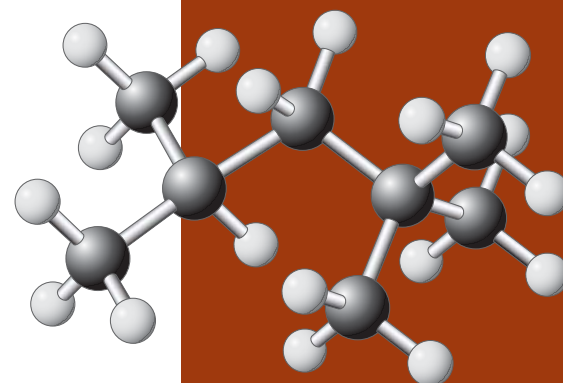


Structure and Reactivity

Acids and Bases, Polar and Nonpolar Molecules

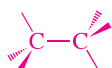


In Chapter 1, we saw organic molecules containing several different types of bonds between various elements. Can we predict, on the basis of these structures, what kinds of chemical reactivity these substances will display? This chapter will begin to answer this question by showing how certain structural combinations of atoms in organic molecules, called functional groups, display characteristic and predictable behavior. We will see how the chemistry of acids and bases serves as a simple model for understanding the reactions of many functional groups, especially those containing polar bonds. We will pursue this analogy throughout the course, through the concepts of electrophiles and nucleophiles.

Most organic molecules contain a structural skeleton that carries the functional groups. This skeleton is a relatively nonpolar assembly consisting of carbon and hydrogen atoms connected by single bonds. The simplest class of organic compounds, the alkanes, lacks functional groups and is constructed entirely of singly bonded carbon and hydrogen. Therefore, alkanes serve as excellent models for the backbones of functionalized organic molecules. They are also useful compounds in their own right, as illustrated by the structure shown at the top of this page, which is called 2,2,4-trimethylpentane and is an alkane in gasoline. By studying the alkanes we can prepare ourselves to better understand the properties of molecules containing functional groups. Therefore, in this chapter we will explore the names, physical properties, and structural characteristics of the members of the alkane family.



The branched alkane 2,2,4-trimethylpentane is an important component of gasoline and the standard on which the "octane rating" system for fuel efficiency is based. The car engine shown above requires high-octane fuel to achieve the performance for which it is famous.



Alkane single bond

2-1 Kinetics and Thermodynamics of Simple Chemical Processes

The simplest chemical reactions may be described as equilibration between two distinct species. Such processes are governed by two fundamental considerations:

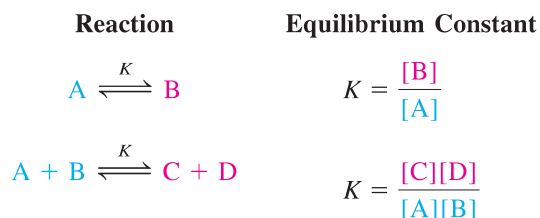
1. **Chemical thermodynamics**, which deals with the changes in energy that take place when processes such as chemical reactions occur. Thermodynamics controls the *extent* to which a reaction goes to completion.
2. **Chemical kinetics**, which concerns the velocity or rate at which the concentrations of reactants and products change. In other words, kinetics describes the *speed* at which a reaction goes to completion.

These two principles are frequently related, but not necessarily so. Reactions that are thermodynamically very favorable often proceed faster than do less favorable ones. Conversely, some reactions are faster than others even though they result in a comparatively less stable product. A transformation that yields the most stable products is said to be under **thermodynamic control**. Its outcome is determined by the net favorable change in energy in going from starting materials to products. A reaction in which the product obtained is the one formed fastest is defined as being under **kinetic control**. Such a product may not be the thermodynamically most stable one. Let us put these statements on a more quantitative footing.

Equilibria are governed by the thermodynamics of chemical change

All chemical reactions are reversible, and reactants and products interconvert to various degrees. When the concentrations of reactants and products no longer change, the reaction is in a **state of equilibrium**. In many cases, equilibrium lies extensively (say, more than 99.9%) on the side of the products. When this occurs, the reaction is said to *go to completion*. (In such cases, the arrow indicating the reverse reaction is usually omitted and, for practical purposes, the reaction is considered to be irreversible.)

Equilibria are described by **equilibrium constants, K** . To find an equilibrium constant, divide the arithmetic product of the concentrations of the components on the right side of the reaction by that of the components on the left, all given in units of moles per liter (mol L^{-1}). A large value for K indicates that a reaction goes to completion; it is said to have a large **driving force**.



If a reaction has gone to completion, a certain amount of energy has been released. The equilibrium constant can be related directly to the thermodynamic function called the **Gibbs* standard free energy change, ΔG°** .[†] At equilibrium,

$$\Delta G^\circ = -RT \ln K = -2.303 RT \log K \text{ (in kcal mol}^{-1} \text{ or kJ mol}^{-1}\text{)}$$

*Professor Josiah Willard Gibbs (1839–1903), Yale University, Connecticut.

[†]The symbol ΔG° refers to the free energy of a reaction with the molecules in their standard states (e.g., ideal molar solutions) after the reaction has reached equilibrium.