state of lower energy than the transition state for protonation to give a primary carbocation. The stabilities of the carbocations themselves do not determine which reaction is faster; the relative free energies of the transition states for carbocation formation determine the relative rates of the two processes. Only the validity of Hammond’s postulate allows us to make the connection between carbocation energy and transition-state energy.

We need Hammond’s postulate because the structures of transition states are uncertain, whereas the structures of reactants, products, and reactive intermediates are known. Therefore, knowing that a transition state resembles a particular species (for example, a carbocation) helps us to make a good guess about the transition-state structure. In this text, we’ll frequently analyze or predict reaction rates by considering the structures and stabilities of reactive intermediates such as carbocations. When we do this, we are assuming that the transition states and the corresponding reactive intermediates have similar structures and energies; in other words, we are invoking Hammond’s postulate.

**Problem 4.31** Apply Hammond’s postulate to decide which reaction is faster: addition of HBr to 2-methylpropene or addition of HBr to *trans*-2-butene. Assume that the energy difference between the starting alkenes can be ignored. Why is this assumption necessary?

### 4.9 CATALYSIS

Some reactions take place much more rapidly in the presence of certain substances that are themselves left unchanged by the reaction. A substance that increases the rate of a reaction without being consumed is called a **catalyst**. A practical example of a catalyst is platinum in the catalytic converter on the modern automobile. The platinum catalyst in the converter
brings about the rapid oxidation (combustion) of hydrocarbon exhaust emissions. This reaction would not occur were it not for the catalyst; yet the catalyst is left unchanged by the combustion reaction. The catalyst increases the rate of the combustion reaction by many orders of magnitude.

Here are some important points about catalysts.

1. A catalyst increases the reaction rate. This means that it lowers the standard free energy of activation for a reaction (Fig. 4.16).
2. A catalyst is not consumed. It may be consumed in one step of a catalyzed reaction, but if so, it is regenerated in a subsequent step.
   An implication of points 1 and 2 is that a catalyst that strongly accelerates a reaction can be used in very small amounts. Many expensive catalysts are practical for this reason.
3. A catalyst does not affect the energies of reactants and products. In other words, a catalyst does not affect the $\Delta G^\circ$ of a reaction and consequently also does not affect the equilibrium constant (Fig. 4.16).
4. A catalyst accelerates both the forward and reverse of a reaction by the same factor.

The last point follows from the fact that, at equilibrium, the rates of a reaction and its reverse are equal. If a catalyst does not affect the equilibrium constant (point 3) but increases the reaction rate in one direction, equality of rates at equilibrium requires that the rate of the reverse reaction must be increased by the same factor.

When a catalyst and the reactants exist in separate phases, the catalyst is called a **heterogeneous catalyst**. The catalyst in the catalytic converter of an automobile is a heterogeneous catalyst because it is a solid and the reactants are gases. In other cases, a reaction in solution may be catalyzed by a soluble catalyst. A catalyst that is soluble in a reaction solution is called a **homogeneous catalyst**.

![Figure 4.16 A reaction free-energy diagram comparing a hypothetical catalyzed reaction (red curve) to the uncatalyzed reaction (blue curve).](image)
A large number of organic reactions are catalyzed. In this section, we’ll introduce the idea of catalysis by considering three examples of catalyzed alkene reactions. The first example, catalytic hydrogenation, is a very important example of heterogeneous catalysis. The second example, hydration, is an example of homogeneous catalysis. The last example involves catalysis of a biological reaction by an enzyme.

**A. Catalytic Hydrogenation of Alkenes**

When a solution of an alkene is stirred under an atmosphere of hydrogen, nothing happens. But if the same solution is stirred under hydrogen in the presence of a metal catalyst, the hydrogen is rapidly absorbed by the solution. The hydrogen is consumed because it undergoes an addition to the alkene double bond.

These reactions are examples of catalytic hydrogenation, an addition of hydrogen to an alkene in the presence of a catalyst. Catalytic hydrogenation is one of the best ways to convert alkenes into alkanes. Catalytic hydrogenation is an important reaction in both industry and the laboratory. The inconvenience of using a special apparatus for the handling of a flammable gas (dihydrogen) is more than offset by the great utility of the reaction.

In the preceding reactions, the catalyst is written over the reaction arrows. Pt/C is read as “Platinum supported on carbon” or simply “Platinum on carbon.” This catalyst is a finely divided platinum metal that has been precipitated, or “supported,” on activated charcoal. A number of noble metals, such as platinum, palladium, and nickel, are useful as hydrogenation catalysts, and they are often used in conjunction with solid support materials such as alumina (Al₂O₃), barium sulfate (BaSO₄), or, as in the previous examples, activated carbon. Hydrogenation can be carried out at room temperature and pressure or, for especially difficult cases, at higher temperature and pressure in a “bomb” (a closed vessel designed to withstand high pressures).

Because hydrogenation catalysts are insoluble in the reaction solution, they are examples of heterogeneous catalysts. (Soluble hydrogenation catalysts are also known and, although important, are not so widely used; Sec. 18.6D.) Even though they involve relatively expensive noble metals, heterogeneous hydrogenation catalysts are very practical because they can
be filtered off and reused. Furthermore, because they are exceedingly effective, they can be used in very small amounts. For example, typical catalytic hydrogenation reactions can be run with reactant-to-catalyst ratios of 100 or more.

How do hydrogenation catalysts work? Research has shown that both the hydrogen and the alkene must be adsorbed on the surface of the catalyst for a reaction to occur. The catalyst is believed to form reactive metal–carbon and metal–hydrogen bonds that ultimately are broken to form the products and to regenerate the catalyst sites. Beyond this, the chemical details of catalytic hydrogenation are poorly understood. This is not a reaction for which a simple curved-arrow mechanism can be written. The mechanism of noble-metal catalysis is an active area of research in many branches of chemistry.

The benzene ring is inert to conditions under which normal double bonds react readily:

\[
\text{ styrene } + \text{H}_2 \xrightarrow{\text{Pt/C}} \text{ethylbenzene}
\]

(Benzene rings can be hydrogenated, however, with certain catalysts under conditions of high temperature and pressure.) You will learn that many other alkene reactions do not affect the “double bonds” of a benzene ring. The relative inertness of benzene rings toward the conditions of alkene reactions was one of the great puzzles of organic chemistry that was ultimately explained by the theory of aromaticity, which is introduced in Chapter 15.

### PROBLEMS

4.32 Give the product formed when each of the following alkenes reacts with a large excess of hydrogen in the presence of Pd/C.
   (a) 1-pentene  (b) (E)-1,3-hexadiene

4.33 (a) Give the structures of five alkenes, each with the formula C\(_6\)H\(_{12}\), that would give hexane as the product of catalytic hydrogenation.
   (b) How many alkenes containing one double bond can react with H\(_2\) over a Pt/C catalyst to give methylcyclopentane? Give their structures. (*Hint:* See Study Problem 4.9, p. 153.)

### B. Hydration of Alkenes

The alkene double bond undergoes reversible addition of water in the presence of moderately concentrated strong acids such as H\(_2\)SO\(_4\), HClO\(_4\), and HNO\(_3\).

\[
\text{2-methylpropene} + \text{H}_2\text{O} \xrightleftharpoons{1 \text{M HNO}_3} \text{2-methyl-2-propanol}
\]

The addition of the elements of water is in general called **hydration**. Hence, the addition of water to the alkene double bond is called **alkene hydration**.

Hydration does not occur at a measurable rate in the absence of an acid, and the acid is not consumed in the reaction. Hence, alkene hydration is an **acid-catalyzed reaction**. Because the catalyzing acid is soluble in the reaction solution, it is a **homogeneous catalyst**.
Notice that this reaction, like the addition of HBr, is regioselective. As in the addition of HBr, the hydrogen adds to the carbon of the double bond with the smaller number of alkyl substituents. The more electronegative partner of the H—OH bond, the OH group, like the Br in HBr addition, adds to the carbon of the double bond with the greater number of alkyl substituents.

In this reaction, the manner in which the catalyst functions can be understood by considering the mechanism of the reaction, which is very similar to that of HBr addition. In the first step of the reaction, which is the rate-limiting step, the double bond is protonated so as to give the more stable carbocation. Because water is present, the actual acid is the hydrated proton (H$_3$O$^+$).

This is a Brønsted acid–base reaction. Because this is the rate-limiting step, the rate of the hydration reaction increases when the rate of this step increases. The strong acid H$_3$O$^+$ is more effective than the considerably weaker acid water in protonating a weak base (the alkene). If a strong acid is not present, the reaction does not occur because water alone is too weak an acid to protonate the alkene.

In the next step of the hydration reaction, the Lewis base water combines with the carbocation in a Lewis acid–base association reaction:

Finally, a proton is lost to solvent in another Brønsted acid–base reaction to give the alcohol product and regenerate the catalyzing acid H$_3$O$^+$:

Notice three things about this mechanism. First, it consists entirely of Lewis acid–base and Brønsted acid–base reactions. Second, although the proton consumed in Eq. 4.42a is not the same as the one produced in Eq. 4.42c, there is no net consumption of protons. Finally, the base is Eq. 4.42c is water. Some students are tempted to use hydroxide ion in a situation like this because it is a stronger base. However, there is essentially no hydroxide in a 1 M nitric acid or sulfuric acid solution. Nor is hydroxide needed, because the acid on the left of Eq. 4.42c is a strong acid. Whenever H$_3$O$^+$ acts as an acid, its conjugate base H$_2$O acts as the base. (Read again about amphoteric compounds on p. 97 if this isn’t clear.) More generally, acids and their conjugate bases always act in tandem in acid–base catalysis.

Because the hydration reaction involves carbocation intermediates, some alkenes give rearranged hydration products.
The equilibrium constants for many alkene hydrations are close enough to unity that the hydration reaction can be run in reverse. The reverse of alkene hydration is called alcohol dehydration. The direction in which the reaction is run depends on the application of Le Châtelier’s principle, which states that if an equilibrium is disturbed, it will react so as to offset the disturbance. For example, if the alkene is a gas (as in Eq. 4.41), the reaction vessel can be pressurized with the alkene. The equilibrium reacts to the excess of alkene by forming more alcohol. Neutralization of the acid catalyst stops the reaction and permits isolation of the alcohol. This strategy is used particularly in industrial applications. One such application of alkene hydration is the commercial preparation of ethyl alcohol (ethanol) from ethylene:

\[ H_2C\equiv CH_2 + H_2O \xrightarrow{H_3PO_4 (\text{absorbed on solid support})} 300^\circ C \]  

\[ H_3C\overset{\text{CH}_2=\text{OH}}{\xrightarrow{\text{H}_3\text{PO}_4 (\text{absorbed on solid support})}} 300^\circ C \]

A high temperature is required because the hydration of ethylene is very slow at ordinary temperatures (see Problem 4.37). Recall (Sec. 4.8B) that increasing the temperature accelerates a reaction. This reaction was at one time a major source of industrial ethanol. Although it is still used, its importance has decreased as the fermentation of sugars from biomass (for example, corn) has become more prevalent.

To run the hydration reaction in the reverse (dehydration) direction, the alkene is removed as it is formed, typically by distillation. (Alkenes have significantly lower boiling points than alcohols, as we’ll further discuss in Sec. 8.3B.) The equilibrium responds by forming more alkene. Alcohol dehydration is more widely used than alkene hydration in the laboratory. We’ll consider this reaction in Sec. 10.1.

Alkene hydration and alcohol dehydration illustrate two important points. First is one of the key points about catalysis: a catalyst accelerates the forward and reverse reactions of an equilibrium by the same factor. For example, because alkene hydration is acid-catalyzed, alcohol dehydration is acid-catalyzed as well. A second point is that alkene hydration and alcohol dehydration occur by the forward and reverse of the same mechanism. Generally, if a reaction occurs by a certain mechanism, the reverse reaction under the same conditions occurs by the exact reverse of that mechanism. This statement is called the principle of microscopic reversibility. Microscopic reversibility requires, for example, that if you know the mechanism of alkene hydration, then you know the mechanism of alcohol dehydration as well. A consequence of microscopic reversibility is that the rate-limiting transition states of a reaction and its reverse are the same. For example, if the rate-limiting step of alkene hydration is protonation of the double bond to form the carbocation intermediate (Eq. 4.42a), then the rate-limiting step of alcohol dehydration is the reverse of the same equation—deprotonation of the carbocation to give the alkene.
Alkenes are compounds containing carbon–carbon double bonds. Alkene carbon atoms, as well as other trigonal planar atoms, are $sp^2$-hybridized.

The carbon–carbon double bond consists of a $\sigma$ bond and a $\pi$ bond. The $\pi$ electrons are more reactive than the $\sigma$ electrons and can be donated to Brønsted or Lewis acids.

In the IUPAC substitutive nomenclature of alkenes, the principal chain, which is the carbon chain containing the greatest number of double bonds, is...