept to keep in mind is that the entropy of the universe

is positive. All of the matter in the universe is believed to have been together at one time until the Big Bang occurred. Since then, the universe has been expanding, which explains why processes in the universe favor a positive value for ΔS . Think about the last time you dropped an egg by accident. When was the last time you saw the egg white, yolk, and shell come back together on its own to re-form the egg?

Calorimetry

HEAT

Heat is closely associated with temperature, but they are very different quantities. **Heat**, or **thermal energy**, is a form of energy that depends on a change of temperature and can be converted to work and other forms of energy. The quantity of heat Q gained or lost by a body is related to the temperature difference ΔT by the following equation:

$$Q = mc\Delta T$$

where m is the mass of the body and c is a proportionality constant termed the specific heat capacity. **Specific heat capacity** is the heat needed to raise the temperature of 1 g of a substance by 1°C . It has the symbol c and the units $\text{J/g } ^\circ\text{C}$. Thus, $Q = mc\Delta T$, where ΔT is the difference in the initial and final temperatures. The following table lists the specific heats of some common substances.

TABLE 10-1 The Specific Heat of Some Common Substances

Substance	Specific Heat in $\text{J/g } ^\circ\text{C}$
Al	0.900
Au	0.129
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H_2O	4.184

EXAMPLE: Calculate the heat needed to raise the temperature of 85.3 g of iron from 35.0°C to 275.0°C .

SOLUTION:

- The ΔT is $275.0^\circ\text{C} - 35.0^\circ\text{C} = 240.0^\circ\text{C}$.
- The c for iron is $0.444 \text{ J/g } ^\circ\text{C}$, given from the table.
- Plug the values into the equation and solve for Q :

$$Q = mc\Delta T = (0.444 \text{ J/g } ^\circ\text{C}) (85.3 \text{ g}) (240.0^\circ\text{C}) = 9.09 \times 10^3 \text{ J}$$

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Calorimetry involves the use of an insulated container at room pressure to measure the heat changes that occur during a physical or chemical process. Because the calorimeter is insulated, no heat can leave or enter the system, and all of the heat changes that occur within the calorimeter are zero. In other words, the heat that is given off equals the heat that is gained.

Heat released = heat absorbed

and $\Delta T = \text{higher temperature} - \text{lower temperature}$

The calorimeter itself is ignored in the following calculations.

EXAMPLE: Calculate the final temperature of the system when an 18.4-g sample of aluminum at 215 °C is added to a calorimeter that contains 120.0 g water at 24.5 °C.

SOLUTION:

- ▶ The c for water is 4.184 J/g °C.
- ▶ The c for aluminum is 0.900 J/g °C, given from the table.
- ▶ The ΔT for the water is $x - 24.5$ °C, where x is the final temperature. For water, x is the higher temperature.
- ▶ The ΔT for the aluminum is 215 °C $- x$, where x is the final temperature. For the aluminum, 215 °C is the higher temperature.
- ▶ Plugging into the equation $(mc\Delta T)_{\text{H}_2\text{O}} = (mc\Delta T)_{\text{Al}}$ and solving for x :

$$(120.0 \text{ g})(4.184 \text{ J/g } ^\circ\text{C})(x - 24.5 \text{ } ^\circ\text{C}) = (18.4 \text{ g})(0.900 \text{ J/g } ^\circ\text{C})(215 \text{ } ^\circ\text{C} - x)$$

$$x = 30.6 \text{ } ^\circ\text{C}$$

Heat of transformation is similar to the specific heat capacity, but it accounts for changes in the phase of the body. The specific heat of a body assumes that no change in phase occurs during a temperature change. In order for a substance to change states of matter—that is, from solid to liquid or from liquid to gas—heat energy must be added to or removed from the substance. The amount of heat required to change the phase of 1 kg of a substance is the heat of transformation L . Thus, the total amount of heat Q gained or lost by a substance of mass m during a change between phases is:

$$Q = mL$$

where L is the heat of transformation unique to the substance. The heat of transformation exists in two forms, according to the particular phase transformation:

- ▶ **Heat of fusion.** L_f is the amount of heat energy required to change 1 kg of solid matter to liquid or the amount of energy released when changing 1 kg of liquid matter to solid.
- ▶ **Heat of vaporization.** L_v is the amount of heat energy required to change 1 kg of liquid matter to gas or the amount of energy released when changing 1 kg of gas matter to liquid.

Heat Transfer

There are three mechanisms of heat transfer: conduction, convection, and radiation, each dependent on the state of matter of the object.

Conduction is the method of heat energy transfer that occurs in solids—for example, the warming of a spoon when cream is stirred in coffee. In conduction, heat energy is transferred by collisions between the rapidly moving molecules of the hot region and the slower-moving molecules of the cooler region. A portion of the kinetic energy from the rapidly moving molecules is transferred to the slower-moving molecules, causing an increase in heat energy at the cooler end and a subsequent increase in the flow of heat.

Convection is the method of heat energy transfer that occurs in liquids and gases—for example, the cooling of coffee after cream is poured into it. Convection represents the transfer of heat energy due to the physical motion or flow of the heated substance, carrying heat energy with it to cooler regions of the substance. In contrast to conduction, convection is the primary mechanism of heat transfer in fluids.

Radiation is the method of heat energy transfer that occurs in space, for example, Earth's surface being warmed by the sun. Radiation represents the transfer of heat energy by electromagnetic waves that are emitted by rapidly vibrating, electrically-charged particles. The electromagnetic waves propagate from the heated body or source at the speed of light.

Endothermic and Exothermic Reactions

Heat is an energy that flows into or out of a system due to a difference between the temperature of the system and its surroundings when they are in thermal contact. Heat flows from hotter to cooler areas and has the symbol Q . If heat is added to a system, Q is positive. If heat is removed from a system, Q is negative. The units of heat are joules (J) or calories. One calorie equals 4.184 J.

A reaction from which heat is given off and has a negative Q is called an **exothermic reaction**. A reaction that requires heat to be added and has a positive Q is called an **endothermic reaction**.

ENTHALPY AND STANDARD HEATS OF REACTION AND FORMATION

Enthalpy is a state function and it is used to denote heat changes in a chemical reaction. It is given the symbol H . Because it depends only on the initial and final states of the system, the difference between these states is ΔH . At standard pressure (1 atm), $Q = \Delta H$.

ΔH_f° is called the **enthalpy of formation** of a substance. It denotes the heat that is absorbed or given off when a substance is produced from its elements at standard temperature (25 °C) and pressure (1 atm).

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$\Delta H_{\text{rxn}}^{\circ}$ is called the **enthalpy of reaction**. It denotes the amount of heat that is given off ($-\Delta H$) or absorbed ($+\Delta H$) by a reaction at standard temperature and pressure.

The $\Delta H_{\text{rxn}}^{\circ}$ can be calculated from ΔH_f° values. For the reaction

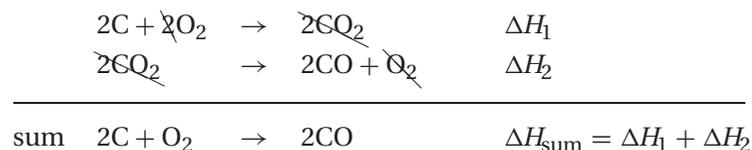


the $\Delta H_{\text{rxn}}^{\circ}$ is

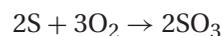
$$\Delta H_{\text{rxn}}^{\circ} = \left[\sum c(\Delta H_f^{\circ}(\text{C})) + d(\Delta H_f^{\circ}(\text{D})) \right] - \left[\sum a(\Delta H_f^{\circ}(\text{A})) + b(\Delta H_f^{\circ}(\text{B})) \right]$$

HESS'S LAW OF HEAT SUMMATION

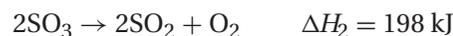
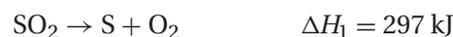
Some reactions are the sum of individual reaction steps. To sum reactions, any compound that shows up on the left side of one equation and on the right side of another equation cancels out. **Hess's law** states that the sum of the ΔH s for each individual equation sum to the ΔH_{rxn} for the net equation.



EXAMPLE: Determine the ΔH of the following reaction:

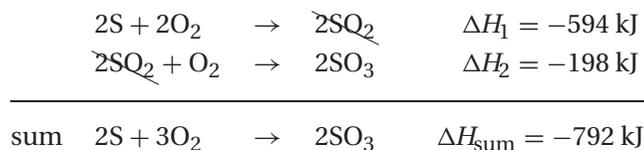


given these reactions and their ΔH s



SOLUTION:

- ▶ First, reverse the first equation and reverse the sign of ΔH_1 .
- ▶ Next, double the first equation and double the ΔH_1 .
- ▶ Then, reverse the second equation and reverse the sign of ΔH_2 .



Bond Dissociation Energy

If the equation is doubled, then the $\Delta H_{\text{rxn}}^{\circ}$ doubles as well.

The ΔH_f° of a compound can be calculated using bond dissociation energies, found in the following table. The formula is:

$$\Delta H_f^\circ = \sum \text{BE of bonds broken} - \sum \text{BE of bonds formed}$$

where BE is the bond energy per mole of bonds.

TABLE 10-2 Dissociation Energies of Selected Single Bonds in kJ/mole

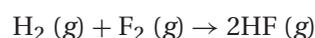
	H	C	N	O	S	F	Cl	Br	I
H	432								
C	411	346							
N	386	305	167						
O	459	358	201	142					
S	363	272			226				
F	565	485	283	190	284	155			
Cl	428	327	313	218	255	249	240		
Br	362	285		201	217	249	216	190	
I	295	213		201		278	208	175	149

Data from Huheey, J. E., Keiter, E. A., and Keiter, R. L., *Inorganic Chemistry*, 4th ed. New York: Harper Collins, 1993; pp. A21–A34.

EXAMPLE: Determine the ΔH_f° of HF using bond dissociation energies.

SOLUTION:

- First write the equation for the formation of HF from its elements:



- For H_2 , the BE = 432 kJ/mole.
- For F_2 , the BE = 155 kJ/mole.
- For HF, the BE = 565 kJ/mole.
- Substitute the values into the equation and solve for ΔH_f° :

$$\begin{aligned} \Delta H_f^\circ &= [(1 \text{ mole H}_2)(432 \text{ kJ/mole}) + (1 \text{ mole F}_2)(155 \text{ kJ/mole})] \\ &\quad - [(2 \text{ mole HF})(565 \text{ kJ/mole})] = -544 \text{ kJ} \end{aligned}$$

Free Energy

Free energy has the symbol G and is defined as $H - TS$. One can predict the spontaneity of a process from the sign of $\Delta G_{\text{rxn}}^\circ$. Free energy is useful because it eliminates the need to worry about the surroundings.

SPONTANEOUS ENERGY

The equation used is $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. When ΔG° is negative, the reaction is spontaneous as written. When ΔG° is positive, the reaction is spontaneous in the opposite direction.

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The maximum work for a spontaneous reaction is equivalent to ΔG . The free energy change is the maximum energy available to do useful work.

THE RELATIONSHIP BETWEEN THE EQUILIBRIUM CONSTANT K AND ΔG

When not at equilibrium, $\Delta G = \Delta G^\circ + RT \ln Q$, where Q is the reaction quotient. Therefore, because $\Delta G = 0$ at equilibrium, $\Delta G^\circ = -RT \ln K$.

EXAMPLE: Calculate K for a reaction for which $\Delta G^\circ = -13.6$ kilojoules (kJ)

SOLUTION:

$$\ln K = \frac{-13,600 \text{ J}}{(-8.314 \text{ J/mol K})(298.2 \text{ K})} = 5.49$$

$$K = e^{5.49} = 242 \quad \text{large } K, \text{ spontaneous reaction}$$

ΔG AND TEMPERATURE

Because $\Delta H^\circ - T\Delta S^\circ = \Delta G^\circ$, the signs of each variable determine the sign of ΔG° . If both ΔH° and ΔS° are positive, ΔG° is negative at high temperatures. If both ΔH° and ΔS° are negative, ΔG° is negative at low temperatures. If ΔH° is negative and ΔS° is positive, ΔG° is always negative. The last case is if ΔH° is positive and ΔS° is negative; in this case, ΔG° is always positive.

EXAMPLE: Estimate the temperature above which a certain reaction becomes spontaneous, if $\Delta H = 178.3$ kJ and $\Delta S = 159$ J/K.

SOLUTION:

- ▶ At the point between spontaneity and nonspontaneity, at equilibrium, $\Delta G^\circ = 0$
- ▶ Plug in the values into $T = \Delta H^\circ / \Delta S^\circ$.

$$T = 178,300 \text{ J} / 159 \text{ J/K} = 1121 \text{ K}$$

Thermal Expansion

Thermal expansion is a physical phenomenon in which increases in temperature can cause substances in the solid, liquid, and gaseous states to expand.

LINEAR EXPANSION OF SOLIDS

A solid subjected to an increase in temperature ΔT experiences an increase in length ΔL that is proportional to the original length L_o of the solid. The relation for the linear expansion of solids is:

$$\Delta L = \alpha L_o \Delta T$$

where the proportionality constant α is the coefficient of linear expansion and is expressed in units of inverse temperature.

EXAMPLE: A metal cylindrical rod of length $L = 4.0$ meters (m) is heated from 25°C to 225°C . Given a coefficient of linear expansion of $11 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, determine the change in length following expansion.

SOLUTION: The equation needed to solve this problem is:

$$\Delta L = \alpha L_o \Delta T = (11 \times 10^{-6} \text{ }^\circ\text{C}^{-1}) (4.0 \text{ m}) (225^\circ\text{C} - 25^\circ\text{C}) = 8.8 \text{ mm}$$

VOLUMETRIC EXPANSION OF LIQUIDS

A liquid subjected to an increase in temperature ΔT experiences an increase in volume ΔV that is proportional to the original volume V_o of the liquid. The relation for the volumetric expansion of liquids is:

$$\Delta V = \beta V_o \Delta T$$

where the proportionality constant β is the coefficient of volumetric expansion and is equal to 3α . As is the case for α , the units of β are inverse temperature.

VOLUMETRIC EXPANSION OF GASES

The volumetric expansion of gases can be summarized by two important gas laws: Charles's law and Boyle's law, which can be combined in the ideal gas law.

Charles's law states that at constant pressure P , the volume V occupied by a given mass of gas is directly proportional to the absolute temperature T by:

$$V = kT \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$P = \text{constant}$ and k is a proportionality constant.

Boyle's law states that at constant temperature, the volume V occupied by a given mass of gas is inversely proportional to the pressure P exerted on it:

$$PV = k \quad \text{or} \quad P_1 V_1 = P_2 V_2$$

$T = \text{constant}$ and k is a proportionality constant.

The **ideal gas law** combines the relations from Charles's law and Boyle's law to yield:

$$PV = nRT \quad \text{or} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

where R is the universal gas constant ($R = 0.082 \text{ L atm/mol K}$) and n is the number of moles.

Heats of Vaporization and Fusion

The equation for heat given previously cannot be used for a phase change, because there is no temperature difference during a phase change. The temperature remains

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the same during the freezing/melting process or during the boiling/condensation process. So for an equation that denotes a phase change, such as:



the heat change is the heat needed to convert 1 mole of solid water to 1 mole of liquid water at 0 °C, and is called the **heat of fusion**, ΔH_{fus} .

For the boiling process,



The heat change is the heat needed to convert 1 mole of liquid water to 1 mole of water vapor at 100.0°C, and is called the **heat of vaporization**, ΔH_{vap} .

The preceding can be summarized in the following table:

TABLE 10-3 Summary of Phase Transformations

Phase Transformation	Descriptive Term	Temperature Point	Heat of Transformation
Solid state → Liquid state	Melting	Melting point	Heat of fusion
Liquid state → Solid state	Freezing	Melting point	Heat of fusion
Liquid state → Gas state	Boiling	Boiling point	Heat of vaporization
Gas state → Liquid state	Condensation	Boiling point	Heat of vaporization

Phase Diagrams

Phase changes occur due to a change in temperature, pressure, or both. The most common phases are solid, liquid, and gas. The names of the phase changes are as follows:

TABLE 10-4 Summary of Phase-to-Phase Changes

Solid to liquid	Melting
Solid to gas	Sublimation
Liquid to solid	Freezing
Liquid to gas	Evaporation
Gas to liquid	Condensation
Gas to solid	Deposition

A **phase diagram** shows the different phases that a substance is in over a range of temperatures and pressures. A simple phase diagram is shown in Figure 10-4.

The lines in Figure 10-4 represent the boundaries between the phases. Each point on a line represents a certain temperature and pressure for that phase transition. The solid–liquid boundary line extends indefinitely, but the liquid–gas boundary ends at the point C, which is called the **critical point**, and it represents the beginning of the supercritical fluid phase. At all temperatures and pressures beyond those at point C, the substance is in a phase that is in between liquid and gas called **supercritical fluid**.

Point T is called the **triple point**. At this pressure and temperature, all three phases coexist in an equilibrium mixture. This means that the actual number of molecules

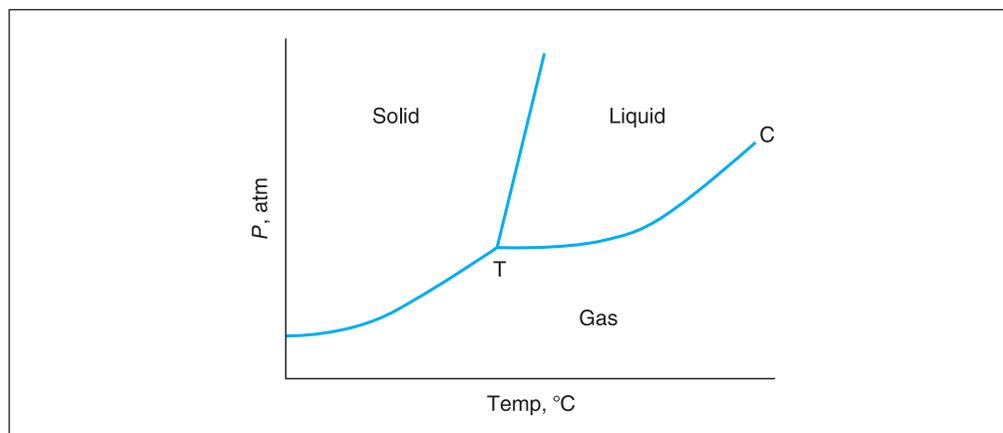


FIGURE 10-4 A typical pressure–temperature diagram.

in each phase remains the same, but the individual molecules are changing their phase.

The boiling and freezing points at 1 atmosphere (atm) pressure are called the **normal boiling point** and the **normal freezing point**. To determine these values, find the temperature that corresponds to 1 atm pressure on the liquid–gas boundary and on the solid–liquid boundary.

The **density** of a substance increases with pressure. Therefore, the relative densities of the phases can be determined by following the phases as the pressure is increased. The phase that exists at the highest pressures is the densest phase. For water, the densest phase is the liquid phase. For most other substances, the solid phase is the densest phase.

KINETICS AND EQUILIBRIUM: RATE PROCESSES IN CHEMICAL REACTIONS

Kinetics is the study of how fast reactions occur; this is called the **reaction rate**. Reaction rates are dependent on the temperature at which the reaction is taking place, on the concentrations of the reactants, and on whether a catalyst is present.

Reaction Rates

Reaction rates are measured experimentally. If the reactant is colored, its absorbance can be followed. At the beginning of the reaction, the absorbance is at a maximum, and it decreases as the reactant disappears (turns into product; see Figure 10-5).

The rate equals the change in concentration with time. The rate is fastest at the beginning of the reaction. An **instantaneous rate** is the change in the concentration of the reactant divided by the change in time, or:

$$\Delta[\text{reactant}]/\Delta t$$

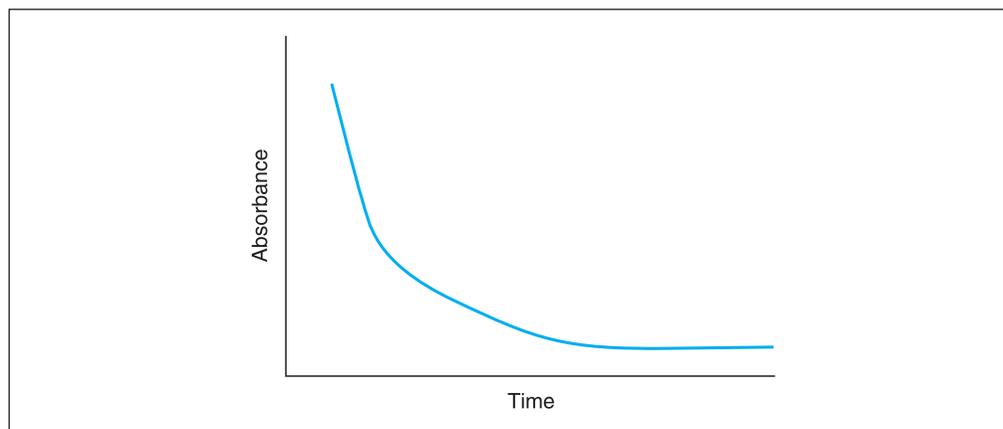


FIGURE 10-5 Reaction rate.

when the change in time, or Δt , is a very small increment of time. This is seen as the tangent to the curve, at any point. The tangent has the steepest slope at the beginning of the reaction (fastest rate), and the flattest slope at the end of the reaction (slowest rate). So the reaction slows with time.

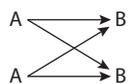
FACTORS THAT INFLUENCE REACTION RATE

The rate at which reactants become products can be manipulated via a number of methods. By no means should you confuse these methods for obtaining more products with the methods for shifting an equilibrium to obtain more product. Two conditions that are needed for a reaction to occur are (1) the reactants' molecules need to collide, and (2) they must do so effectively.

Concentration of Reactants. In order to make more products, reactants need to be in contact with each other. Increasing the concentration of the reactants increases the frequency and likelihood that this process will occur. Consider the following situation. When less A and B are present, their likelihood of collision is low:



But if you double the number of A and B, you see that there are more possibilities:

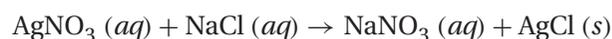


Temperature. An increase in temperature will increase the average kinetic energy of the molecules. With more kinetic energy, the molecules will have a greater velocity according to the equation $KE = \frac{1}{2}mv^2$. If the molecules collide with more kinetic energy, their collisions will be more effective. Therefore, with an increase in kinetic energy, the rate of reaction increases as well.

Activation Energy. Energy, no matter its quantity or its form, is needed to start a reaction. The energy barrier that reactants need to overcome to react is called the

activation energy, E_a . For an exothermic reaction, the activation energy will be small compared to the activation energy for the reverse reaction. A good example is a stick of dynamite. It takes only a little bit of fire (activation energy) from a match to light the fuse, but the amount of energy released will be enormous in comparison. For an endothermic reaction, the activation energy will be far greater than the activation energy for the reverse reaction.

Physical State. The physical state of the reactants can greatly determine how long it will take for a reaction to take place. Consider the reaction between aqueous silver nitrate and aqueous sodium chloride. When the two reactants are mixed, the following reaction occurs:



The mixing of the two clear aqueous solutions immediately produces a white precipitate, silver chloride. The aqueous ionic solutions have their ions ready to react upon contact.

In contrast, consider a reaction between two covalently bonded compounds such as an alcohol and a carboxylic acid. Even though the reaction is typically catalyzed by sulfuric acid, it needs to be refluxed for multiple hours to ensure a high yield of the ester. In order to get the reactants to form an activated complex and start forming products, covalent bonds need to be broken with a sufficient amount of energy. This is a much slower process when compared to aqueous ions.

CATALYSTS

Catalysts speed a reaction rate by lowering the **activation energy** of the reaction. The catalyst may be involved in the formation of the activated complex, the high-energy compound that is partly starting material and partly product, but it is regenerated at the end of the reaction.

Catalysts can be in the same phase as the reactants (homogeneous) or in a different phase (heterogeneous). They can be inorganic or organic. Biological catalysts are called **enzymes**, and they catalyze every biochemical reaction in the body. Enzymes are very specific for their starting material, which is called its **substrate**. They often interact with the substrate like a key fitting into a lock. A three-dimensional site on the substrate acts as the lock, and the enzyme fits into the site, called the **active site**, like a key. Enzymes work optimally within a very narrow range of temperature and pH.

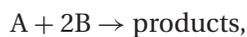
RATE LAW AND RATE CONSTANT

Kinetics studies how the reaction rate changes when the concentrations of the reactants change. This rate data is used to determine the rate law for the reaction. The **rate law** expresses how the rate is affected by the concentrations and by the rate constant.

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For a reaction



the rate law is written

$$\text{Rate} = k[A]^x [B]^y$$

where $[A]$ is the molarity of A, $[B]$ is the molarity of B, x is the order with respect to A, and y is the order with respect to B.

The rate constant can be used to determine the concentration of the reactant at any point. For a first-order reaction (overall), the equation is:

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

where \ln means natural log, $[A]_0$ is the concentration of A at the beginning of the reaction ($t = 0$), and $[A]_t$ is the concentration of A at time t ; k is the rate constant, and t is the time.

EXAMPLE: For a first-order reaction



the rate constant is $3.02 \times 10^{-3} \text{ s}^{-1}$. The concentration of A initially is 0.025 M.

SOLUTION:

1. Calculate the $[A]$ after 172 s.
2. Calculate the time for the $[A]$ to reach $1.13 \times 10^{-3} \text{ M}$.
3. Calculate the time needed for 98% of the $[A]$ to react.

► Plug in $[A]_0 = 0.0250 \text{ M}$, $t = 172 \text{ s}$, $k = 3.02 \times 10^{-3} \text{ s}^{-1}$

$$\begin{aligned} \ln [A]_t &= \ln 0.0250 - (3.02 \times 10^{-3} \text{ s}^{-1})(172 \text{ s}) \\ &= -3.69 - 0.519 \\ &= -4.21 \end{aligned}$$

$$[A]_t = e^{-4.21} = 0.015 \text{ M}$$

►
$$\frac{\ln[A]_t}{\ln[A]_0} = -kt$$

$$\ln \frac{0.015}{0.0250} = -(3.02 \times 10^{-3} \text{ s}^{-1}) \cdot t$$

$$-0.511 = -3.02 \times 10^{-3} \text{ s}^{-1} \cdot t$$

$$t = \frac{0.511}{3.02 \times 10^{-3} \text{ s}^{-1}} = 169 \text{ s}$$

$$\begin{aligned} \text{> } \quad \frac{\ln[A]_t}{\ln[A]_0} &= -kt \\ \ln \frac{2\%}{100\%} &= -(3.02 \times 10^{-3} \text{ s}^{-1}) \cdot t \\ t &= 1294 \text{ s} \end{aligned}$$

REACTION ORDER

Rates usually relate to the concentration of a reactant in one of three ways: by not changing, by changing proportionately to the change in concentration, or by changing as the square of the change of the concentration.

- ▶ As the concentration of A is changed, the rate does not change (see Figure 10-6a). The rate is unaffected; the order with respect to A is 0.
- ▶ As the concentration of A is changed, the rate changes proportionally (see Figure 10-6b). If [A] is doubled, the rate doubles, and so on. The order with respect to A is 1.
- ▶ As the concentration of A is changed, the rate changes as the square of the change in the concentration (see Figure 10-6c). If [A] is doubled, the rate quadruples, for instance. The order with respect to A is 2.

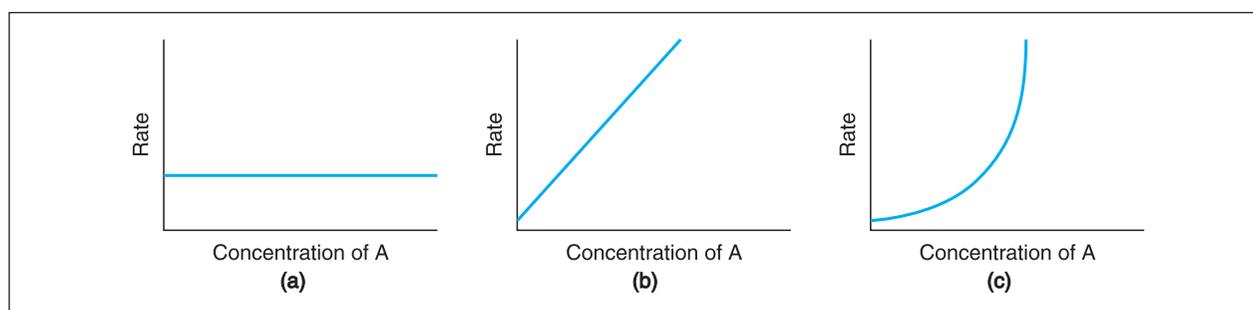
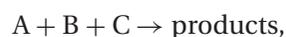


FIGURE 10-6 Relation of rate to concentration of reactant.

The orders of each reactant are thus determined by observing how the rate is affected by the change in the concentration of each reactant. Only one order can be determined at a time. All other concentrations must remain constant; only the concentration of the reactant being studied is changed. The rates are shown under various conditions; these are used to determine the rate law and the rate constant, k , is then calculated.

EXAMPLE: For the reaction



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determine the rate law and calculate the rate constant using the following data:

Run	[A] (M)	[B] (M)	[C] (M)	Rate (M/s)
1	0.003	0.001	1.0	1.8×10^4
2	0.003	0.002	1.0	3.6×10^4
3	0.006	0.002	1.0	7.2×10^4
4	0.003	0.001	2.0	7.2×10^4

SOLUTION:

- ▶ From run 1 to 2, the [B] is doubled. The rate doubles, so the order of B is 1. (The rate is directly proportional to the concentration of B.)
- ▶ From run 2 to 3, the [A] is doubled. The rate doubles, so the order of A is 1. (The rate is directly proportional to the concentration of A.)
- ▶ From run 1 to 4, the [C] is doubled. The rate quadruples, so the order of C is 2. (The rate is proportional to the square of the concentration of C.)
- ▶ So the rate law is:

$$\text{rate} = k[\text{A}] [\text{B}] [\text{C}]^2$$

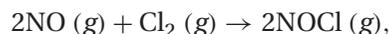
- ▶ Using the data from run 1, the rate constant k is calculated:

$$1.8 \times 10^{-4} = k[0.003] [0.001] [1]^2$$

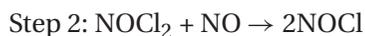
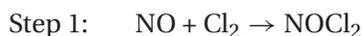
$$k = 60 \text{ M}^{-3}\text{s}^{-1}$$

Rate-Determining Step

Not all reactions take place in a single step. Instead, many reactions have multiple steps, each with its own activation energy. These individual steps are called elementary steps and, when added together, produce the overall reaction. The step with the greatest energy barrier to overcome will be the slowest step. It is considered to be the **rate-determining step**. For example, when you consider the overall reaction:



there are actually two elementary steps:



To actually know the rate-determining step, you must know the observed rate law. For this particular reaction, the slower step is the second elementary step.

How would you know if the reaction takes place in one step? According to the overall reaction, two molecules of nitric oxide gas, $\text{NO}(g)$, must make contact and react with chlorine gas to form the product. It is highly unlikely that a termolecular reaction will

take place. Instead, you see that there are bimolecular reactions taking place to form an intermediate, which is consumed in the next step. If one substance were to form a product or intermediate, that type of reaction would be considered to be unimolecular.

Activated Complex or Transition State

Activation energy is needed to provide reactants with enough energy to produce an intermediate between the reactants and products. Once this energy has been achieved, the reaction then reaches a **transition state** in which the reactants start to form the products. This transition state is also called the **activated complex**. The complex formed has its own potential energy called the **potential energy of the activated complex**. This point of a potential energy diagram will be a maximum level, meaning that the complex is less stable and that the next steps of the reaction will be exothermic. This complex is usually a short-lived substance. Once the complex is formed, the products begin to form immediately so as to become a lower-energy, more stable substance.

Interpretation of Energy Profiles

In order to track the energy changes over the course of a reaction, an energy profile (or reaction coordinate diagram) is used. A typical energy profile looks like Figure 10-7.

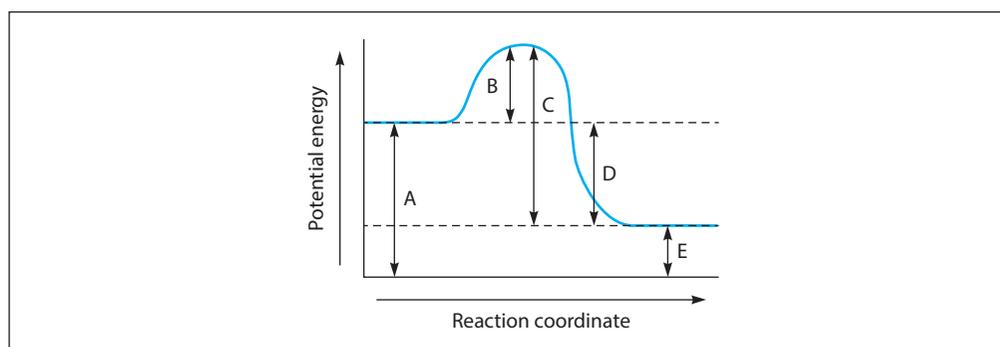


FIGURE 10-7 Typical energy profile.

Figure 10-7 has the following features:

- A: The potential energy of the reactants
- B: The activation energy of the forward reaction
- C: The activation energy of the reverse reaction
- D: The heat of reaction, ΔH
- E: The potential energy of the products

An example of a multistep energy profile is demonstrated in Figure 10-8. The first energy barrier, requiring more activation energy, would be the rate-determining step for this sample reaction.

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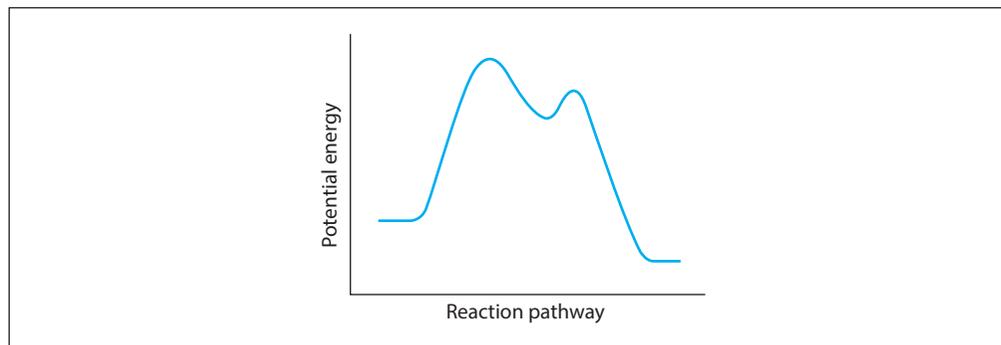
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FIGURE 10-8 Multistep energy profile.

ARRHENIUS EQUATION

If the **energy of activation**, E_a , for a reaction is known (this is the minimum energy needed for a reaction to occur), and the rate constant for one temperature is known, the rate constant at any other temperature can be calculated using the **Arrhenius equation**:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} (1/T_1 - 1/T_2)$$

where k_1 is the rate constant at temperature T_1 , k_2 is the rate constant at temperature T_2 , T_1 and T_2 are in Kelvin, $R = 8.314$ joules (J)/mole K, and E_a is the activation energy.

EXAMPLE: For a certain first-order reaction, the rate constant at 190 °C is 2.61×10^{-3} and the rate constant at 250 °C is 3.02×10^{-3} . Calculate the energy of activation of this reaction.

SOLUTION:

$$k_1 = 2.61 \times 10^{-3} \quad \text{at } T_1 = 463.2 \text{ K}$$

$$k_2 = 3.02 \times 10^{-3} \quad \text{at } T_2 = 523.2 \text{ K}$$

So

$$\ln \frac{3.02 \times 10^{-3}}{2.61 \times 10^{-3}} = \frac{E_a}{8.314} \left(\frac{1}{463.2} - \frac{1}{523.2} \right)$$

$$\ln 1.16 = \frac{E_a(2.48 \times 10^{-4})}{8.314}$$

$$\frac{0.148(8.314)}{2.48 \times 10^{-4}} = E_a$$

$$5.0 \times 10^3 \text{ J/mole} = E_a$$

Kinetic Control Versus Thermodynamic Control of a Reaction

Sometimes a reaction has competing pathways that can lead to different products, even though the reactants are exactly the same. One pathway may require a lower

activation energy, or one may form a more stable product than another. The reaction that is governed by a lower activation energy will produce a kinetically-controlled product. A reaction that is favored because it forms a more stable product does so by forming a thermodynamically-favored product. The energy profile shown in Figure 10-9 summarizes these two competing possibilities.

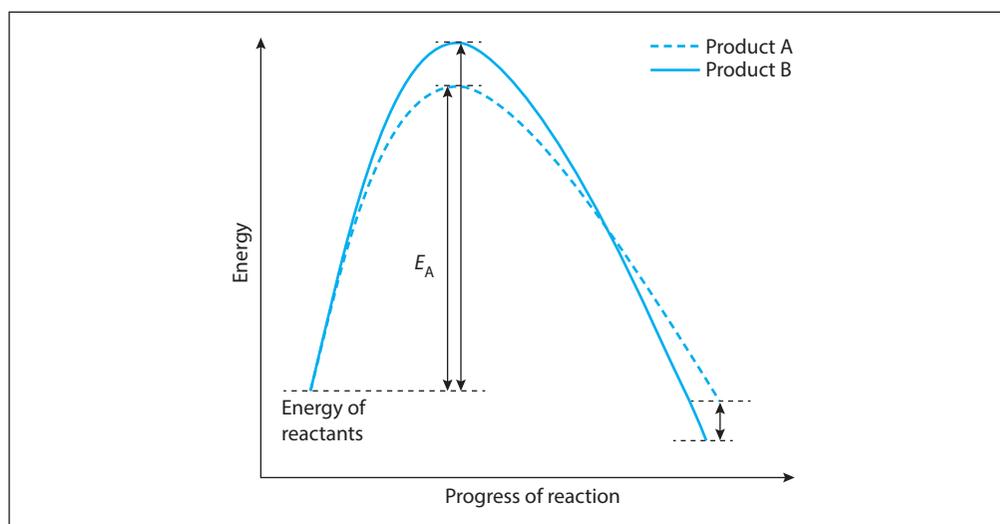


FIGURE 10-9 Kinetic control versus thermodynamic control.

Product A was the kinetically-favored (lower activation energy) product, while Product B was formed via a thermodynamically-favored pathway (more stable product).

Equilibrium in Reversible Chemical Reactions

Equilibrium occurs with reactions that are reversible when the **forward reaction rate** equals the **reverse reaction rate**. Using various formulas, the rate at which a reaction occurs before reaching equilibrium and the concentrations of the products can be determined.

For a reversible reaction, the starting material (on the left) is converted into the product (on the right) at a rate equal to $k[A]^x$:



At a certain point in the progress of the reaction, some of the B that has formed begins to convert to A at a rate equal to $k_{-1}[B]^y$. There comes a point when the forward rate and the reverse rate are equal, and the concentrations of A and B no longer change, although each reaction is still proceeding. This is called the **equilibrium point**. The net numbers of A and B present in the reaction flask remain the same. It appears that the reaction has stopped.

EXAMPLE: If one begins with 100 molecules of A, A begins immediately to turn into B. When enough B's are present, they start to turn back into A. At the equilibrium point, there are, for example, 60 A's and 40 B's. The reactions, both forward and reverse, are still proceeding, but the reaction rates are equal, so there remain at all times 60 A's and 40 B's.

LAW OF MASS ACTION

For a reaction at equilibrium, there is a method in which chemists express the concentration of products formed to the reactants remaining. This is called the **law of mass action**. For example, the following reaction is at equilibrium: $wW + xX \rightleftharpoons yY + zZ$. The law of mass action expresses the ratio of products formed to reactants remaining where the concentration of each substance is raised to a power that is equal to their coefficient. Using the preceding reaction at equilibrium, the law of mass action would look like:

$$K_{\text{eq}} = [Y]^y[Z]^z/[W]^w[X]^x$$

A good mnemonic device to remember is, "Products over reactants; coefficients become powers."

The phases of the substances involved in the equilibrium are important to note as well. The law of mass action will include only aqueous substances (*aq*) or gaseous substances (*g*). It will not include solids (*s*) or liquids (*l*). When including an aqueous substance, the concentration should be noted in molarity, *M*. When gases are involved, the partial pressure of each gas is used. Applying these rules to a purely hypothetical reaction at equilibrium: $2W(aq) + 3X(s) \rightleftharpoons 4Y(l) + 5Z(g)$ the law of mass action would result in:

$$K_{\text{eq}} = [Z]^5/[W]^2$$

EQUILIBRIUM CONSTANT

The **equilibrium constant** *K* describes the extent to which the forward reaction proceeds before reaching the equilibrium point. Is there a lot of A left over, or just a little? *K* is a constant value at a constant temperature; it does change with temperature.

If *K* is large (>1), there is mostly product and very little starting material left at the equilibrium point. This is a **product-favored reaction**.

If *K* is small ($<10^{-4}$), there is mostly starting material left over, and very little product formed at the equilibrium point. This is a **reactant-favored reaction**.

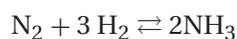
With a medium *K* (between 1 and 10^{-4}), a lot of product is formed, but there are still substantial quantities of starting material left.

Factors Affecting Equilibrium Constant—Equilibrium Expression. The equilibrium constant K depends on temperature and is related to the amounts of starting material and product in the following manner:



where a , b , and c are the molar coefficients and $[\] =$ mole per liter (mol/L)

EXAMPLE:

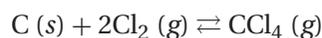


SOLUTION:

$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} \text{ in terms of pressure}$$

Only gases (with pressures) and species in solution (with concentrations) affect the equilibrium. Solids and liquids do not appear in the equilibrium expression.

EXAMPLE:



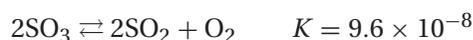
SOLUTION:

$$K_p = \frac{(P_{CCl_4})}{(P_{Cl_2})^2}$$

Given the K and the initial conditions (concentrations or pressures), you can calculate the equilibrium conditions of the products.

If the K is $<10^{-4}$, the reaction does not proceed far before equilibrium. Very little product is formed, and the amount of starting material has changed very little. You can neglect the change in the starting material because it is such a small amount.

EXAMPLE: If you start with 0.240 mole SO_3 in a 3.00-L container, calculate the equilibrium concentrations of SO_2 and O_2 in the reaction:



SOLUTION:

- The balanced chemical equation is used to set up an ICE (Initial, Change, Equilibrium) table

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TABLE 10-5 ICE Table for a Balanced Chemical Equation

Initial	2SO_3 0.080 M	\rightleftharpoons	2SO_2 0	+	O_2 0	Initial amounts in M or pressure
Δ	$-2x$		$+2x$		$+x$	For every 2 moles of SO_3 that react, 2 moles of SO_2 and 1 mole of O_2 are formed.
Equilibrium	0.080 M		$2x$		x	Add the values in the column to get the equilibrium value; you can neglect the change to the SO_2 ; these values go into the K expression.

- Write the K expression:

$$K = \frac{[\text{SO}_2]^2 [\text{O}_2]}{[\text{SO}_3]^2}$$

- Plug in the equilibrium values and solve for x :

$$9.6 \times 10^{-8} = \frac{[2x]^2 [x]}{[0.080]^2}$$

- $x = 5.4 \times 10^{-4}$

- So the equilibrium concentrations of SO_2 and O_2 are:

$$[\text{SO}_2] = 2x = 1.1 \times 10^{-3} \text{ M}$$

$$[\text{O}_2] = x = 5.4 \times 10^{-4} \text{ M}$$

You can calculate the K if given the initial conditions (concentrations or pressures) and either the percentage of starting material that reacts or one of the actual equilibrium values.

EXAMPLE: You have 0.40 atm of CH_4 and 0.65 atm of H_2S initially. Calculate the K of the following reaction if 25% of the CH_4 remains at the equilibrium point.

SOLUTION:

Initial	CH_4 (g) 0.40	+ $2\text{H}_2\text{S}$ (g) 0.65	\rightleftharpoons	CS_2 (g) 0	+ 4H_2 (g) 0
Δ	$-x$	$-2x$		$+x$	$+4x$
At equilibrium	0.10	0.05		0.30	1.20

- The numbers on the bottom line were determined using the information given in the problem. If you start with 0.40 atm of CH_4 and 25% remains at the equilibrium point, then $(0.40 \text{ atm}) (0.25) = 0.10 \text{ atm}$ is what remains of the CH_4 at equilibrium.
- Then using the equation $0.40 - x = 0.10$, you get $x = 0.30 \text{ atm}$.
- Plugging in this value for x on the change line and adding the columns, the

other equilibrium values are obtained.

- ▶ Now you write the K expression.

$$K = \frac{(P_{\text{CS}_2}) (P_{\text{H}_2})^4}{(P_{\text{CH}_4}) (P_{\text{H}_2\text{S}})^2}$$

- ▶ Plug in the bottom line values to calculate K .

$$K = \frac{(0.30) (1.20)^4}{(0.10) (0.05)^2} = 2.5 \times 10^3$$

LE CHATELIER'S PRINCIPLE

Le Chatelier's principle states that if you subject a system that is at equilibrium, to some change in conditions, the equilibrium shifts so as to counteract the change. For example, note the following reaction:

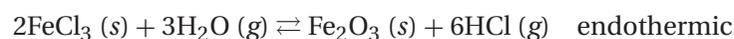


TABLE 10-6 Summary of Changes in Reactions in Equilibrium

Change	Counteraction	Direction of Equilibrium Shift
Add some water vapor	Remove the water vapor	→
Remove some HCl	Make more HCl	→
Remove some Fe_2O_3	No counteraction	No change
Add some HCl	Remove some HCl	←
Increase the volume (decrease the pressure)	Increase the pressure (make more gas molecules)	→
Decrease the volume (increase the pressure)	Decrease the pressure (remove gas molecules)	←
Heat the reaction	Remove the heat	→
Cool the reaction	Increase the heat content	←

