Chapter 2 Lecture **Chapter 7 Lecture**

Fundamentals of General, Organic, and Biological Chemistry

7th Edition McMurry, Ballantine, Hoeger, Peterson

Chapter Seven

Chemical Reactions: Energy, Rates, and Equilibrium

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ALWAYS LEARNING

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Outline

- 7.1 Energy and Chemical Bonds
- 7.2 Heat Changes during Chemical Reactions
- 7.3 Exothermic and Endothermic Reactions
- 7.4 Why Do Chemical Reactions Occur? Free Energy
- 7.5 How Do Chemical Reactions Occur? Reaction Rates
- 7.6 Effects of Temperature, Concentration, and Catalysis on Reaction Rates
- 7.7 Reversible Reactions and Chemical Equilibrium
- 7.8 Equilibrium Equations and Equilibrium Constants
- 7.9 Le Châtelier's Principle: The Effect of Changing Conditions on Equilibria

Goals

- **1. What energy changes take place during reactions?** Be able to explain the factors that influence energy changes in chemical reactions.
- 2. What is "free energy," and what is the criterion for spontaneity **in chemistry?**

Be able to define enthalpy, entropy, and free-energy changes, and explain how the values of these quantities affect chemical reactions.

- **3. What determines the rate of a chemical reaction?** Be able to explain activation energy and other factors that determine reaction rate.
- **4. What is chemical equilibrium?**

Be able to describe what occurs in a reaction at equilibrium and write the equilibrium equation for a given reaction.

5. What is Le Châteliers principle?

Be able to state Le Châtelier's principle and use it to predict the effect of changes in temperature, pressure, and concentration on reactions.

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7.1 Energy and Chemical Bonds

- **Potential energy** is stored energy.
	- The water in a reservoir behind a dam
	- An automobile poised to coast downhill
	- A coiled spring
- **Kinetic energy** is the energy of motion.
	- Water falls over a dam and turns a turbine.
	- The car rolls downhill.
	- The spring uncoils and makes the hands on a clock move.

7.1 Energy and Chemical Bonds

- The attractive forces between ions or atoms are a form of potential energy.
- When these attractive forces result in the formation of ionic or covalent bonds, the potential energy is often converted into **heat**.
- Heat is a measure of the kinetic energy of the particles that make up the molecule.
- Breaking these bonds requires an input of energy.

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7.1 Energy and Chemical Bonds

- In reactions, some bonds break (energy in) so that new bonds can form (energy out).
- If the products have less potential energy than the reactants, the products are *more stable* than the reactants.
- *Stable* describes a substance that has little remaining potential energy and, consequently, little tendency to undergo further change.

7.1 Energy and Chemical Bonds

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• Whether a reaction occurs, and how much energy or heat is associated with the reaction, depends on the difference in the amount of potential energy contained in the reactants and products.

7.2 Heat Changes during Chemical Reactions

- The strength of a covalent bond is measured by the amount of energy that must be supplied to break the bond.
- **Bond dissociation energy** is the amount of energy that must be supplied to break a bond and separate the atoms in an isolated gaseous molecule.
- The greater the bond dissociation energy, the more stable the chemical bond.
- The more stable a molecule, the less reactive it is.

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7.2 Heat Changes during Chemical Reactions

- Bond breaking is **endothermic**, from the Greek words *endon* (within) and *therme* (heat), meaning that heat is put in.
- Bond formation *releases* heat and is described as **exothermic**, from the Greek *exo* (outside), meaning that heat goes out.
- The amount of energy released in forming a bond is numerically the same as that absorbed in breaking it.

7.2 Heat Changes during Chemical Reactions

- The amount of heat transferred during a change in one direction is numerically equal to the amount of heat transferred during the change in the opposite direction.
- Only the *direction* of the heat transfer is different.
- This relationship reflects a fundamental law of nature.

7.2 Heat Changes during Chemical Reactions

- The **law of conservation of energy** states that energy can be neither created nor destroyed in any physical or chemical change.
- In every chemical reaction, some bonds in the reactants are broken and new bonds are formed in the products.
- The difference between the heat absorbed in breaking bonds and the heat released in forming bonds is the **heat of reaction**.

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7.2 Heat Changes during Chemical Reactions

- Heats of reaction measured at constant pressure are abbreviated !*H.*
- \bullet Δ (the Greek capital letter delta) is a symbol used to indicate "a change in."
- *H* is a quantity called **enthalpy**.
- The terms *enthalpy change* and *heat of reaction* are often used interchangeably.
- Heat of reaction, or enthalpy change (ΔH) is the difference between the heat energy absorbed in breaking bonds and the heat energy released in forming bonds.

7.3 Exothermic and Endothermic Reactions

• Heat of reaction can be calculated as the difference between the bond dissociation energies in the products and the bond dissociation energies of the reactants.

 $\Delta H = \Sigma ($ Bond dissociation energies)_{reactants} - Σ (Bond dissociation energies)_{products}

• If the input of energy to break bonds is less than the amount of energy released when forming bonds, the excess is released as heat and the reaction is exothermic (ΔH = negative).

7.3 Exothermic and Endothermic Reactions

- If the input of energy to break bonds is more than the amount of energy released when forming bonds, the excess is absorbed and the reaction is endothermic $(AH =$ negative).
- Tabular bond energies are average values. Actual bond energies may vary depending on the chemical environment in which the bond is found.

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7.3 Exothermic and Endothermic Reactions

Important Points about Heat Transfers and Chemical Reactions

- An exothermic reaction releases heat to the surroundings; ΔH is negative.
- An endothermic reaction absorbs heat from the surroundings; ΔH is positive.
- The reverse of an exothermic reaction is endothermic.
- The reverse of an endothermic reaction is exothermic.
- The amount of heat absorbed or released in the reverse of a reaction is equal to that released or absorbed in the forward reaction, but ΔH has the opposite sign.

7.3 Exothermic and Endothermic Reactions

Energy from Food

- Food is "burned" in the body to yield H_2O , CO_2 and energy.
- The "caloric value" of a food is the heat of reaction for complete combustion of the food (minus a small correction factor).
- One gram of protein releases 4 kcal, 1 g of table sugar (a carbohydrate) releases 4 kcal, and 1 g of fat releases 9 kcal
- The caloric value of a food is usually given in "Calories" (note the capital C), where 1 Calorie = 1000 cal= 1 kcal = 4.184 kJ.
- A food sample is placed together with oxygen into an instrument called a *calorimeter*, the food is ignited, the temperature change is measured, and the amount of heat given off is calculated from the temperature change.
- The total heat released or absorbed in going from reactants to products is the same, no matter how many reactions are involved.
- The body applies this principle by withdrawing energy from food a bit at a time in a long series of interconnected reactions rather than all at once in a single reaction.

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7.4 Why Do Reactions Occur? Free Energy

- Events that lead to lower energy tend to occur spontaneously.
- Many, but not all, exothermic processes take place spontaneously, and many, but not all, endothermic processes are nonspontaneous.
- A **spontaneous process** is a process or reaction that, once started, proceeds on its own without any external influence.

7.4 Why Do Reactions Occur? Free Energy

- The value of the free-energy change determines spontaneity.
	- A negative value means that free energy is released and the reaction or process is spontaneous. Such events are **exergonic**.
	- A positive value means that free energy must be added and the process is nonspontaneous. Such events are **endergonic**.

7.4 Why Do Reactions Occur? Free Energy

Important Points about Spontaneity and Free Energy

- A spontaneous process, once begun, proceeds without any external assistance and is exergonic; that is, free energy is released and it has a negative value of ΔG .
- A nonspontaneous process requires continuous external influence and is endergonic; that is, free energy is added and it has a positive value of ΔG .
- The value of ΔG for the reverse of a reaction is numerically equal to the value of ΔG for the forward reaction, but has the opposite sign.
- Some nonspontaneous processes become spontaneous with a change in temperature.

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energy change, ΔG.

- A catalyst increases reaction rate either by letting a reaction take place through an alternative pathway with a lower energy barrier, or by orienting the reacting molecules appropriately.
- The catalyzed reaction has a lower activation energy.
- The free-energy change for a reaction depends *only* on the difference in the energy levels of the reactants and products, and *not* on the pathway of the reaction.
- A catalyzed reaction releases (or absorbs) the same amount of energy as an uncatalyzed reaction, but occurs more rapidly.

TABLE 7.3 Effects of Changes in Reaction Conditions on Reaction Rates

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Looking Ahead

– The thousands of biochemical reactions continually taking place in our bodies are catalyzed by large protein molecules called *enzymes*, which control the orientation of the reacting molecules. The study of enzymes is a central part of biochemistry.

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7.6 Effects of Temperature, Concentration, and Catalysts on Reaction Rates

Regulation of Body Temperature

- If the body is unable to maintain a temperature of 37 °C, the rates of the chemical reactions that take place in the body will change.
- *Hypothermia* occurs when the body is unable to generate enough heat to maintain normal temperature. All chemical reactions in the body slow down because of the lower temperature, energy production drops, and death can result.
- During open-heart surgery, the heart is stopped and maintained at about 15 °C, while the body, which receives oxygenated blood from an external pump, is cooled to 25–32 °C.
- *Hyperthermia* is an uncontrolled rise in body temperature. Chemical reactions in the body are accelerated, the heart struggles to supply increased oxygen, and brain damage can result if the body temperature rises above 41 °C.

Regulation of Body Temperature (Continued)

- Body temperature is maintained by the thyroid gland and the hypothalamus region of the brain, which regulate metabolic rate. Temperature receptors in the skin, spinal cord, and abdomen send signals to the hypothalamus, which contains heat- and coldsensitive neurons.
- Stimulation of heat-sensitive neurons stimulate the sweat glands, dilates the blood vessels of the skin, decreases muscular activity, and reduces metabolic rate.
- Stimulation of cold-sensitive neurons stimulates metabolic rate, and causes contraction of peripheral blood vessels and increased muscular contractions, resulting in shivering and "goosebumps."
- Alcohol causes blood vessels to dilate. This results in a warm feeling as blood flow to the skin increases, but body temperature drops as heat is lost through the skin at an increased rate.

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7.7 Reversible Reactions and Chemical Equilibrium

- Many chemical reactions result in the virtually complete conversion of reactants into products.
- When the reactants and products are of approximately equal stability, the reaction is *reversible*.
- A **reversible reaction** is one that can go in either direction, from products to reactants or reactants to products.

7.7 Reversible Reactions and Chemical Equilibrium

7.7 Reversible Reactions and Chemical Equilibrium • The forward reaction takes place rapidly at

- the beginning of the reaction then slows down as reactant concentrations decrease.
- The reverse reaction takes place slowly at the beginning but then speeds up as product concentrations increase.
- Ultimately, the forward and reverse rates become equal.

- For a reversible reaction, the rates of both the forward *and* the reverse reactions must depend on the concentration of reactants and products.
- Is it possible to predict what the equilibrium conditions will be for any given reaction?
- Numerous experiments have led to a general equation that is valid for any reaction.

7.8 Equilibrium Equations and Equilibrium Constants

- If there is no coefficient for a reactant or product in the reaction equation it is assumed to be 1.
- The value of *K* varies with temperature— 25 °C is assumed unless specified.
- Units are usually omitted.
- For reactions that involve pure solids or liquids, these pure substances are omitted when writing the equilibrium constant expression.

7.9 Le Châteliers Principle: The Effect of Changing Conditions on Equilibria

- **Le Châteliers principle**—When a stress is applied to a system at equilibrium, the equilibrium shifts to relieve the stress.
- The word "stress" means anything that disturbs the original equilibrium.
- Changes in concentration, temperature, and pressure affect equilibria, but addition of a catalyst does not (except to reduce the time it takes to reach equilibrium).

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7.9 Le Châteliers Principle: The Effect of Changing Conditions on Equilibria

Effect of Changes in Concentration

- Once equilibrium is reached, the concentrations of reactants and products are constant, and the forward and reverse reaction rates are equal.
- If the concentration of a reactant is increased, the rate of the forward reaction must increase. The equilibrium is "pushed" to the right.
- Ultimately, the forward and reverse reaction rates adjust until they are again equal, and equilibrium is reestablished.
- The value of the equilibrium constant *K* remains constant.

7.9 Le Châteliers Principle: The Effect of Changing Conditions on Equilibria

Effect of Changes in Concentration

- If more product is added to the reaction at equilibrium, the rate of the reverse reaction will increase until equilibrium is reestablished.
- If a reactant is continuously supplied or a product is continuously removed, equilibrium can never be reached.
- Metabolic reactions sometimes take advantage of this effect, with one reaction prevented from reaching equilibrium by the continuous consumption of its product in a further reaction.

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7.9 Le Châteliers Principle: The Effect of Changing Conditions on Equilibria

Effect of Changes in Temperature and Pressure

- The reverse of an exothermic reaction is always endothermic. Equilibrium reactions are therefore, exothermic in one direction and endothermic in the other.
- An increase in temperature will cause an equilibrium to shift in favor of the endothermic reaction so the additional heat is absorbed.
- A decrease in temperature will cause an equilibrium to shift in favor of the exothermic reaction so additional heat is released.
- Heat is a reactant or product whose increase or decrease stresses an equilibrium, just as a change in reactant or product concentration does.

7.9 Le Châteliers Principle: The Effect of Changing Conditions on Equilibria

Coupled Reactions

- Coupling of reactions is a common strategy in both biochemical and industrial applications.
- An endergonic reaction will not proceed spontaneously, but can be coupled to an exergonic reaction so that it will proceed.
- An important example of coupled reactions in biochemistry is the endergonic phosphorylation of glucose, which is combined with the hydrolysis of adenosine triphosphate (ATP) to form adenosine diphosphate (ADP), an exergonic process.
- Heat generated by the coupled reactions can be used to maintain body temperature.

Chapter Summary

1. What energy changes take place during reactions?

- The strength of a covalent bond is measured by its *bond dissociation energy*, the amount of energy that must be supplied to break the bond in an isolated gaseous molecule.
- For any reaction, the heat released or absorbed by changes in bonding is called the *heat of reaction*, or *enthalpy change*.
- If the total strength of the bonds formed in a reaction is greater than the total strength of the bonds broken, then heat is released and the reaction is said to be *exothermic*.
- If the total strength of the bonds formed in a reaction is less than the total strength of the bonds broken, then heat is absorbed and the reaction is said to be *endothermic*.

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Chapter Summary, *Continued*

- 2. What is "free energy," and what is the criterion for **spontaneity in chemistry?**
- *Spontaneous reactions* are those that, once started, continue without external influence.
- Nonspontaneous reactions require a continuous external influence.
- Spontaneity depends on the amount of heat absorbed or released in a reaction (ΔH) and the *entropy change* (ΔS), which measures the change in molecular disorder in a reaction.
- Spontaneous reactions are favored by a release of heat (negative ΔH) and an increase in disorder (positive ΔS).
- The *free-energy change* ∆G takes both factors into account, according to the equation $\Delta G = \Delta H - T \Delta S$.
- A negative value for ΔG indicates spontaneity, and a positive value for ΔG indicates nonspontaneity.

Chapter Summary, *Continued* **3. What determines the rate of a chemical reaction?** • A chemical reaction occurs when reactant particles collide with proper orientation and sufficient energy.

- The exact amount of collision energy necessary is called the *activation energy*.
- A high activation energy results in a slow reaction because few collisions occur with sufficient force, whereas a low activation energy results in a fast reaction.
- Reaction rates can be increased by raising the temperature, by raising the concentrations of reactants, or by adding a *catalyst*, which accelerates a reaction without itself undergoing any change.

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Chapter Summary, *Continued*

- **4. What is chemical equilibrium?**
- A reaction that can occur in either the forward or reverse direction is *reversible* and will ultimately reach a state of *chemical equilibrium*.
- At equilibrium, the forward and reverse reactions occur at the same rate, and the concentrations of reactants and products are constant.
- Every reversible reaction has a characteristic *equilibrium constant* (*K*), given by an *equilibrium equation*.

Chapter Summary, *Continued*

5. What is Le Châteliers principle?

- *Le Châteliers principle* states that when a stress is applied to a system in equilibrium, the equilibrium shifts so that the stress is relieved.
- Applying this principle allows prediction of the effects of changes in temperature, pressure, and concentration.