

INTRODUCTION TO CATALYSIS

PRÉCIS

In the last few chapters we have been discussing principles of reactions, with a particular emphasis on reactions in the gas phase. However, now we will be changing topics and start to discuss how one can change the rate of a reaction by changing the chemical environment where the reaction occurs. In particular, we will discuss how one can use a catalyst or solvent to promote a desired reaction. Our approach will be a little bit nonstandard in that we start by asking what we can do to increase rates. We will develop the ideas into predictive tools later in this book.

12.1 INTRODUCTION

So far we have been discussing how reactions occur when the reactants are isolated from their environment. However, in most cases one does not run reactions that way. Instead, one runs the reaction in solution and/or in the presence of a catalyst. The solvent and catalyst are active participants in the reaction. If you run the reaction in the wrong solvent, you will not get as much desired product. Usually the solvent and catalysts are carefully chosen to maximize the rate of production of some desired product or to eliminate some side reaction. In the remainder of this chapter, we will give an overview of how catalysts or solvents work. Additional details will be given in later chapters.

Let's start with catalysts.

Ostwald defined a catalyst as a substance that changes the rate of reaction but that is not itself consumed in the process.

When students read Ostwald's definition, students often think that the catalysts are not active participants in the reaction. However, in reality, the catalysts are active participants

in the reaction. The catalyst usually reacts with the reactants to form a stable complex:



Then the complex rearranges to yield products and regenerate the catalyst:



Notice that the catalyst is regenerated at the end of the reaction so there is no net consumption of catalyst.

One way to think about a catalytic reaction is to consider the catalyst to be analogous to a printing press. A printing press takes in reactants, paper and ink, goes through a cycle of steps, and produces a product: a printed page. The printing press is not changed during the process. In the same way a catalyst takes in reactants goes through a series of steps and produces products. The catalyst is not changed in the process.

People often talk about catalytic reactions in terms of a catalytic cycle. The catalytic cycle is the sequence of steps that the system goes through, starting with reactants and ending with products. For example, Figure 12.1 shows a catalytic cycle for the formation of acetic acid via the Monsanto process:



There are two catalysts: HI and $[\text{Rh}(\text{CO})_2\text{I}_2]^-$. Both catalysts are active participants in the reaction. The HI reacts with the alcohol in the first step of the reaction. The $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ reacts with the product of the HI reaction. Still, both catalysts cycle through the reaction and are regenerated. The catalysts are not consumed even though the catalysts are active participants in the reaction.

Most catalytic reactions look like the reaction in Figure 12.1. The catalyst participates in the reaction, but the catalyst is regenerated, so the catalyst is not consumed in the reaction.

Table 12.1 lists the catalysts used to promote some common reactions. The rate enhancement seen under typical conditions is also included in the table. Rates typically increase by factors of 10^3 – 10^9 with gas-phase catalysts. Solid- or liquid-phase catalysts can often increase rates by factors of 10^{10} – 10^{20} , and there are cases where rate enhancements as large as 10^{40} are seen. Clearly, these effects are large enough that they need to be understood.

Table 12.1 The rate enhancement of a number of reactions in the presence of a catalyst

Reaction	Catalyst	Rate Enhancement	Temperature, K
Ortho $\text{H}_2 \rightleftharpoons$ para H_2	Pt (solid)	10^{40}	300
$2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$	Mo (solid)	10^{20}	600
$\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$	Pt (solid)	10^{12}	300
$\text{H}_2 + \text{Br}_2 \rightleftharpoons 2\text{HBr}$	Pt (solid)	1×10^8	300
$2\text{NO} + 2\text{H}_2 \rightleftharpoons \text{N}_2 + 2\text{H}_2\text{O}$	Ru (solid)	3×10^{16}	500
$\text{CH}_3\text{COH} \rightleftharpoons \text{CH}_4 + \text{CO}$	I_2 (gas)	4×10^6	500
$\text{CH}_3\text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$	NO_2 (gas)	1×10^9	750
$(\text{CH}_3)_3\text{COH} \rightleftharpoons (\text{CH}_3)_2\text{CH}_2\text{CH}_2 + \text{H}_2\text{O}$	HBr (gas)	3×10^8	750

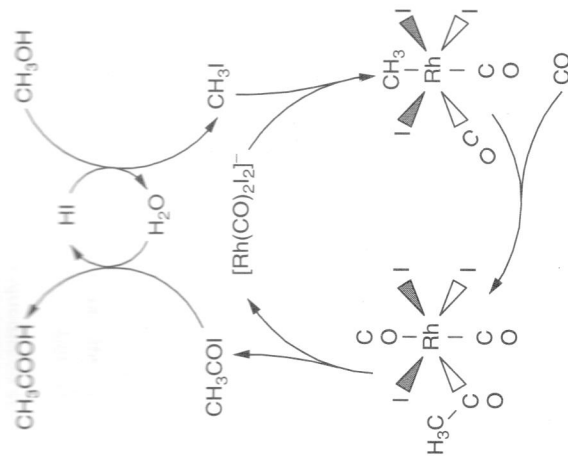


Figure 12.1 A schematic of the catalytic cycle for acetic acid production via the Monsanto process. The arrows in this figure are as described in Chapter 5.

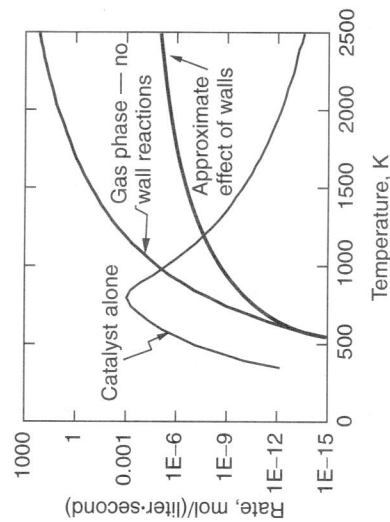


Figure 12.2 The rate of hydrogen oxidation on a platinum-coated pore calculated with (a) only heterogeneous (catalytic) reactions, (b) only radical reactions, and (c) combined radical-homogeneous reactions.

Another key experimental observation is that catalysts do not work over a wide range of conditions. For example, Figure 12.2 shows some rates of reaction calculated for hydrogen oxidation in a small pore. Notice that the rate of reaction reaches a maximum at an intermediate temperature, and then declines. The catalyst is ineffective at high temperature.

Interestingly, at very high temperatures, the gas-phase reactions are much faster than the catalytic reactions. At the highest temperatures, the catalyst slows down the reaction by promoting termination reactions.

12.1.1 Classes of Catalysts

Next we want to change topics and discuss the various types of catalysts. There are two broad classes of catalysts: **homogeneous catalysts** and **heterogeneous catalysts**. Homogeneous catalysts are substances you add to a reacting phase to speed up a given reaction, while heterogeneous catalysts act at the boundary of a phase to promote reactions.

In the next few sections we will list some of the key catalyst systems. The sections are written to provide a general overview of the kinds of materials that are catalytically active and not to teach people why the catalysts work. When I teach the course, my students often find the breadth of the material overwhelming. However, I usually tell students to just memorize the material, particularly the material in the tables, and then reread the chapter.

12.2 OVERVIEW OF HOMOGENEOUS CATALYSTS

Let's start with homogeneous catalysts. Homogeneous catalysts are substances that are added to a reacting phase to speed up some desired reaction. Examples of homogeneous catalysts include.

- Acids or bases
- Metal salts
- Enzymes
- Radical initiators
- Solvents

In the next several sections we will list several examples of acid catalysts, metal catalysts, and enzyme and radical initiators. The lists are not meant to be complete. However, we wanted to give the reader a picture of the wide variety of materials that show catalytic properties.

12.2.1 Acids and Bases

Table 12.2 lists a number of reactions commonly catalyzed by acids or bases. Acid catalysis includes acids such as HF or H₂SO₄ and organic acids such as acetic acid or trifluoroacetic acid. Basic catalysts include compounds such as sodium hydroxide. Generally any strong acid or strong base can be used to catalyze reactions.

Acids and bases act by interacting with various hydrocarbon species to form **carbocations**. Recall that a carbocation is a hydrocarbon ion with a positive charge. Carbocations are very reactive species. The production of the very reactive species allows the reaction to occur at an enhanced rate. For example, during the acid-catalyzed alkylation reaction



a proton reacts with the ethylene to form an ethyl ion:



Table 12.2 Some reactions commonly catalyzed by acids and bases

Reaction	Example	Typical Application
Isomerization (rearranging the structure of a molecule)	$\text{CH}_2=\text{CHCH}_2\text{CH}_3 \Rightarrow \text{CH}_3\text{CH}=\text{CHCH}_3$	Octane enhancement, monomer production, paraxylene production,
Alkylation (making very small molecules into a bigger molecule)	$\text{CH}_3\text{CH}=\text{CHCH}_3 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \Rightarrow (\text{CH}_3\text{CH}_2)\text{CH}(\text{CH}_3)(\text{C}_4\text{H}_9)$	Pharmaceutical production, monomer production Fine chemicals; butane + olefin \Rightarrow octane
Cracking (taking a big molecule and breaking it into two smaller ones)	$\text{C}_{12}\text{H}_{24} \Rightarrow \text{C}_7\text{H}_{14} + \text{C}_5\text{H}_{10}$	Crude-oil conversion, digestion
Esterification (attaching an acid to a base eliminating water)	$\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \Rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O}$	Soap production, fragrance production
Aldol condensation reactions (combining two aldehydes by eliminating water)	$2\text{CH}_3\text{CH}_2\text{CHO} \Rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{CHO})\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}$	Fine chemicals pharmaceutical production
Alcohol dehydration (removing a hydrogen and an OH from an alcohol, producing a double bond)	$\text{CH}_3\text{CH}_2\text{OH} \Rightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$	Alternative fuels
Cationic polymerization	Propylene \Rightarrow polypropylene	Polymer production

The ethyl ion reacts with benzene to yield an ethylbenzene ion:



Then the ethylbenzene ion loses a proton:

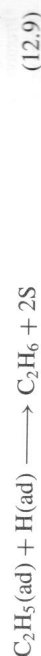


Reaction (12.2) has a significant Pauli repulsion, but reactions (12.3)–(12.5) do not. The absence of Pauli repulsions makes acid-catalyzed reactions much quicker than the corresponding uncatalyzed reactions.

We discussed some of the reactions of carbocations in Chapter 5. Most industrial carbocation reactions are catalyzed by acids or bases.

12.2.2 Metal Atoms

Metal atoms can also be used as homogeneous catalysts. Table 12.3 shows the most important examples. Generally the transition metal catalysts work by binding to the intermediates of a reaction, thereby increasing the concentration of the key intermediates. For example, the Wilkinson catalyst, Rh(P(C₆H₅)₃)Cl, catalyzes the hydrogenation of ethylene. The reaction occurs via the following steps:



where S is an empty site on the rhodium cluster, and the (ads) denote species attached to the cluster. In this case the cluster is stabilizing hydrogen atoms and ethyl groups. In Chapter 4, we showed that the rate of a cyclic reaction is proportional to the concentration of the intermediates of the reaction. In fact, the Wilkinson catalyst stabilizes

Table 12.3 Examples of reactions catalyzed by homogeneous transition metal catalysts

Reaction	Catalyst
Olefin polymerization	$[\text{TiCl}_2(\text{C}_5\text{H}_5)_2]^{2+}$ or $\text{TiCl}_2/\text{Al}(\text{C}_2\text{H}_5)_3$ (Ziegler-Natta catalyst)
Olefin hydrogenation	$\text{Rh}(\text{P}(\text{C}_6\text{H}_5)_3)_3\text{Cl}$ (Wilkinson catalyst)
$\text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow$ acetaldehyde (Wacker process)	$\text{PdCl}_2(\text{OH})_2$
$\text{C}_2\text{H}_4 + \text{H}_2 + \text{CO} \rightarrow$ propylaldehyde (hydroformylation)	$\text{HCo}(\text{CO})_4$
$\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}$ (monsanto carbonylation process)	$[\text{Rh}(\text{CO})_2\text{I}]^-$
$\text{H}_2\text{O}_2 + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + 2\text{H}_2\text{O}$	Fe^{2+}

Table 12.4 Some examples of enzymes listed in the Brookhaven National Labs' protein

Oxidoreductases ^a	Transferases ^b	Hydrolases ^c
NADH peroxidase (oxidizes NADH with peroxides)	Dimethylallyl-transferase (transfers dimethylallyl groups)	Carboxylesterase (promotes hydrolysis of ester linkages)
Ferroxidase (oxidizes Iron)	4Fe ²⁺ + O ₂ ⇒ 4Fe ³⁺ + 2H ₂ O	A carboxylic ester + H ₂ O ⇒ an alcohol + a carboxylic anion
Glucose oxidase (oxidizes glucose)	β-D-Glucose + O ₂ ⇒ D-glucono-1,5-lactone + H ₂ O ₂	1,4-D-Glucan glucanohydrolase (also called-amylase)
		Hydrolysis of 1,4-glucosidic linkages in oligosaccharides and polysaccharides
		Charidases
		Release of interleukin 1-β by specific hydrolysis at 116-Asp-1-Ala-117 and 27-Asp-1-Gly-28 bonds

^aPromote oxidation reduction reactions.

^bPromote transfer of functional groups.

^cPromote hydrolysis/cleavage reactions.

^dPromote addition of CO₂, H₂O and NH₃ to double bonds or formations of double bonds via elimination of CO₂, H₂O or NH₃.

^ePromote isomerization reactions.

^fPromote bond formation; generally used to catalyze entothermic reactions requiring ATP.

the intermediate. That raises the concentration of the intermediates. As a result, the rate of reaction is tremendously enhanced.

The mechanism of metal catalysts will be discussed in detail in Chapter 14. However, the thing to remember for now is that metal atoms stabilize radical intermediates. The stabilization speeds up rates.

Industrially, hydroformylation is the largest application of homogeneous catalysts. The Monsanto process is also the main route that people use to produce acetic acid. Ziegler-Natta catalysts are used to produce polyethylene. There are many other examples of reactions catalyzed by transition metal compounds in solution; however, Table 12.3 lists the main reactions used commercially.

12.2.3 Enzymes

Enzymes are another very important class of catalysts. Enzymes are complicated proteins. They work principally by four different routes:

database

	Lyases ^d	Isomerases ^e	Ligases ^f
Carbonate dehydratase (dehydrates carbonates)	$\text{H}_2\text{CO}_3 \leftrightarrow \text{CO}_2 + \text{H}_2\text{O}$	Maleate isomerase (promotes <i>cis-trans</i> isomerization of Maleate)	Leucine-tRNA ligase
Citrate dehydratase	$\text{Citrate} \leftrightarrow \text{cis-aconitate} + \text{H}_2\text{O}$	Cholesterol δ^9 -isomerase	Pyruvate carboxylase
		5- α -Cholesterol-7-en-3- β -ol \Rightarrow 5- α -cholest-8-en-3- β -ol	ATP + pyruvate + (HCO ₃) ⁻ \Rightarrow ADP + phosphate + oxalacetate
Pyruvate decarboxylase	A 2-oxo acid \leftrightarrow an aldehyde + CO ₂	Mannose isomerase	Aspartate-ammonia ligase
		D-Mannose \Rightarrow D-fructose	ATP + L-aspartate + NH ₃ \Rightarrow AMP + diphosphate + L-asparagine

- Enzymes bind to the reactants in such a way that key bonds in the reactants are stretched. That makes bonds easier to break.
- Enzymes lower the energy of the transition state. The analysis in Chapter 9 shows that lowering the transition state energy enhances the rate of reaction.
- Enzymes work like metals to stabilize key intermediates.
- When you have a bond-forming reaction, the enzymes push the reactants together. That also promotes reaction.

Table 12.4 lists several different enzymes. Basically, enzymes are classified according to what they do rather than how they are constructed. For example, NADH peroxidase is an enzyme used to react NADH (nicotinamide adenine dinucleotide) with hydrogen peroxide and superoxide (H_2O_2^-) where NADH is a key molecule in the energy cycle of cells. In Table 12.4 we list “NADH peroxidase” as though NADH peroxidase were a single enzyme. In fact, NADH peroxidase represents a whole family of enzymes. For example, horseradish NADH peroxidase is slightly different from mammalian NADH peroxidase.

Another important idea is that enzymes often work with “cofactors”, which are additional substances needed to get the enzyme to work. So, for example, FAD (flavine adenine dinucleotide) is a cofactor for NADH peroxidase.

Table 12.4 lists six key classes of enzymes:

- Oxidoreductases
- Transferases
- Hydrolases
- Lyases
- Isomerases
- Ligases

Oxidoreductases are enzymes that promote oxidation–reduction reactions. Transferases are enzymes that promote transfer of functional groups from a donor molecule to an acceptor molecule. Hydrolases are enzymes that promote hydrolysis reactions (i.e. scission of bonds with additions of water). Lyases are enzymes that promote elimination of CO_2 , H_2O , and NH_3 from organic molecules leading to the formation of double bonds, and the reverse reactions where water, CO_2 , NH_3 , are added to double bonds. Isomerases are enzymes that promote unimolecular isomerization reactions. Ligases are enzymes that promote endothermic bond-formation processes, consuming ATP in the process.

Enzymes are discussed in detail in elsewhere. See Faber (2000), Jencks (1987), Fersht (1999), or Sinnott (1997). The thing to remember for now is that there are many different enzymes, and they each perform a specific function.

Another key point is that if you want to find an enzyme to do a specific reaction, you can look in a standard table and find out whether a suitable enzyme exists. I usually look things up in the protein database at which in 2000 was at <http://www.rcsb.org/pdb/> or <http://www.chem.qmw.ac.uk/iubmb/enzyme/>

12.2.4 Radical Initiators

Radical initiators represent a fourth important class of catalysts. Recall that in many reactions, the slow step is the initiation step where radicals are formed. If one can find

a way to form the radicals more easily, the rate of reaction will be enhanced. Radical initiators are molecules that decompose into radicals very easily, possibly in the presence of light. The radicals then initiate the reaction.

For example, in Chapters 5 and 10 we considered the reaction



and found that the slow step was the initiation step where the C–C bond broke. Well, an iodine–iodine bond is much easier to break than a carbon–carbon bond. Consequently, the iodine can decompose at modest temperatures:



Then the iodine can react with ethane to start the reaction:



There are many variations of this. For example, the carbon–carbon bonds in acetaldehyde are much weaker than the carbon–carbon bonds in ethane. Consequently, acetaldehyde is a useful initiator for ethane dehydration.

Free-radical initiators are most important for polymerization reactions. Molecules like ethane are hard to decompose into radicals, and you need radicals or ions to start free-radical polymerization. Consequently one adds a molecule that is easy to decompose, like benzoyl peroxide. The benzoyl peroxide decomposes into radicals:



Then the radical reacts with the ethylene to start the polymerization process:



Free-radical initiators tend to give polymers with varying properties because of chain transfer reactions, so they are less useful than the transition metal polymerization catalysts. Still, the catalysts are used when one wants a soft material.

Free-radical processes are also important to atmospheric chemistry. Chlorine atoms produced from photolysis of chlorocarbons catalyze the destruction of ozone via the process:



The ClO can then react via a number of processes to reduce the ozone layer. One particular reaction is



Others reactions also occur.

Table 12.5 gives several other examples of free-radical initiators. They are used extensively.

Table 12.5 Some examples of reactions initiated or catalyzed by free radicals and similar species

Reaction	Initiator	Reaction	Catalyst
Olefin polymerization	Peroxides, (Ph) ₃ CC(Ph) ₃	2SO ₂ + O ₂ ⇒ SO ₃ (lead chamber process)	NO/NO ₂
Hydrocarbon dehydrogenation	Iodine, NO ₂ , chlorine atoms	Ozone depletion	Cl
Hydrocarbon oxidations	[(CH ₃ CH ₂) ₄ N][I], [(CH ₃ CH ₂) ₄ N] [C ₆ H ₅ COO]	—	—

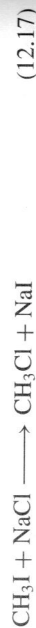
Table 12.6 The rate of reaction (12.17) in several solvents^a

Solvent	Rate constant, liter/(mol·second)
Gas phase	≈10 ⁻⁴⁵
Water	3.5 × 10 ⁻⁵
Methol	3 × 10 ⁻⁶
Methyl cyanide	0.13
DMF	2.5

^aAll measurements have been extrapolated to 25°C.

12.2.5 Solvents

There is one other class of homogeneous catalysts that is usually discussed separately from all other types of homogeneous catalysts: solvents. Solvents can act just like catalysts. They speed up reactions and change selectivities. For example, Table 12.6 shows some data for the rate of the reaction



Notice that the rate in DMF is a factor of 10⁶ larger than that in water, and 10⁴⁵ larger than that in the gas phase. Clearly DMF is acting like a catalyst.

In the literature, people seldom discuss solvents as catalysts, but solvents can act just like catalysts. Generally solvents speed up rates of ionic reactions by factors of 10³⁰ or more. Increases in rates of nonionic reactions are more unusual. Solvents are less able to selectively catalyze reactions than are the other types of homogeneous catalysts. Still, many solvents show considerable catalytic activity. Therefore I consider solvents to be a class of homogeneous catalysts.

12.3 INTRODUCTION TO HETEROGENEOUS CATALYSTS

At this point, we will be changing topics. So far we have been surveying homogeneous catalysts; however, now we move on and start to discuss heterogeneous catalysts.

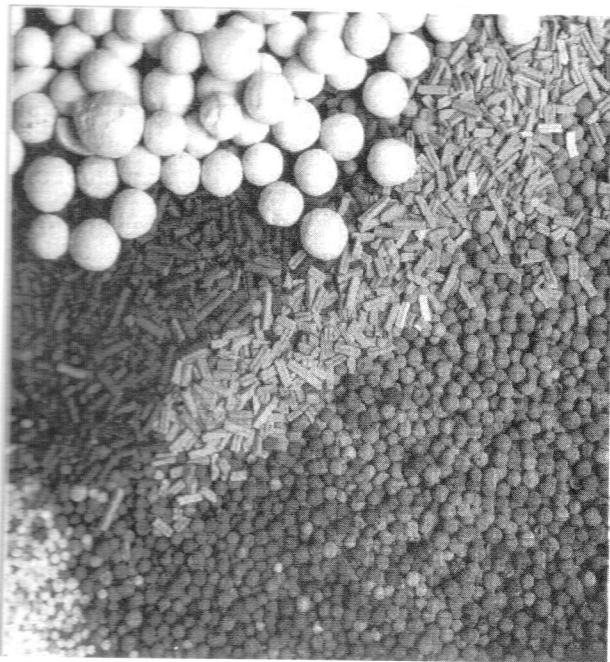


Figure 12.3 Pictures of some heterogeneous catalysts. [From Wjngaarden and Westertep (1991) With permission.]

Figure 12.3 shows pictures of some heterogeneous catalysts. Heterogeneous catalysts can be pellets, powders or other solids.

Heterogeneous catalysts are quite similar chemically to homogeneous catalysts. They are substances that are added to a reacting mixture to speed up a reaction. However, while homogeneous catalysts are generally substances that dissolve into the reacting mixture, heterogeneous catalysts are solids that do not dissolve. Instead, reaction occurs at or near the interface between the solid and the reactant mixture.

The fact that the reaction occurs at an interface means that reactants have to diffuse to the interface before the reaction can occur. Consequently, heterogeneously catalyzed reactions are often a little slower than homogeneously catalyzed ones.

Still, industrially, heterogeneous catalysts are almost always preferred over homogeneous catalysts. Recall that with a homogeneous catalyst, the catalyst is added to the reacting phase. When the reaction is completed, either the catalyst must be separated from the products, or you end up losing the catalyst. Many catalysts contain expensive metals, such as rhodium. You would not want to throw rhodium away. Other catalysts contain acids; the acids are disposal problems. In contrast, a heterogeneous catalyst is a solid. The solid is easily separated from the reacting mixture. As a result, it is generally much easier to use a heterogeneous catalyst rather than a homogeneous catalyst in a chemical process. Examples of heterogeneous catalysts include

- Supported metals
- Transition metal oxides and sulfides
- Solid acids and bases
- Immobilized enzymes and other polymer-bound species

Generally, heterogeneous catalysts are just like homogeneous catalysts except that the active species are attached to a solid. The solid allows the catalyst to be separated from the reaction mixture quite easily. The easy separation generally makes heterogeneous catalysts preferred over homogeneous catalysts in industrial practice.

In the next several sections we will list several examples of catalysts in each of these classes. The lists are not meant to be complete. However, we wanted to give the reader a picture of the wide variety of materials that show catalytic properties so that the reader will have a general idea about what is available.

12.3.1 Supported Metal Catalysts

The simplest heterogeneous catalyst is a supported metal catalyst. Figure 12.4 shows a diagram of a supported metal catalyst. The catalyst consists of a series of small platinum particles on an inert silica (SiO_2) support. Generally, the platinum provides most of the catalytic activity. However, the silica is there to both add mechanical strength to the catalyst, and to spread out the platinum over more surface area.

Supported metals are fundamentally similar to the homogeneous transition metal catalysts discussed in Section 12.2.2. The catalyst contains an active metal that does chemistry similar to that discussed in Section 12.2. However, the metal is attached to the support. The support spreads out the metal and holds the metal in place, so the catalyst is easy to separate from the reacting mixture. Supports tend to be high-surface-area materials; aluminum oxide, silicon dioxide, and activated carbon. Generally, most supported metal catalysts contain group VIII or group Ib metals, although other transition metals and rare earths also show catalytic activity.

Table 12.7 shows a selection of the reactions commonly run on supported metal catalysts. Generally metals are used to hydrogenate and dehydrogenate hydrocarbons, to oxidize substances, and to generally catalyze hydrocarbon conversions. Supported metal catalysts are used in the catalytic converter in your car and your wood stove. People

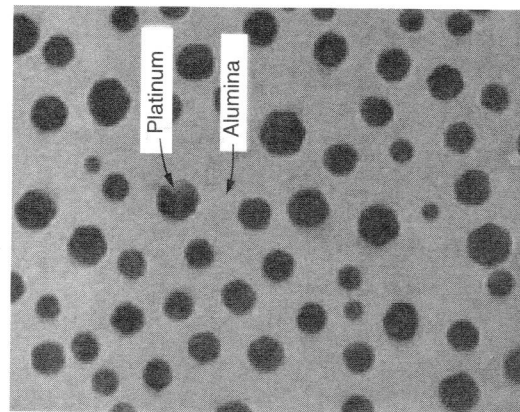


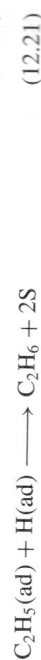
Figure 12.4 A supported metal catalyst.

Table 12.7 A selection of the reactions catalyzed by supported metals

Reaction	Catalyst	Reaction	Catalyst
Hydrocarbon hydrogenation, Dehydrogenation	Pt, Pd, Ni	$\text{CO} + \text{H}_2 \Rightarrow$ hydrocarbons (Fischer-Tropsch)	Fe, Rh
(CO) oxidation, total oxidation of hydrocarbons	Pt, Pd, Cu, Ni, Fe, Rh, Ru	Steam reforming for production of hydrogen	Ni plus additives
$(\text{C}) + 2\text{H}_2 \Rightarrow \text{CH}_3\text{OH}$	Cu/ZnO	Reforming (isomerization of oil)	Pt/Rc/Al ₂ O ₃
$2\text{CO} + 2\text{NO} \Rightarrow 2\text{CO}_2 + \text{N}_2$	Pt, Rh, Ru (catalytic converter)	$2\text{NH}_3 + \text{O}_2 \Rightarrow \text{N}_2\text{O}_3 + 3\text{H}_2\text{O}$	Pt
$\text{N}_2 + 3\text{H}_2 \Rightarrow 2\text{NH}_3$	Fe, Ru, Rh	Alcohols + $\text{O}_2 \Rightarrow$ aldehydes + H_2O , e.g., $2\text{CH}_3\text{OH} + \text{O}_2 \Rightarrow 2\text{H}_2\text{CO} + \text{H}_2\text{O}$	Ag, Cu
$2\text{C}_2\text{H}_4 + \text{O}_2 \Rightarrow$ 2-ethylene oxide	Ag, Cu	$\text{R}-\text{R}' + \text{H}_2 \Rightarrow \text{RH} + \text{HR}'$ (hydrogenolysis)	Ni, Co, Rh, Ru

are starting to sell supported metal catalysts to clean the air in your home. Most major industrial chemicals are made with a supported metal or a metal oxide catalyst. Chapter 14 will be devoted to a detailed discussion of supported metal catalysts. However, the thing to remember for now is that virtually all reactions where you add or subtract an atom from a molecule are run on a supported metal catalysts or a metal oxide catalyst.

Supported metal catalysts work just like homogeneous transition metal catalysts. For example, platinum catalyses the hydrogenation of ethylene via the same series of steps as the Wilkinson catalyst:



where S is an empty site on the surface of the platinum and the (ad) denote species attached to the surface of the platinum. In this case the platinum is stabilizing hydrogen atoms and ethyl groups. The stabilization tremendously speeds up the rate of reaction as discussed in Section 1.2.

12.3.2 Special Reactions on Supported Metal

Reactions (12.18)–(12.21) can occur on either a cluster or a supported metal catalyst. However, there are a few reactions that occur only on supported metal catalysts.

For example, the conversion of acetylene to benzene occurs readily on a palladium catalyst, but at the time this book was written, the reaction had not yet been seen on a cluster compound.

The overall reaction is



Physically, in order for reaction (12.22) to occur, the catalyst needs to simultaneously coordinate three acetylene molecules. That is easy on a metal surface because there are many atoms on the surface to hold the acetylene. In contrast, the reaction is difficult on a single transition metal atom in solution. I expect that as people begin to make larger cluster compounds, they will observe reaction (12.22). However, at present, metal cluster compounds with multiple metal atoms are difficult to make. In contrast, it is easy to get a cluster of atoms on a supported metal catalyst.

The mechanism of metal catalysis will be discussed in detail in Chapter 14. However, the thing to remember for now is that like metal atoms, metal surfaces stabilize radical intermediates. In Chapter 4 we found that an increase in the intermediate can tremendously enhance the rate of a reaction.

12.3.3 Transition Metal Oxides, Nitrides, Sulfides, and Carbides

In Table 12.7, we listed reactions that are commonly run on pure metals. However, there are a number of reactions that are instead run on transition metal oxides or sulfides they are listed in Table 12.8. I usually think of a transition metal oxide, nitride, sulfide, or carbide catalyst as being a transition metal catalyst that has been poisoned (i.e., slowed down)

Table 12.8 A selection of the reactions catalyzed by transition metal oxides, nitrides, and sulfides

Reaction	Catalyst	Reaction	Catalyst
$2\text{SO}_2 + \text{O}_2 \Rightarrow 2\text{SO}_3$	V_2O_5	$\text{CO} + \text{H}_2\text{O} \Rightarrow \text{CO}_2 + \text{H}_2$ (water-gas shift)	FeO , CuO , ZnO
Hydrodesulfurization	CoS , MoS , WS	$2(\text{CH}_3)_3\text{COH} \Rightarrow$ $(\text{CH}_3)_3\text{COC}(\text{CH}_3)_3 +$ H_2O	TiO_2
$\text{CH}_3\text{CH}=\text{CH}_2 + \text{O}_2 \Rightarrow$ $\text{CH}_2=\text{CHCHO} +$ H_2O	$(\text{Bi}_2\text{O}_3)_x(\text{MoO}_3)_y$ (bismuth molybdate) uranium antimonate	$2\text{CH}_3\text{CH} =$ $\text{CH}_2 + 3\text{O}_2 + 2\text{NH}_3 \Rightarrow$ $2\text{CH}_2=\text{CHC}\equiv\text{N} +$ $6\text{H}_2\text{O}$ (aminoxidation)	$(\text{FeO})_x(\text{Sb}_2\text{O}_3)_y$
$4\text{NH}_3 + 4\text{NO} + \text{O}_2 \Rightarrow$ $4\text{N}_2 + 6\text{H}_2\text{O}$ (selective catalytic reduction)	V_2O_5 , TiO_2	$\text{Benzene} + \text{O}_2 \Rightarrow$ maleic anhydride + water naphthylene + $\text{O}_2 \Rightarrow$ phthalic anhydride + water	$(\text{V}_2\text{O}_5)_x(\text{PO}_4)_y$
$\text{CH}_3\text{CH}_2(\text{C}_6\text{H}_5) +$ $\text{O}_2 \Rightarrow$ $\text{CH}_2=\text{CH}(\text{C}_6\text{H}_5) +$ H_2O (styrene production)	FeO	Selective oxidation of hydrocarbons	NiO , Fe_2O_3 , V_2O_5 , TiO_2 , CuO , Co_3O_4 , MnO_2
Aromatization, e.g. heptane \Rightarrow toluene H_2 or H_2O	$\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$	Hydrodenitrogenation	NiS , MoS

via addition of oxygen, nitrogen, carbon, or sulfur. The same types of chemistry occur on the metal-metal oxide, nitride, sulfide, or carbide catalyst as on the pure metal. However, the reaction is slower on the metal-metal oxide, nitride, sulfide, or carbide catalyst. In particular, side reactions are suppressed. As a result, metal oxide, nitride, sulfide, and carbide catalysts can sometimes be used to promote very selective transformations.

For example, let's assume that you want to design a system to selectively oxidize ethane to ethylene. You can oxidize ethane to ethylene over a platinum mesh catalyst provided you run the reaction at high temperatures (1000°C), and keep the residence time short (10^{-3} seconds or less). However, if you run the reaction longer, the ethylene is further oxidized to eventually produce CO_2 and water.

One can avoid the need for a short residence time by running the process on a metal oxide catalyst. Commercially, one normally runs the reaction on an iron oxide catalyst. The metal oxide is less reactive than platinum. The primary reaction to produce acetylene is slowed. However, the secondary reaction to produce CO_2 and H_2O is slowed to a greater extent. As a result, the iron catalyst can selectively oxidize the ethane to ethylene and not produce much CO_2 .

Generally, the mechanism of the oxidation of ethylene is similar to the mechanism of the hydrogenation of ethylene [reactions (12.19), (12.20), and (12.21)], except that the reaction occurs in reverse. First the ethane dissociatively adsorbs, then the ethylene is dehydrogenated and then the product desorbs:

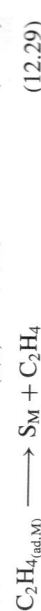
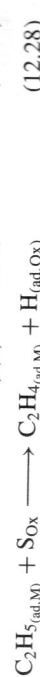
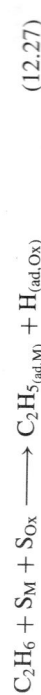


Oxygen then reacts with the hydrogen to produce



All of these steps are the reverse of the steps mentioned in Section 12.3.1.

In the literature, it is unusual to find the mechanism written this way. The reason is that in a metal oxide catalyst, there are two types of sites: (1) metal sites, which I will call S_M sites; and (2) oxygen sites, which I will call S_{Ox} sites. Ethylene normally binds to a metal site while hydrogen prefers to bind to an oxide site. As a result one can rewrite the mechanism as:



where the notation (ad,M) is used to denote a species attached to a metal atom while, $\text{H}(\text{ad},\text{Ox})$ denotes a hydrogen attached to a lattice oxygen. Notice that the $\text{H}(\text{ad},\text{Ox})$ is basically a hydroxyl group. In Chapter 5, we found that hydroxyls can react with hydrocarbons like ethane via the reaction



The $H_{(ad,Ox)}$ can react in the same way:



where the \square represents a lattice site that has been depleted of oxygen.

Reaction (12.31) depletes lattice oxygen, which is replaced via O_2 adsorption:



This example illustrates the one major difference between reactions on transition metals and on transition metal oxides. On transition metals, all of the reacting species are adsorbed on the metal. With metal oxides, the lattice oxygen is a major player in the reaction.

People often think of reactions on metal oxides as oxidation reduction reactions, where metal is reduced, then reoxidized. Generally, there is more going on than just oxidation–reduction. However, oxidation–reduction is a key part of the catalytic cycle.

12.3.4 Solid Acids And Bases

In Section 12.3.2, we discussed transition metal oxides. Transition metal oxides have weak metal–oxygen bonds, and so oxygen can be easily exchanged. By comparison, the metal–oxygen bond in alumina is so strong that the bond is not easily broken. As a result, alumina is not a good oxidation catalyst. Still, there is some important chemistry that occurs on metal oxides with strong metal–oxygen bonds. The objective of this section is to give an overview of the key chemistry.

Generally, metal oxides with strong metal–oxygen bonds are acids or bases. For example, you know that H_2SO_4 is a strong acid. Well, H_2AlO_3 is a strong acid, too. $AlCl_3$ and $FeCl_3$ are strong Lewis acids. There are strong Lewis acid sites on Al_2O_3 . Silica (SiO_2) can stabilize the acid sites, so silica aluminas are quite effective solid acid catalysts.

There are also special acids, like (SbF_5) and sulfated zirconia, which are much stronger acids than H_2SO_4 . These compounds are also effective acid catalysts.

Na_2O and MgO are strong bases. They are used to catalyze basic reactions.

Table (12.9) shows several other examples. All of the materials in Table (12.9) are strong acids or bases.

Industrially, most acid-catalyzed reactions are run on a special class of solid acids called **zeolites**. Zeolites are highly porous silica/aluminas. The pore structure is very uniform. Generally, the structures consist of cages that are stacked one on top of another. Figure 12.5 shows one of the cages in a material called *faugasite*. The uniform pores

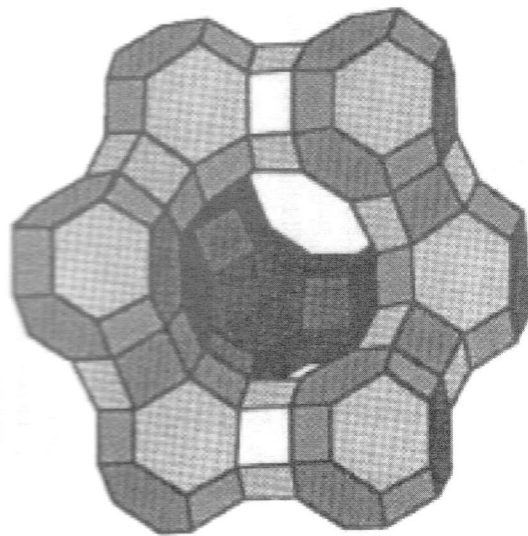


Figure 12.5 A diagram of the pore structure in faugasite.

allow people to design zeolites with special mass transfer properties that enhance the selectivities of reactions. This idea will be discussed in greater detail later in this chapter. Industrially, most of the acid-catalyzed reactions listed in Table 12.2 are actually run on solid acids. The one major exception is butane alkylation, which is still commonly catalyzed with hydrofluoric acid.

12.3.5 Polymer-Bound Catalysts

All of the heterogeneous catalysts we have discussed so far in this chapter were heterogeneous by their nature. The catalysts were solids. Solids have the advantage that they are easy to separate at the end of a reaction, so they are generally cheaper to use than are homogeneous catalysts. In the 1970s and 1980s there was a lot of effort devoted toward starting with a homogeneous catalyst, and anchoring the catalyst to a polymer to produce a material that is catalytically active and easy to separate from the products. For example, immobilized enzymes, that is, enzymes bound to polymer beads, were tried as reusable enzyme catalysts. People also tried bonding transition metal salts to polymers and using the resultant materials as catalysts. Acid groups were also bound to polymers. Acid-bound materials are currently being used as catalysts. When this book was being written, none of the other materials had made it into industrial practice. Still, people continue to discuss polymer bound catalysts in the literature, and so I decided to mention them.

12.3.6 Photocatalysts

There is one other class of catalysts that I did not have a place for anywhere else, so I decided to list separately: photocatalysts. Photocatalysts are catalysts that are inactive under normal conditions, but when the catalysts are irradiated with UV light, the catalysts become activated. At present, there are only three important photocatalysts:

Table 12.9 Some common solid acids and bases

Material	Type	Material	Type
Silica/alumina	Solid acid	Mordenite	Zeolite
Alumina	Solid acid	ZSM-5	Zeolite
Y-zeolite faugasite	Zeolite	VFI	Large-pore zeolite
Sodalite	Zeolite	Offretite	Zeolite
HF– SbF_5	Superacid	HSO_3F	Superacid
$H_2[Ti_6O_4(SO_4)_4(OEt)_{10}]$	Superacid	Sulfated zirconia	Superacid
MgO	Solid base	Na_2O	Base

- TiO_2 and TiSrO_3
- Fe_2O_3
- Mercury vapor

TiO_2 is commonly used as a catalyst for destruction of hydrocarbon wastes in aqueous environments. The main mode of catalytic action is for water to react with the O^{2-} in the titania surface to yield



TiO_2 is a semiconductor. When light hits the semiconductor, the light interacts with the semiconductor to produce free electrons and holes (positive charges). The charges can promote reaction. The holes can then react with the OH^- s to yield OH radicals:



where h^+ is a hole.

The OH radicals then oxidize hydrocarbons:



Electrons react with O_2 to regenerate the O^{2-} lattice:



which can also oxidize species.

Fe_2O_3 works similarly to TiO_2 except that Fe_2O_3 is much less catalytically active than TiO_2 .

Mercury vapor works via a different mechanism. Mercury is relatively unreactive in its ground state, but once the mercury is promoted into the $^3\text{P}_1$ state, the mercury becomes quite reactive. For example, the excited mercury can extract hydrogen from a hydrocarbon:



Then the mercury falls back to its ground ($^1\text{S}_0$) state, releasing the hydrogen:



The result is that mercury vapor can initiate gas-phase radical chemistry and act much like the radical catalysts described earlier in this chapter.

Industrially, people rarely use mercury anymore because mercury is so toxic. However, there are many papers on the topic.

12.3.7 Summary

At this point, then, we have listed many different types of catalysts and briefly mentioned how they work. When I teach this course I find that students are often overwhelmed by all of the variations; and in reality there are reasons to say that the variations are overwhelming. In fact, that has been the main point of the sections so far in this chapter: there are many variations. Many substances can act as catalysts.

As I said earlier, I recommend that the reader memorize everything in Tables 12.2–12.9. The material in these tables will be necessary background for the things that follow.

12.4 GENERAL OVERVIEW OF CATALYTIC ACTION

At this point, we will be changing topics. So far we have been discussing what catalysts are like. Now, we will start to discuss how catalysts work.

Catalysts work by changing the local environment around the reactants. The change in the local environment stabilizes intermediates and modifies the forces between the reactants. These changes can be used to promote a desired reaction.

The idea that rates of reactions can vary with the local environment around the reactants goes back to the early days of kinetics. In 1817, sir Humphry Davy found that he could prevent explosions in coal mines if he surrounded the candles used to illuminate the mines with a platinum shield. A few years later, Michael Faraday examined the fundamental processes in Davy's lamp. In 1834 Faraday proposed that the platinum was catalyzing the termination reactions in the flame by acting in two key ways. The platinum was holding the reactants in close proximity so that they could react. The platinum was also modifying the forces between the reactants to stimulate the reaction.

A few years later, Jöns Berzelius (1836a,b) did extensive studies on catalysts. At that time people did not know about molecules. However, Berzelius proposed that the catalyst changed the rate by modifying the forces between the reactants to stimulate reactions. Another idea in the literature came from the work of Jean-Baptiste Perrin (1919), who suggested that catalysts were able to transfer energy into the reactants and thereby overcome the energy requirements needed to activate molecules. Finally, Paul Sabatier (1913) suggested that the catalysts stabilized intermediates, thereby promoting a reaction.

Over the years there have been many arguments about whether Faraday, Berzelius, Sabatier, or Perrin were correct. However, we now know that they were all correct. Catalysts can work in a variety of different ways, and if you look at different reactions, you can find many different modes of catalyst action. When I teach my catalysis course, I give the following list of ways a catalyst can be designed to work:

- Catalysts can be designed to help initiate reactions.
- Catalysts can be designed to stabilize the intermediates of a reaction.
- Catalysts can be designed to hold the reactants in close proximity.
- Catalysts can be designed to hold the reactants in the right configuration to react.
- Catalysts can be designed to block side reactions.
- Catalysts can be designed to sequentially stretch bonds and otherwise make bonds easier to break.
- Catalysts can be designed to donate and accept electrons.
- Catalysts can be designed to act as efficient means for energy transfer.

It is also important to realize that

- One needs a catalytic cycle to get reactions to happen.
- Mass transfer limitations are more important when a catalyst is present.

There are many ideas here so it is useful to consider an example. Consider the reaction



In chapter 5 we found that the reaction goes via the following mechanism:



In actual practice, the reaction goes through a catalytic cycle, as will be discussed later in this chapter. However, for now we will assume that the reaction goes only once, and try to see how a catalyst can work.

Figure 12.6 shows how the free energy of the system changes during the reaction in the gas phase. The system goes uphill during the initiation step, and more uphill during the first reaction step. Then everything is downhill to products.

The first way a catalyst can work is to help initiate the reaction by reducing the initial steep rise in energy as shown in Figure 12.6b. According to the Polanyi relationship, when you reduce the initial rise, you will decrease the barriers to reaction.

The next way that a catalyst works is to stabilize the intermediates as shown in Figure 12.6c. The idea is to bind to the reactants just enough that the reaction never has to go uphill. That way the overall barrier for reaction is reduced.

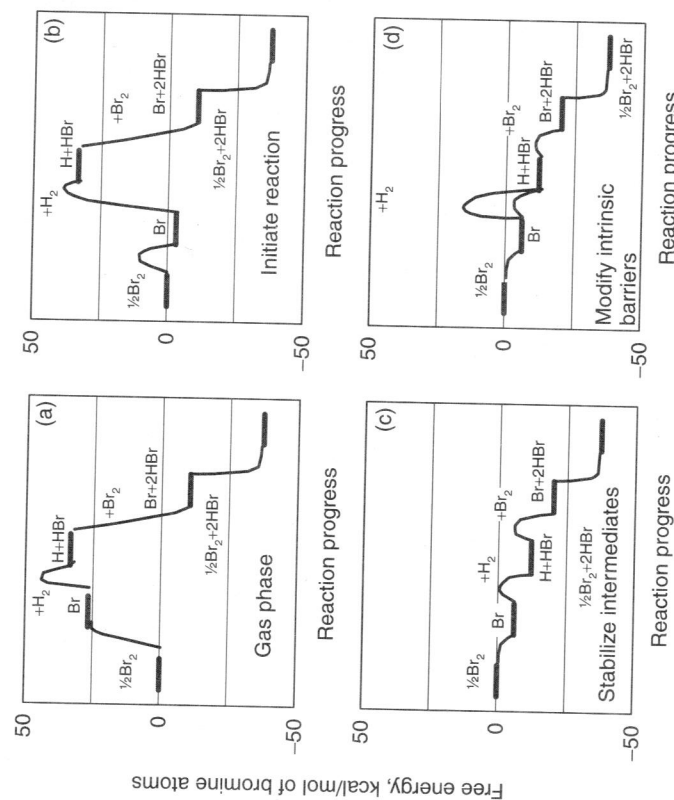


Figure 12.6 An illustration of some of the ways a catalyst can affect the free-energy changes during a reaction.

The third main way a catalyst works is to adjust the intrinsic barriers at each stage of the reaction as indicated in Figure 12.6d. Generally you want to lower the intrinsic barriers for desired reactions and raise the intrinsic barriers for undesirable reactions. One can lower the intrinsic barriers by changing either the entropy or the enthalpy of activation. You can lower the entropy of activation by holding the reactants close together and in the right configuration to react. You can lower the enthalpy of activation by either stretching bonds, thereby making them easier to break, or by adjusting the charge to moderate the Pauli repulsions between the reactants.

These ideas will be discussed in detail in the next several sections. It would be unusual for a catalyst to do all of these things. The very best catalysts might help initiate the reaction, stabilize the reactants, hold the reactants in close proximity and in the right configuration to react, and possibly block side reactions. However, few catalysts work that efficiently. I view the list above as a list of things that you would ideally want the catalyst to do. However, few catalysts do *all* of those things. In the next several sections we will choose examples to illustrate each of these effects.

Another point is that much of the material from here on will be qualitative. People know in a qualitative way how catalytic reactions work. However, very few of the ideas have been quantified enough that one can use them to make practical calculations.

I used the word "catalyst" in the last few paragraphs, but I do not want to restrict the discussion to conventional catalysts. People now know, for example, that a solvent can act like a catalyst. Solvents can modify the forces between reactants, stabilize intermediates, hold the reactants in close proximity, and act as efficient media for energy transfer. Other condensed phases can also act as catalysts. In the literature it has become common to treat the effects of solvents separately from the effects of catalysts. However, we now know that the principles of catalytic action and the principles of solvation are almost the same. Therefore, I find it convenient to treat catalysts and solvents as having fundamentally the same types of influence on rates.

In the next several sections we will discuss how a solvent or a catalyst can modify the rate of a reaction. We will concentrate on the general principles that apply to a large number of systems. Specific information about different catalyst systems will be given in Chapters 13 and 14.

12.5 CATALYSTS CAN BE DESIGNED TO INITIATE REACTIONS

The basis for all of our analysis will be a simple observation, discussed in Masel (1996): Catalysts seldom change the mechanisms of reactions; catalysts change only the initiation processes and the rates and selectivities of reactions. For example, McKenney et al. (1963) found that at 200 K the rate of the reaction



goes up by a factor of about 10^9 if one adds NO_2 to the reacting mixture. The mechanism of reaction (12.41) does not change substantially in the presence of the catalyst. The only major change is in the initiation step.

Recall from Chapter 5 that reaction (12.41) goes via the following mechanism:

Initiation



Transfer



Propagation



Termination



If fact, NO_2 changes the reaction in a very simple way. Recall that NO_2 is paramagnetic. It has an unpaired electron. The presence of the unpaired electron makes NO_2 a "stable radical". NO_2 can do radical chemistry even though NO_2 is a stable species.

Now, let's use the material in Chapter 5 to guess how the presence of NO_2 would affect the rate. Let's consider the reaction



According to the analysis in Chapter 5, when an NO_2 molecule collides with ethane, the main reaction will be a hydrogen transfer process:



Once one forms the C_2H_5 the C_2H_5 can react via reactions (12.44) and (12.45). Reaction (12.50) is about 20 kcal/mol endothermic, and according to the analysis in Chapter 5, it should have an intrinsic barrier of 14 kcal/mol. If one plugs the intrinsic barrier into the Polanyi relationship, one finds that reaction (12.50) should have an activation barrier of about 25 kcal/mol. By comparison, reaction (12.42) has an activation barrier of about 90 kcal/mol. The result is that reaction (12.50) is usually much faster than reaction (12.42). The increase in the initiation process means that reaction (12.41) is much faster in the presence of NO_2 than in the absence of NO_2 .

This example illustrates a key point:

Catalysts can initiate reactions. The mechanisms are similar to the mechanisms without a catalyst, but the initiation process is much faster with the catalyst.

The increase in the initiation rate produces a tremendous increase in the overall rate of reaction. One can quantify the effect using analysis similar to that in Section 12.7. In the case above, the presence of NO_2 increases the rate by a factor of 10^6 at 750 K.

Table 12.10 shows several other examples where catalysts initiate reactions. Notice that a wide range of reactions can be initiated by catalysts. Not all catalysts work this way, of course. However, catalysts can be designed to initiate chemical reactions.

Table 12.10 Some examples of reactions initiated by catalysts

Reaction	Catalyst	Mechanism of Initiation
$\text{CH}_4, \text{C}_2\text{H}_6 \Rightarrow \text{C}_2\text{H}_4 + \text{H}_2$	NO_2	$\text{NO}_2 + \text{CH}_3\text{CH}_3 \rightarrow \text{HNO}_2 + \text{CH}_3\text{CH}_2\cdot$
$\text{CH}_3\text{COH} \Rightarrow \text{CH}_4 + \text{CO}$	I_2	$\text{X} + \text{I}_2 \rightarrow 2\text{I} + \text{X}$ $\text{I} + \text{CH}_3\text{COH} \rightarrow \text{HI} + \text{CH}_3\text{CO}\cdot$
Ethylene \Rightarrow polyethylene	$\cdot\text{ROOR}$	$\text{ROOR} \rightarrow 2\text{RO}\cdot$ $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\cdot + \text{nCH}_2\text{CH}_2 \Rightarrow$ polyethylene $\text{CH}_2 \rightarrow \cdot\text{ROCH}_2\text{CH}_2\cdot$
$\text{H}_2 + \text{Br}_2 \Rightarrow 2\text{HBr}$	Metallic platinum	$\text{Br}_2 + 2\text{S} \rightarrow 2\text{Br}\cdot_{\text{ad}}$
Propylene \Rightarrow polypropylene	Ti^{4+}	$\text{Ti}^{4+} + \text{propylene} \rightarrow \text{CH}_3\text{CHTiCH}_2^+$ $\text{CH}_3\text{CHTiCH}_2^+ + \text{nC}_3\text{H}_6 \Rightarrow$ polypropylene
$\text{C}_2\text{H}_5\text{OH} \Rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$	H^+	$\text{C}_2\text{H}_5\text{OH} + \text{H}^+ \rightarrow [\text{C}_2\text{H}_5\text{OH}_2]^+$ $[\text{C}_2\text{H}_5\text{OH}_2]^+ \rightarrow [\text{C}_2\text{H}_5]^+ + \text{H}_2\text{O}$ $[\text{C}_2\text{H}_5]^+ \rightarrow \text{C}_2\text{H}_4 + \text{H}^+$
$2\text{O}_3 \rightarrow 3\text{O}_2$	Cl	$\text{O}_3 + \text{Cl} \rightarrow \text{O}_2 + \text{ClO}$

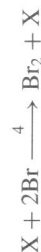
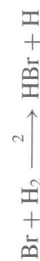
12.6 CATALYSTS CAN BE DESIGNED TO STABILIZE INTERMEDIATES

Another way that catalysts can change rates of reaction is by stabilizing intermediates. In Chapter 2, we noted that at 200°C the rate of the reaction



goes up by a factor of 10^8 in the presence of a platinum catalyst. Well, the mechanism of reaction (12.51) does not change dramatically in the gas phase and on the catalyst. It is just that the rates of many of the elementary reactions are much slower in the gas phase than on the catalyst.

Platinum is able to catalyze reaction (12.51) mainly because the platinum stabilizes the intermediates of the reaction. In Chapter 5 we found that in the gas phase reaction (12.51) goes by the following mechanism:



Focusing on the figure, we see that first the Br_2 dissociates to form bromine atoms. That costs 26.74 kcal/mol. Then the bromine atoms react with H_2 to produce hydrogen atoms and HBr . That reaction is another 6.8 kcal/mol endothermic. Then there is a cycle where a Br_2 reacts with a hydrogen atom to produce HBr and a bromine atom. That reaction is 44 kcal/mol exothermic. Then the bromine atom reacts with H_2 to yield HBr and the hydrogen atom. That reaction is 6.8 kcal/mol endothermic.

The cycle repeats several times. Each time the system goes through the cycle, two molecules of HBr are produced. Consequently, the enthalpy of the system goes down by twice the heat of formation of HBr or 37.16 kcal/mol. We indicated two cycles in the figure, but the system actually goes through the cycle hundreds of times. Eventually, the reaction terminates.

In the literature people often redraw Figure 12.7, assuming that the reaction terminates after completing one cycle. The diagram assuming that the reaction terminates after completing one cycle is shown in Figure 12.8. The key feature of Figure 12.8 is that the reaction needs to go uphill twice for the reaction to proceed. That makes the reaction rather slow.

Figure 12.9 shows how the enthalpy changes that occur during the reaction vary if you run the reaction on a platinum surface. The platinum binds to the intermediates of the reaction. The enthalpy of formation of the intermediate is lowered by the strength of the adsorbate-surface bond. This stabilization of intermediates is a key process on platinum.

Notice that on platinum all of the steps in the mechanism except the termination step lower the enthalpy of the system. There is only one uphill step, and its barrier is small. That makes the reaction $\text{H}_2 + \text{Br}_2 \Rightarrow 2\text{HBr}$ very rapid on $\text{Pt}(111)$.

Most catalysts speed up reactions by binding to some key intermediate and thereby stabilizing the intermediate. That increases the intermediate concentration, and thereby

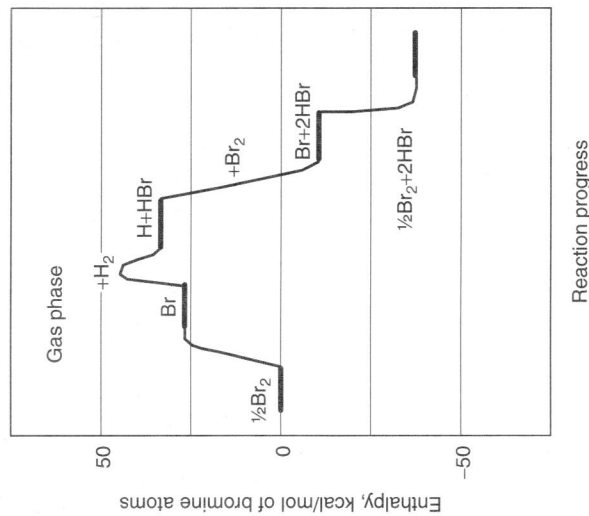


Figure 12.8 The enthalpy changes during the gas-phase reaction $\text{H}_2 + \text{Br}_2 \Rightarrow 2\text{HBr}$ assuming that the reaction terminates after one cycle.

In Chapter 5, we found that during reaction (12.52), most HBr is being produced in a catalytic cycle. First a bromine atom reacts with a H_2 to produce an HBr and an H atom. The hydrogen atom then reacts with the Br_2 to generate more HBr and regenerate the bromine atom. Note that in Section 4.3 we found that the rate of reaction (12.52) is directly proportional to the bromine concentration in the gas phase, so if we could find a way to increase the bromine atom concentration, we would increase the rate.

Now, it should not take much to enhance the rate. One can show that at 200°C , the bromine atom concentration should be about 10^{-17} mol/liter. Bromine atoms are the active centers during reaction (12.52), and with only 10^{-17} mol/liter of bromine atoms, the rate is limited by a shortage of bromine atoms.

One could imagine trying to find a way to increase the concentration of bromine atoms using a solvent. After all, we know that many different molecules will dissociate in solution. If we could find a solvent that dissociated the Br_2 to yield bromine atoms, we would increase the rate of reaction.

I do not know of any simple solvent that will dissociate Br_2 . However, Br_2 does dissociate when Br_2 adsorbs on platinum to yield chemisorbed bromine atoms. Physically, the platinum is acting just like a solvent when it dissociates the Br_2 . The free electrons in the platinum form a cage around the bromine atoms in exactly the same way that a solvent forms a cage around an ion in solution. The solvent cage is different in a metal than in a liquid because electrons behave differently than solvent molecules. Still, the process is fundamentally just like solvation. The electrons in the platinum solvate the bromine atoms, so that bromine atoms are stable on the platinum surface.

Just to quantify things, at saturation, the bromine atom concentration in the adsorbed layer is about 50 mol/liter. By comparison under similar conditions, the bromine atom concentration is about 10^{-17} mol/liter in the gas phase.

This is a general finding. The first key role of any catalyst is to increase the concentration of the active species. Increases of 20 orders of magnitude in the intermediate concentration are typical. That has a tremendous influence on the rate.

In the literature it is common to view the stabilization of intermediates in terms of the changes in the enthalpy of the system. To orient the reader, Figure 12.7 shows the enthalpy changes during the gas-phase reaction $\text{H}_2 + \text{Br}_2 \Rightarrow 2\text{HBr}$. The curve is very similar to that in Figure 12.6 except that the vertical axis is enthalpy, not free energy.

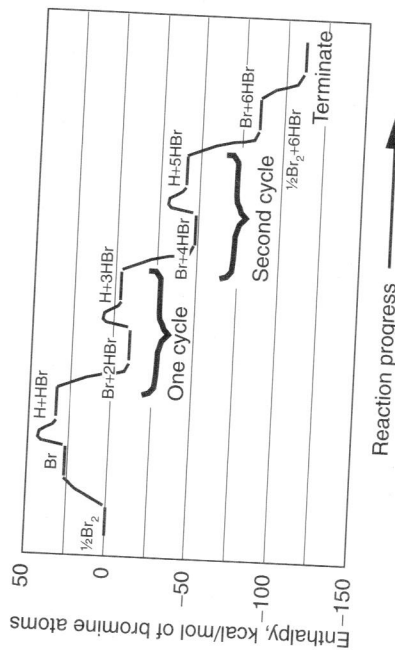


Figure 12.7 The enthalpy changes during the gas-phase reaction $\text{H}_2 + \text{Br}_2 \Rightarrow 2\text{HBr}$. The enthalpy is measured as the enthalpy per mole of bromine atoms produced in the initiation step.

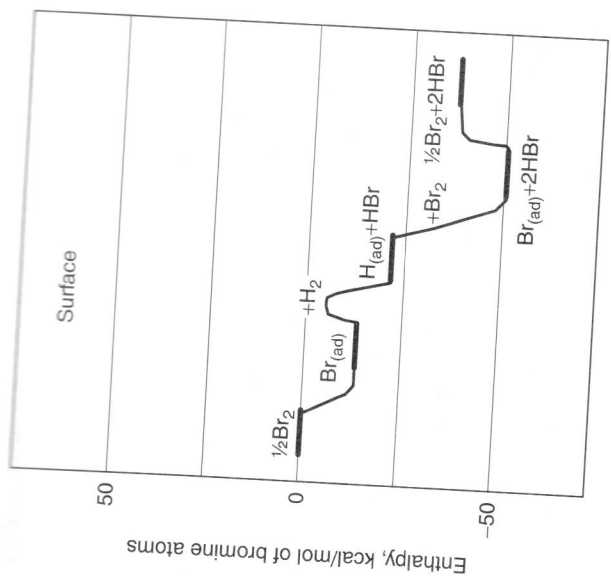


Figure 12.9 The enthalpy changes during the Rideal-Eley surface reaction $H_2 + Br_2 \Rightarrow 2HBr$ on Pt(111) assuming that the reaction terminates after one cycle.

increases the rate. One has to design the catalyst to selectively bind to the desired intermediate, and that is not always possible. However, most catalysts do increase the concentration of key intermediates.

12.6.1 Stabilization of Multiply Bound Intermediates

An alternative is for the catalyst to open up a new reaction pathway that would not be seen in the gas phase. In Section 12.6, we stated that catalysts seldom change the mechanism of a reaction. However, there are exceptions. The exceptions occur because the primary mechanisms of a reaction can vary with conditions. Catalysts can also stabilize intermediates that would be present only at very low concentrations in the gas phase. As a result, a minor reaction pathway in the gas phase can become a major reaction pathway in the presence of a catalyst.

Generally in the gas phase, one sees only monoradicals, that is, radicals with one dangling bond. However, on a solid catalyst one can see di- or triradicals, namely, species with multiple bonds to the catalyst. The ability to form multiple bonds allows reactions to occur that would not occur at reasonable rates in the gas phase. For example, consider a simple reaction:



Reaction (12.53) is extremely slow in the gas phase. According to the analysis in Chapter 5, in the gas phase, reaction (12.53) should occur via an initiation-propagation mechanism:

Initiation



Propagation



Termination



However, according to data in the CRC, reaction (12.55) is about 150 kcal/mol endothermic. Consequently, in the gas phase, reaction (12.55) is extremely slow at any reasonable conditions.

Everything changes in the presence of an iron catalyst. On iron, the nitrogen readily dissociates via the reaction



One can then hydrogenate the adsorbed nitrogen via the following reactions:



Notice that when reaction (12.59) occurs, six nitrogen-surface bonds form. According to Table 6.5, on iron, ΔH_f for forming a single nitrogen surface bond is -14 kcal/mol. Therefore, the heat of reaction of reaction (12.59) is $(-14) \times 6 = -84$ kcal/mol (exothermic). Consequently, there is no thermodynamic barrier to reaction (12.59). Consequently, reaction (12.59) can occur on an iron catalyst even though reaction (12.59) occurs negligibly slowly in the gas phase.

One can use the data in Table 6.4 to show that reactions (12.60)-(12.62) are each 21 kcal/mol endothermic on iron. If we substitute the 21 kcal/mol into the Polanyi relationship, we find that each reaction should have an activation barrier of about 28 kcal/mol. Such reactions are quite feasible at reasonable temperatures, which is why one uses an iron catalyst.

One does not see a similar reaction in the gas phase since according to data in the CRC handbook, in the absence of a catalyst, reaction (12.59) is 225 kcal/mol endothermic.

This example illustrates an important point. Nitrogen radicals with three unpaired bonds are fairly unstable. However, when nitrogen adsorbs onto an iron catalyst, the iron can form multiple bonds to the nitrogen. The possibility of forming multiple bonds allows reaction (12.53) to occur.

One can generalize these results to many other situations. One can design a catalyst that stabilizes covalently bonded di- and triradicals. That allows the catalytic reactions to

go via a reaction pathway that is not available in the gas phase.

Generally, the ability to form multiply bound species allows a catalyst to produce species that would not be produced at reasonable rates in the gas phase.

12.6.2 Stabilization of Ionic Intermediates

Another way that a catalyst can work is to stabilize ionic intermediates, thereby allowing ionic pathways to occur. Consider a simple isomerization reaction:



It is hard to find a feasible mechanism for reaction (12.63) in the gas phase. One possibility is for the R group to break off:



Then there could be an addition reaction:



Then a β -hydrogen elimination:



Reaction (12.64) is 120 kcal/mol endothermic. Further, this mechanism does not have a catalytic cycle. Consequently, according to the results in Section 5.4, the mechanism will have a very slow rate.

On the other hand, if one starts with a proton, H^+ in an acid catalyst, it is easy to find a catalytic cycle. First the proton reacts with the olefin to yield a carbocation:



Then the carbocation isomerizes:



Then the new ion loses a proton to form the products:



Reactions (12.67)–(12.69) have barriers of 20 kcal/mol or less. Notice that the addition of the acid catalyst has allowed the reaction to occur via an ionic species. None of the reactions have large barriers. The result is that the reaction is quite facile (speedy).

This example shows that an acid catalyst can facilitate reactions by helping to create ionic intermediates.

Again, one does have to design the catalyst properly to stabilize the ionic intermediates. Not all catalysts will work. Still, one can design solid acid catalysts that stabilize ionic intermediates and thereby catalyze reactions like reaction (12.63).

12.6.3 The Effect of Intermediate Stabilization on Rates — Can We Have Too Much of a Good Thing?

There is a subtle point in all of this—it is possible to stabilize an intermediate so much that the intermediate becomes unreactive. Therefore, one needs to be careful to choose the catalyst carefully.

In this section, we quantify how much rates go up in the presence of a catalyst and show that one can overstabilize an intermediate and thereby decrease the rate. We will go back to the example in Section 12.6, namely



and derive an expression for the reaction. To put the discussion in perspective, in Section 12.6, we found that the concentration of bromine atoms increases by a factor of 10^{17} in the presence of a platinum catalyst. Yet, the data in Table 12.1 show that the rate increases by a factor of only 10^8 . Other catalysts show much smaller rate enhancements even though the other catalysts increase the bromine atom by a factor of more than 10^{13} . Therefore, it appears that there is something else going on that prevents a 10^{17} increase in the intermediate concentration from producing a 10^{17} increase in rate.

In the remainder of this section, and in the next section, we will try to explain why the rate does not show a 10^{17} increase. To start off, it is useful to recall that a steady-state treatment of mechanism (12.52) shows that the rate of HBr formation via mechanism (12.52) is

$$r_{HBr} = 2k_2[H_2][Br] \quad (12.71)$$

where r_{HBr} is the rate of HBr formation; $[H_2]$ and $[Br]$ are the concentrations of hydrogen molecules and bromine atoms, respectively; and k_2 is the rate constant for the second reaction in mechanism (12.52). Therefore, if everything were equal, and k_2 did not change, one would expect the rate to increase by a factor of 10^{17} when the bromine atom concentration goes up by a factor of 10^{17} . However, experimentally, the rate goes up by a factor of only 10^8 .

There are several reasons why the rate changes by a factor of 10^8 . There are some mass transfer limitations, and there is a second reaction pathway involving a direct reaction between adsorbed hydrogen atoms and adsorbed bromine's. However, the key effect is that when you stabilize the bromine atoms on the platinum surface, the bromine atoms become less reactive so k_2 goes down.

This is also a general effect. Radicals are very reactive in the gas phase. You can stabilize the radicals by solvating them on a metal surface. However, then the radical becomes less reactive.

In the next section, we will quantify this effect. Our main tool will be the Polanyi relationship, which we derived in Chapter 10:

$$E_a = E_a^0 + \gamma_P \Delta H_i \quad (12.72)$$

where E_a is the activation barrier, E_a^0 is the intrinsic barrier to reaction, ΔH_i is the heat of reaction, and γ_P is the transfer coefficient. According to equation (12.72), when you change the heat of reaction, you also change the activation barrier of the reaction. Next, let's work out the implications of the Polanyi relationship for the reaction:



When you stabilize the bromine atoms, the free energy of the bromine atoms goes down. The enthalpy of the bromine atoms goes down, too, which means that the ΔH_f of reaction (12.73) becomes more positive. According to equation (12.72), when ΔH_f becomes more positive, the activation barrier for reaction (12.73) will increase. Consequently, k_2 will go down. Therefore, the implication of equation (12.72) is that when we stabilize the bromine atoms, the rate constants for reaction (12.73) will always go down.

Again, this is also a general effect. Whenever you stabilize a reactive intermediate, you increase the concentration of the intermediate. That generally increases the rate. However, there is always the secondary effect that the intermediate becomes less reactive. The loss of reactivity of the intermediate tends to partially counteract the effects of the increased stability of the intermediate, so the rate does not increase as much as the intermediate concentration increases.

Interestingly, there are some cases where one stabilizes the intermediate so much that the reaction slows down. For example, Sachtler and Fahrenfort (1958) and Fahrenfort et al. (1960) examined the decomposition of formic acid on a number of catalysts. Additional data is in Sachtler (1960). They found that the main reaction is



Sachtler and Fahrenfort (1958) suggested that reaction (12.74) occurred via a very simple mechanism: The formic acid first adsorbs to form a formate intermediate. Then the formate intermediate decomposes to yield CO_2 and H_2 .

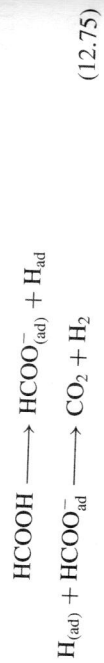


Figure 12.10 shows how the rate of formic acid decomposition changes as one changes the binding energy of the formate intermediate. Notice that the rate increases, reaches a maximum, and then declines. People call plots with a maximum like those in Figure 12.10 **volcano plots**. Most catalytic systems follow volcano plots.

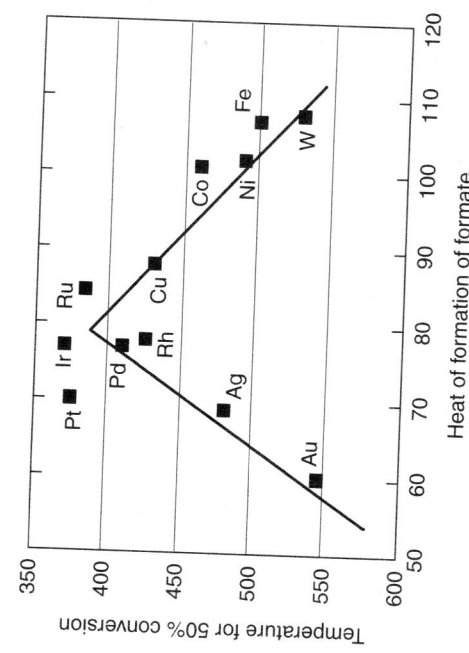


Figure 12.10 The rate of formic acid decomposition changes as a function of the binding energy of the formate intermediate.

The idea that rates reach a maximum was discovered by Sabatier (1913). Sabatier suggested that all reactions will follow a volcano plot. After all, an increase in the intermediate concentration will usually increase the rate. Still, Sabatier noted that you do not want the intermediate to be so stable that you produce the intermediate and not the product. Therefore, Sabatier proposed that volcano plots would be a universal phenomenon.

Sabatier also proposed what is now called **the principle of Sabatier**:

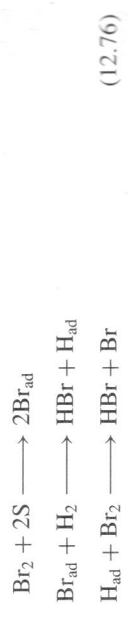
The best catalysts are substances that bind the reactants strongly, but not too strongly.

If you have a weakly bound intermediate, increasing the binding energy will increase the intermediate concentration, thus increasing the rate. On the other hand, if you have a strongly bound intermediate, the intermediate concentration is already high. In such a case, increasing the binding energy of the intermediate does not increase the intermediate concentration substantially. However, k_2 decreases. According to equation (12.71), if k_2 decreases, and the intermediate concentration does not increase by a comparable amount, the rate should decrease.

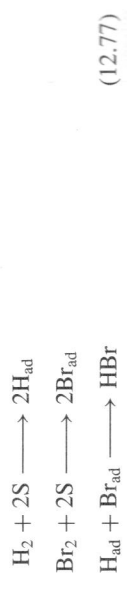
In actual practice, however, Sabatier's principle is not quite a universal phenomenon. There are few reactions where one observes a leveling off rather than a decline of the rate when you stabilize the intermediates too much. However, this is the exception. Most catalytic reactions follow Sabatier's principle.

12.7 DERIVATION OF SABATIER'S PRINCIPLE

Next, we want to show how the maxima arises in detail. Our approach will be to work out an equation for the rate, and use the equation to see if there is a maximum. Let's go back to reaction (12.51), HBr formation, and assume that we are running the reaction in an adsorbed layer. There are two reaction pathways for HBr formation: a Rideal-Eley mechanism



and a Langmuir-Hinshelwood mechanism



Where the names Rideal-Eley and Langmuir-Hinshelwood were discussed in Chapter 5. The Rideal-Eley mechanism is very similar to the gas-phase reaction, while the Langmuir-Hinshelwood reaction usually occurs only on a surface. For the purposes of this section we will ignore the Langmuir-Hinshelwood reaction, (12.77), even though on a real catalyst, the Langmuir-Hinshelwood reaction is faster than the Rideal-Eley reaction at moderate pressures. The Rideal-Eley reaction dominates at high pressures, however.

Following the discussion in Chapter 5, we will assume that the adsorption of bromine goes via the reaction



where S is a site on the surface that is available to hold gas as described in Chapter 5. We will also assume that reaction (12.78) is in equilibrium. At equilibrium, the bromine concentration is given by the following equation:

$$K_{\text{Br}} = \frac{[\text{Br}_{\text{ad}}]}{[\text{S}][\text{Br}_2]^{1/2}} \quad (12.79)$$

In equation (12.79), K_{Br} is the equilibrium constant for the adsorption process; $[\text{Br}_2]$, $[\text{Br}_{\text{ad}}]$, and $[\text{S}]$ are the concentrations of Br_2 , adsorbed bromine atoms, and bare surface sites.

Solving equation (12.79) for $[\text{Br}_{\text{ad}}]$, and substituting the result into equation (12.71) yields

$$r_{\text{HBr}} = 2k_2 K_{\text{Br}} [\text{H}_2][\text{S}][\text{Br}_2]^{1/2} \quad (12.80)$$

Next, we will attempt to consider how changes in the binding energy of the bromine atoms changes the rate of HBr formation. Well, when the binding energy of the bromine changes, K_{Br} goes up and k_2 goes down. In order to quantify the effect, we will assume that K_{Br} is given by

$$K_{\text{Br}} = \exp\left(\frac{-\Delta G_{\text{ad}}}{k_{\text{B}} T}\right) = \exp\left(\frac{-(\Delta H_{\text{ad}} - T\Delta S_{\text{ad}})}{k_{\text{B}} T}\right) \quad (12.81)$$

where ΔG_{ad} is the free energy of adsorption, ΔH_{ad} is the heat of adsorption, ΔS_{ad} is the entropy of adsorption, k_{B} is Boltzmann's constant, and T is the absolute temperature. According to Arrhenius' law, k_2 is given by

$$k_2 = k_2^0 \exp\left(\frac{-E_{\text{a},2}}{k_{\text{B}} T}\right) \quad (12.82)$$

where k_2^0 is the preexponential and $E_{\text{a},2}$ is the activation barrier for reaction 2. Substituting equation (12.72) into equation (12.82) yields

$$k_2 = k_2^0 \exp\left(\frac{-(E_{\text{a},2} + \gamma_{\text{P},2}\Delta H_{\text{r},2})}{k_{\text{B}} T}\right) \quad (12.83)$$

where $E_{\text{a},2}$ is the intrinsic barrier for reaction 2 in mechanism (12.76), $\Delta H_{\text{r},2}$ is the heat of reaction, and $\gamma_{\text{P},2}$ is the transfer reaction.

Note that as we change the heat of adsorption, ΔH_{r} changes, too. Let's define ΔH_0 as the heat of reaction when the heat of adsorption is zero. It is easy to show that when the heat of adsorption is nonzero, ΔH_{r} , the heat of reaction, is given by

$$\Delta H_{\text{r},2} = \Delta H_0 - \Delta H_{\text{ad}} \quad (12.84)$$

Substituting equations (12.81) and (12.83) into equation (12.80) and then substituting in equation (12.84) yields

$$r_{\text{HBr}} = 2k_{\text{Br}} \exp\left(\frac{(1 - \gamma_{\text{P},2})\Delta H_{\text{ad}}}{k_{\text{B}} T}\right) [\text{H}_2][\text{S}][\text{Br}_2]^{1/2} \quad (12.85)$$

with

$$k_{\text{Br}} = 2k_2^0 \exp\left(\frac{-(E_{\text{a},2} - \gamma_{\text{P},2}\Delta H_0 + T\Delta S_{\text{ad}})}{k_{\text{B}} T}\right) \quad (12.86)$$

There are two interesting cases to consider: (1) the case where $[\text{S}]$ is constant, so that there is no limit to the adsorbed bromine concentration; and (2) a case where $[\text{S}]$ decreases as bromine adsorbs, so that the surface can hold only a finite amount of bromine.

Figure 12.11 shows a plot of the rate of HBr formation as calculated from equation (12.85), assuming that $[\text{S}]$ is constant. Notice that the rate of HBr formation increases monotonically as the binding energy of the Br increases. Physically, if we assume that $[\text{S}]$, the number of bare sites, is constant, we are in effect assuming that there is nothing to slow down the adsorption of bromine. In such a case, the bromine concentration continues to increase as the binding energy of the bromine increases, and so the reaction rate increases monotonically with coverage.

Quite a different effect occurs if one assumes that the reaction follows a Langmuir adsorption isotherm. According to the analysis later in this chapter, if one adsorbs hydrogen and bromine onto the platinum catalyst, the hydrogen and bromine take up sites. $[\text{S}]$, the number of free sites, decreases as hydrogen and bromine adsorb. One can quantify this effect using an equation that we will derive in Section 12.17:

$$[\text{S}] = \frac{S_0}{1 + K_{\text{Br}_2} \sqrt{P_{\text{Br}_2}} + K_{\text{H}_2} \sqrt{P_{\text{H}_2}}} \quad (12.87)$$

Figure 12.12 shows a plot of the rate of HBr formation calculated from equation (12.85), with $[\text{S}]$ from equation (12.87) and $\gamma_{\text{P}} = 0.5$. Notice that Figure 12.12 shows a volcano plot similar to that in Figure 12.10, where the rate reaches a maximum a heat of adsorption (i.e., heats of formation of the intermediate) and then declines. Physically, when ΔH_{a}

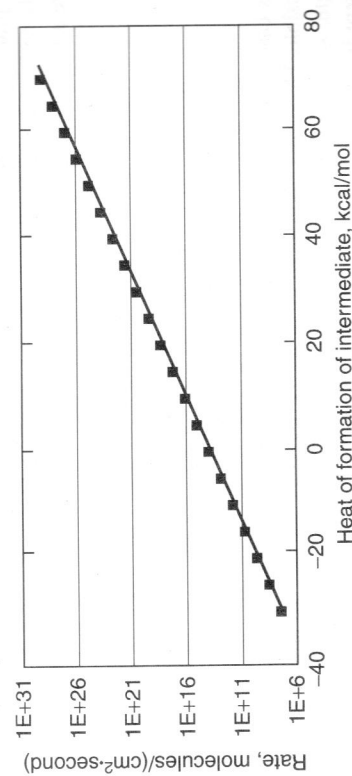


Figure 12.11 The rate of HBr formation as calculated from equation (12.85), with $[\text{S}] = 1 \times 10^{14} \text{ cm}^{-2}$ and $\gamma_{\text{P}} = 0.5$, $T = 500 \text{ K}$, $P_{\text{H}_2} = P_{\text{Br}_2} = 1 \text{ atm}$.

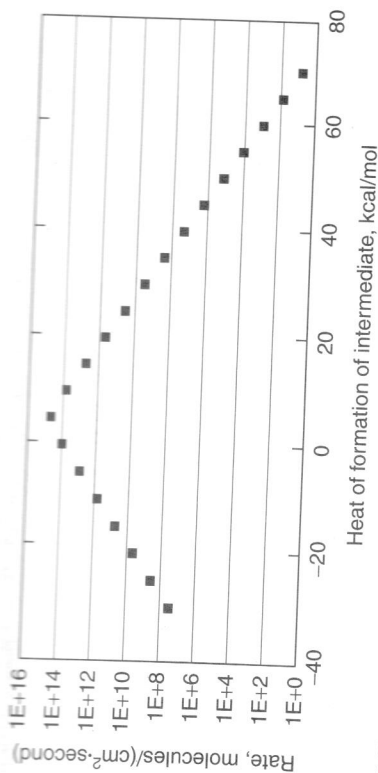


Figure 12.12 The rate of HBr formation calculated from equation (12.85), with [S] from equation (12.87) and $\gamma_p = 0.5$, $T = 500$ K, $P_{H_2} = P_{Br_2} = 1$ atm.

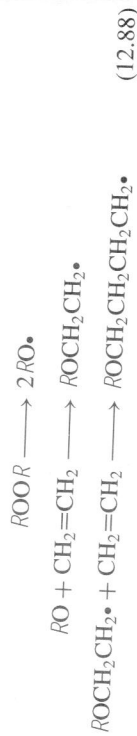
is small, increases in ΔH_a increase the intermediate concentration substantially. The increases in ΔH_a also decrease the reactivity of the intermediate since the intermediate is being stabilized, but that is a smaller effect. The net result is that the rate increases.

In contrast, once the surface fills up with reactants, further increases in ΔH_a do not produce substantial increases in the intermediate concentration. However, the increases in ΔH_a still decrease the reactivity of the intermediate. The net result is that the rate decreases. If one works through the numbers, one finds that there is a maximum rate at intermediate values of ΔH_a .

One also finds that for a given reaction on a given catalyst, there is an optimal temperature where the rate is maximized. That is why there is a maximum in Figures 2.16 and 12.2.

In actual practice, one almost always observes a maximum in the rate of reaction with increasing intermediate bond strength. Physically, with a heterogeneous catalyst, there are always a finite number of sites on the catalysts to hold reactants. Once all of the sites are filled, further increases in the bond strength of the intermediates mainly decreases the reactivity. With a homogeneous catalyst, there are only a finite number of complexes that you can make, before the catalysts are saturated. Once all the catalyst molecules are attached to reactants, further increases in bond strength decrease the activity.

In practice, Sabatier's principle works for most real catalysts. The one exception is in polymerization catalysts, such as a free-radical initiator. For example, a peroxide can initiate a free-radical polymerization via the mechanism



In this case, one wants the initiator, $RO\cdot$, to have as strong of a bond with the reactants as possible. Physically, the reactivity of the radical does not decline with increasing bond strength, so a high bond strength is helpful.

There is one other detail of note. One does not need to know the heat of adsorption of the key intermediates to construct a plot like Figure 12.12. Instead, one can use any measure of the bond strength as the x axis in Figure 12.12, and one will still get a

similar curve. This is very important because it often is quite difficult to know the heat of formation of a reactive intermediate. However, if one can find some other measure of the bond strength that is proportional to the heat of formation of the reactive intermediate, one can still construct a volcano plot.

In the literature, people often plot volcano plots as a function of the heat of formation of the bulk oxide per mole of oxygen. Figure 12.13 shows a plot of the heat of adsorption of a number of adsorbed intermediates as a function of the heat of formation of the bulk oxide per mole of oxygen. Notice that the heat of formation of the bulk oxide per mole of oxygen is proportional to the heat of adsorption of the reactive intermediate. A surface that binds some intermediates strongly tends to bind most adsorbates strongly as well. Therefore, one can construct a volcano plot using the heat of formation of the bulk oxides as the x axis (abscissa).

The advantage of this approach is that one can construct the volcano plot from data that are readily available, and so one can construct volcano plots for a wide number of reactions. Table 12.11 lists the heats of formation of a number of oxides. One can use the data in the table to construct volcano plots.

There is one subtlety in all of this. Table 12.11 gives the total heat of formation per mole of oxide. We actually want to scale the heat of formation to moles of adsorbate. Well, in the literature, there are two approaches to go to moles of adsorbate. One idea is to assume that the heat of formation of the intermediate is proportional to the heat of formation of the oxide *per mole of oxygen*. The second idea is to assume that the heat of formation of the intermediate is proportional to the heat of formation of the oxide *per mole of metal*. One also customarily assumes that if there are multiple oxides, the strongest oxide is the most important. If one makes these assumptions, one can plot the rate of a catalytic reaction versus the heat of formation of the oxide, and expect to observe a volcanolike curve.

There are two key types of plots in the literature:

- Plots of the log of the reaction rate versus the heat of formation of the oxide *per mole of oxygen*

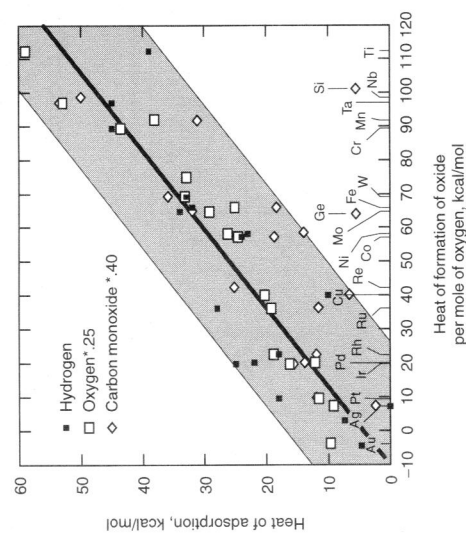


Figure 12.13 The heat of formation of adsorbed oxygen, hydrogen, and carbon monoxide on a number of metals as a function of the heat of formation of the corresponding oxide per mole of oxygen.

In summary, then, the results in this section show that if a substance binds the intermediates of a reaction strongly, but not too strongly, the substance will show some catalytic activity. However, one does not want to overdo the bond strength, or else the substance will be catalytically inactive.

12.8 CATALYSTS CAN BE DESIGNED TO HOLD THE REACTANTS IN CLOSE PROXIMITY

Another way that a catalyst can work is to hold the reactants in close proximity to each other. For example, in Section 12.1 we noted that in 1817, Davy discovered that if one surrounded a candle with a platinum gauze, the platinum would prevent the flame from causing an explosion. In this case, the platinum is acting to catalyze the termination reactions in the flame so the candle does not cause an explosion.

In 1834, Faraday proposed that the main role of the catalyst is to hold the reactants in close proximity so they can react.

The reactions in a flame are pretty complex. There are many catalytic cycles. Still, the most important intermediates are the hydroxyls and the hydrogen atoms. Figure 12.15 shows a catalytic cycle for the hydroxyls.

As noted above, Davy found that platinum can catalyze the termination reactions in a flame. In the gas phase, the main quenching reactions are



Both reactions are slow in the gas phase because the concentration of intermediates is low. When you add a platinum catalyst, the catalyst concentrates the intermediates. Hydrogens adsorb on the catalyst and wait for another hydrogen atom or hydroxyl to hit the catalyst and react with the hydrogen. The catalyst in effect concentrates the reactants. That speeds up the termination reaction.

There are some subtleties here because the platinum also speeds up the initiation reactions. For example, if you put a platinum wire into a hydrogen/oxygen mixture, the platinum speeds up the initiation process more than the platinum speeds up the termination process. In that case, the flame is initiated by platinum. On the other hand, with a candle

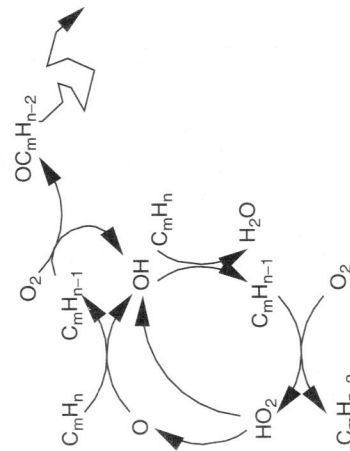


Figure 12.15 A simplified version of the reactions in a flame.

Table 12.11 The heat of formation of several metal oxides

Oxide	Heat of Formation, kcal/mol	Oxide	Heat of Formation, kcal/mol
AgO	-7.3	IrO ₂	-40.1
Ag ₂ O	-6.3	FeO	-63.7
As ₂ O ₅	-218.6	Fe ₂ O ₃	-197.5
Au ₂ O ₃	+19.3	PbO	-52.4
Bi ₂ O ₃	-137.9	MnO ₂	-125.5
CdO	-60.9	Mn ₂ O ₃	-232.1
CoO	-57.2	HgO	-21.7
Cr ₂ O ₃	-269.7	MoO ₂	-130
CuO	-37.1	MoO ₃	-180.3
Cu ₂ O	-39.8	NiO	-58.4
Ga ₂ O ₃	-258	PbO	-52.4
In ₂ O ₃	-222.5	PdO	-20.4
		ZnO	-83.17

Source: Data from the CRC or Landolt-Bornstein.

- Plots of the log of the reaction rate versus the heat of formation of the oxide per mole of metal

Plots of the log of the reaction rate versus the heat of formation of the oxide per mole of oxygen are called **Sachtler-Fahrenfort** plots (Sachtler and Fahrenfort, 1958). Plots of the log of the reaction rate versus the heat of formation of the oxide per mole of metal are called **Tanaka-Tamaru** plots. (Tanaka and Tamaru, 1963)

Figure 12.14 shows a Sachtler-Fahrenfort plot and a Tanaka-Tamaru plot for the hydrogenation of ethylene. Both plots show some correlation to the data, although clearly there are lots of variations. (Without the line, the figures look like scatterplots.) Generally, Sachtler-Fahrenfort plots fit better than do Tanaka-Tamaru plots.

One has to be careful not to extrapolate these plots too far. Selenium, mercury, and lead are inactive for ethylene hydrogenation even though they have the heat of formation of the oxides is similar to those for the transition metal. Still, the Sachtler-Fahrenfort plots are a useful way to correlate data, even though they do not fit exactly.

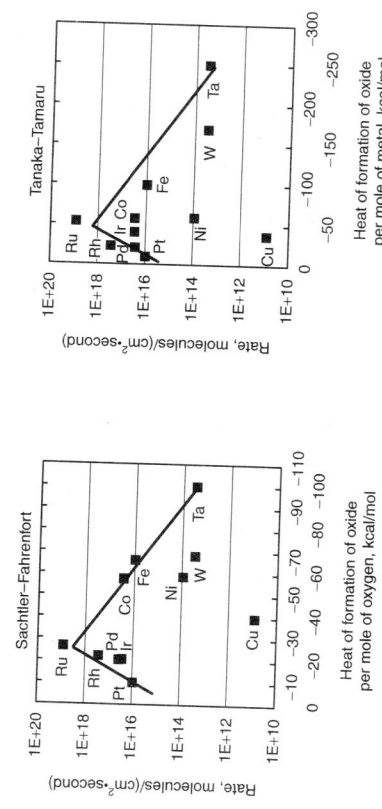


Figure 12.14 A Sachtler-Fahrenfort and Tanaka-Tamaru plots for the hydrogenation of ethylene.

(i.e., a paraffin flame), the platinum speeds up the termination reactions more than the initiation reactions. As a result, the platinum quenches the flame.
 In both cases, the platinum is concentrating the intermediates of the reaction so that the reactants are in close proximity to react. It is just that in one case the platinum speeds the initiation reactions more than the termination reactions while in the other case the opposite occurs.

12.9 CATALYSTS CAN BE DESIGNED TO HOLD THE REACTANTS IN THE CORRECT CONFIGURATION TO REACT

In the previous section, we noted that catalysts hold the reactants in close proximity and thereby speed up rates of reaction. Still, it is interesting to note that one could get even higher increases in rate if the catalyst could also hold the reactants in just the right configuration to react. Pushing the reactants together would also produce an additional increase in rate. It is, in fact, possible to design a catalyst that holds the reactants in just the right configuration to react. Very few catalysts do this, but the ones that do are especially efficient.

There is one specific example that illustrates the effects particularly well: the conversion of acetylene to benzene:



Reaction (12.91) is very rapid on a palladium catalyst. Figure 12.16 shows what is called the *active site* on the catalyst. The active site is defined as the arrangement of surface atoms where the reaction occurs. It happens that when acetylene adsorbs on palladium, the acetylene binds in what is called a "bridge bound state," where the acetylene is held off center of what is called a "threefold hollow" on the palladium surface. The bonding position is shown in Figure 12.16. It happens that if you put three acetylenes onto the palladium, the three acetylenes form a hexagonal structure similar to the hexagonal structure in benzene. The bond lengths are also about right for benzene. That promotes benzene formation.

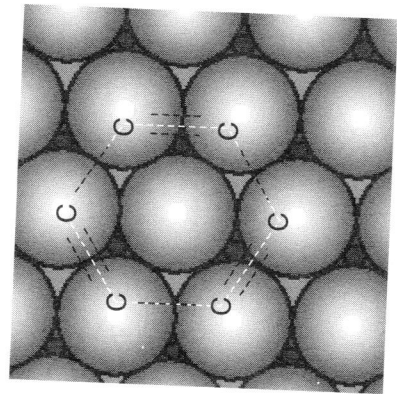


Figure 12.16 The active site for reaction (12.91) on a palladium catalyst.

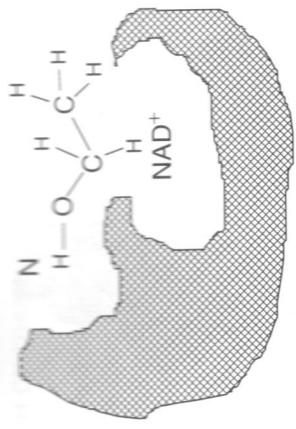


Figure 12.17 A cartoon of the reaction of ethanol and NAD⁺ on the active site of liver alcohol dehydrogenase. [Adapted from Oppenheimer and Handlon (1992).]

If one changes the geometry by, for example, going to a square surface, the reaction is not observed. This example clearly illustrates the idea that if a catalyst holds the reaction in the right configuration to react, the reaction will occur at an unusually high rate.

This process commonly happens in enzyme-catalyzed reactions. For example, the first step in the destruction of alcohol by your liver is a hydrogen transfer from the alcohol to an ion called NAD⁺ [nicotinamide adenine dinucleotide (oxidized form)]:



Reaction (12.92) occurs on an enzyme called *liver alcohol dehydrogenase*. Figure 12.17 shows how the reaction occurs in liver alcohol dehydrogenase. The diagram is adapted from Oppenheimer and Handlon (1992). The NAD⁺ fits into a pocket in the enzyme. The alcohol sits over the NAD⁺ in a bent configuration, with a hydrogen in the alcohol pushing into the NAD⁺. The close proximity of the alcohol and the NAD⁺ facilitates the reaction.

12.10 CATALYSTS STRETCH BONDS AND OTHERWISE MAKE BONDS EASIER TO BREAK

Some enzymes work in another way, too. They stretch bonds and otherwise make bonds easier to break. For example, Figure 12.18 shows a diagram of an enzyme called *Lysozyme 161L*. The name Lysozyme means that the molecule is part of a wide class of enzymes made in a part of a cell called a lysosome. The number 161L is the listing in the protein database. (The listings go in order.) Generally, lysozymes are enzymes that animals use to kill bacteria. For example, there are lysozymes in your tears that kill bacteria in your eyes.

Microbiologists say that lysozymes work by catalyzing the hydrolysis of polysaccharides in the cell walls of the bacteria, causing the cell walls to rupture. Let me translate. Polysaccharides are carbohydrates (sugars). In this case the polysaccharides consist of NAM (*N*-acetylmuramic acid) and NAG (*N*-acetylglucosamine) units. Both molecules are shown in Figure 12.19. Lysozyme catalyzes the hydrolysis of the bond between the NAG and NAM units:



one is mixing excited states into the ground state of a system. If one can stabilize those antibonding orbitals, one will also stabilize the transition state. As a result, one can lower the energy of the transition state and thereby facilitate a reaction. Generally d electrons are able to interact with antibonding orbitals to stabilize them. S and p electrons are less able to facilitate reactions.

For example, consider the dissociation of hydrogen on platinum:



Reaction (12.95) is a classic four-centered symmetry-forbidden reaction. So, on the basis of the analysis in Section 10.9, one would expect reaction (12.95) to have a large intrinsic barrier. Well, on aluminum the reaction does have a large barrier. People observe little dissociation of energies up to 50 kcal/mol even though the reaction is 60 kcal/mol exothermic. If one plugs these measurements into the Polanyi relationship with a γ_P of 0.5, one finds that the intrinsic barrier is at least 80 kcal/mol. An intrinsic barrier of 80 kcal/mol is consistent with our expectations for a symmetry forbidden reaction.

On platinum, however, the reaction is unactivated. The heat of adsorption is 13 kcal/mol, and so if we plug into the Polanyi relationship, we find that the intrinsic barrier is less than 7 kcal/mol. Clearly, H_2 dissociation on platinum does not have the large intrinsic barrier one expects for a symmetry-forbidden reaction.

This occurs because the reaction is no longer symmetry-forbidden on platinum. Figure 12.20 shows a correlation diagram for reaction (12.95). In the absence of the platinum, the $\sigma\sigma^*$ state is lost and a $\sigma^*\sigma$ state forms. This is a standard symmetry-forbidden reaction.

When the platinum is present, everything changes. The d bands in the platinum add some extra states, which I have labeled A and E in the diagram, both of which are partially filled with electrons. In the material that follows we will show that during the reaction, the electrons from the $\sigma\sigma^*$ state can flow into the A band, while electrons from the E band can flow into the $\sigma^*\sigma$ state. That allows the reaction to occur with a minimal barrier.

A good way to understand this interaction is to look at what happens when electrons flow into the $\sigma^*\sigma$ state. The $\sigma^*\sigma$ state consists of an antibonding state in the H_2 plus a corresponding state in the metal. Figure 12.21 shows a diagram of the antibonding state.

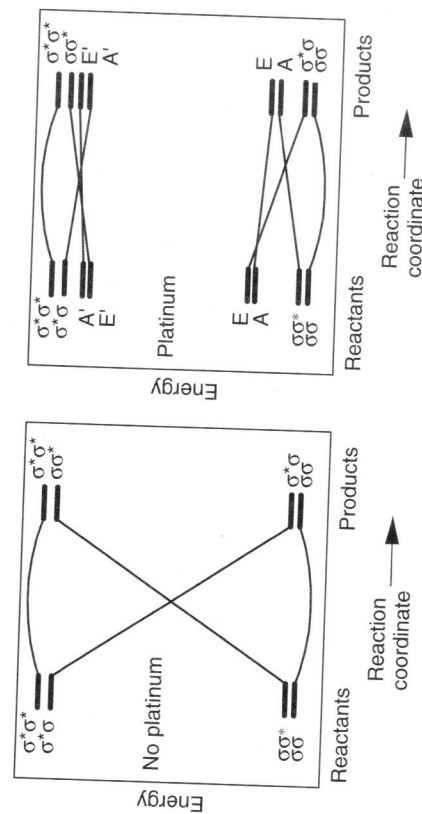


Figure 12.20 A correlation diagram for reaction (12.95) with and without platinum.

Notice that there is a sign change in the antibonding state. Consequently, according to the material in Section 10.11, if one has a state in the metal with a similar sign change, and one can take electrons out of that state, then one can get the reaction to occur smoothly as shown in Figure 10.35.

Figure 12.21 shows a diagram of the key orbitals during the reaction. There are two kinds of orbitals in platinum: s orbitals and d orbitals. The s orbitals spread out over the whole surface. There are no big sign changes, so the s band cannot interact with the antibonding orbitals on the H_2 . In contrast, the E states in the d bands have the same sign changes as in the antibonding orbitals in the H_2 . Consequently, one can transfer electrons from the d bands to the antibonding orbitals in the H_2 with minimal difficulty.

In fact, there is some subtlety to the arguments, because one wants to break the H-H bond, not simply stabilize the antibonding orbitals. Well, the d bands do that, too. Recall that orbitals of the same sign attract while orbitals of different sign repel. If one looks at the s bands, one finds that there is an attractive interaction on one side of the hydrogen but a repulsive interaction on the other side. The net effect is that the s bands do not attract the antibonding orbitals. On the other hand, if one orients the hydrogen as shown in the lower diagram in Figure 12.21, both sides of the antibonding orbitals on the hydrogen will be attracted to the d bands on the platinum. The overlap increases as the hydrogen dissociates. The net effect is that the antibonding orbitals in the hydrogen are pulled toward the platinum atoms. That rips the hydrogen apart.

The net effect is that the intrinsic barrier for the reaction has been reduced by over 70 kcal/mol. Generally, the 70 kcal/mol or more reduction in intrinsic barriers occurs only for symmetry-forbidden reactions: dissociation of diatomic molecules into two atoms, or scission of double or triple bonds. Most other reactions show similar intrinsic barriers on both transition metals and nontransition metals.

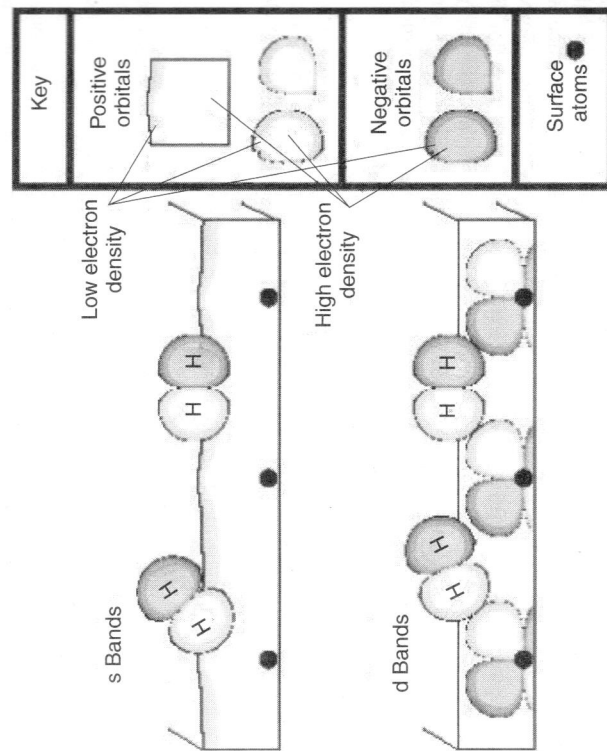


Figure 12.21 A diagram of the key interactions during the dissociation of hydrogen on platinum.

12.11.3 Acid Catalysts

Another way that catalysts can change the intrinsic barriers is to change the net charges on the reacting species. The idea is simple. An electronegative catalyst can remove charge from the reactants. That can produce changes in the barriers to reaction.

In order to see how that works, consider the reaction discussed in Section 12.6.2:



In Section 12.6.2 we noted that in acid solution the proton reacts with the olefin to yield a carbocation:



Then the carbocation isomerizes:



Then the new ion loses a proton to form the products:



In this case the acid is doing several things. The acid is initiating the reaction. However, the acid solution is also stabilizing the charged species. The stabilization of the charges is important to the reaction. In the material that follows we will discuss how the charges affect the barriers to reaction.

In order to determine how the charge on the molecule affects the barriers to reaction, it is useful to consider a reaction where a neutral hydrogen atom reacts with the olefin to yield a radical:



Then the radical isomerizes:



Then there is loss of a hydrogen atom:



First, let us consider reaction (12.100).

Figure 12.22 shows some of the key orbitals during reaction (12.100). The reactant, $RHC=C\overset{R}{R}H$, starts with a π -bond. Recall that a π -bond forms when two p orbitals line up and bind together. The π bond looks like an extended p orbital as shown in Figure 12.22. The hydrogen starts out with a spherical orbital as we saw in Chapter 10.

Now consider what happens when reaction (12.100) starts. When reaction (12.100) starts, the hydrogen approaches the ethylene. In Chapter 10, we found that there will be a bonding and antibonding interaction. Figure 12.22 shows the bonding and antibonding molecular orbitals. The two MOs look almost the same, except that in the bonding MO

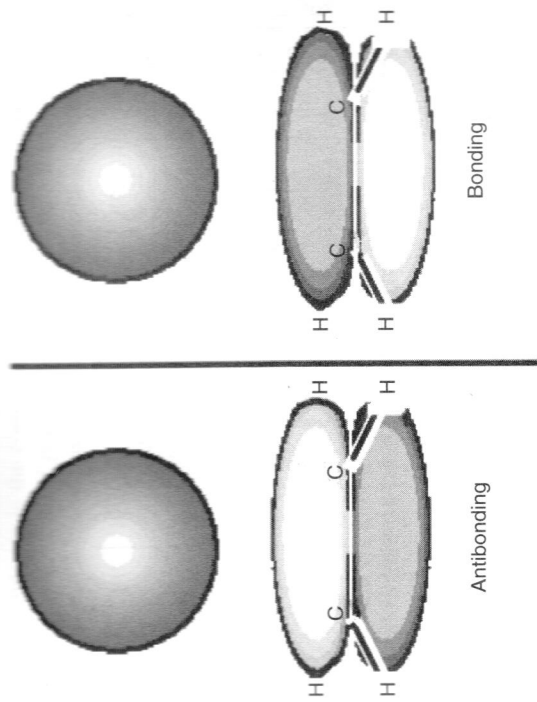


Figure 12.22 A diagram of the key MOs during reaction(12.100).

the top lobe on the ethylene has the same sign as the s orbital while in the antibonding MO, the lobe has a sign different from that of the s orbital.

Now consider what happens when the orbitals come together. This case is very similar to the cases we discussed in Section 10.6.3. Notice that in the antibonding state, a positive orbital is pushing up against a negative orbital. Physically, we are pushing one balloon of electrons into another, so there is a repulsion exactly like the repulsions discussed in Chapter 10. The repulsive interaction pushes up the energy of the system. Consequently the reaction is activated.

A more detailed analysis shows that the repulsion occurs because there are three electrons in the system. If there were only two electrons, we could put both electrons into the bonding state, and so we would not have to put electrons into orbitals of different signs. Consequently, one could eliminate the repulsive antibonding interaction. However, the bonding MO can hold only two electrons. If one has three electrons, one of the electrons must be put into the antibonding MO. That produces the repulsive interaction.

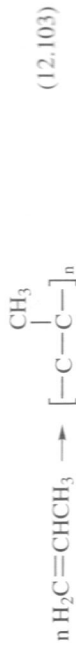
Notice that if one starts with H^+ , there will be only two electrons in the system, so there will be no repulsion. Consequently, the fact that one has protons or hydroniums, rather than neutral hydrogen atoms, in acid solution eliminates most of the barriers to reaction (12.100).

One can also run reaction (12.100) on a solid. Solid catalysts are great because one can modify the charges on the protons. Recall that in a covalently bonded molecule such as water, the hydrogen has a small net positive charge. That is why water has a net dipole. In a solid, one can increase the charge. On certain solids, called **superacid catalysts** the charge is nearly +1. That promotes easy proton transfer. Consequently, superacid catalysts are able to lower the intrinsic barriers to reaction (12.100)

The superacid catalysts also promote reaction (12.101). Reaction (12.101) is more complex than reaction (12.100). Reaction (12.101) starts with a radical. There is a half-filled p orbital on one carbon, and a C-R bond on the other carbon. Figure 12.23 shows a very approximate diagram of the key orbitals during reaction (12.101).

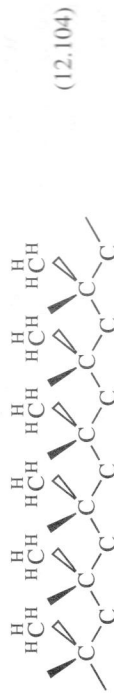
only when the reactants are in the correct configuration to react via the desired pathway. The result is that you get desired reaction and not an undesired one.

One specific example where this effect is very important is in the polymerization of propylene:

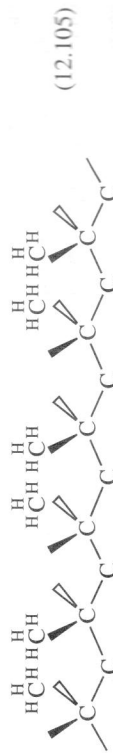


Polypropylene undergoes free-radical or cationic polymerization as discussed in Chapter 5. When the free-radical reaction occurs, the methyl group can go on the top or the bottom of the molecule. If the methyl groups are distributed randomly, the polymer has poor mechanical properties. As a result, the polymer cannot be used in many applications. In contrast, if one can control the positions of the methyl groups, one can produce polymers with much better mechanical properties. Such polymers are very valuable.

There are two key forms of oriented polypropylene: isotactic polypropylene, where all of the methyl groups are on one side



and syndiotactic polypropylene, where the methyl groups alternate from side to side:



Consider making isotactic polyethylene. Figure 12.24 shows a diagram of a step during the production of isotactic polypropylene where a single propylene unit is added to a growing polymer chain. Notice that one can add the propylene, with a methyl group facing in the correct direction or in the wrong direction. If one would add the propylene with the methyl group facing the wrong way, polymerization would still occur, but one would not end up with isotactic polypropylene.

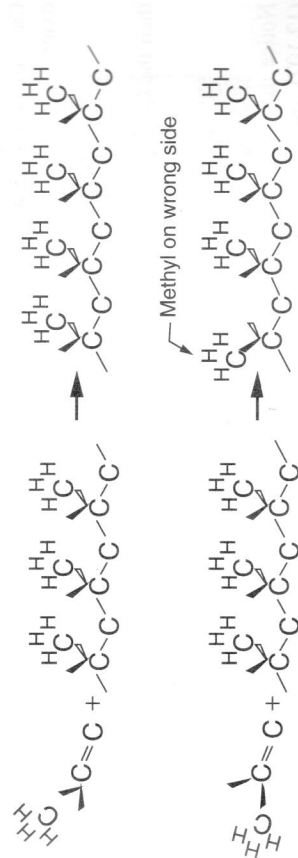


Figure 12.24 A rough diagram of one step during the production of isotactic polypropylene.

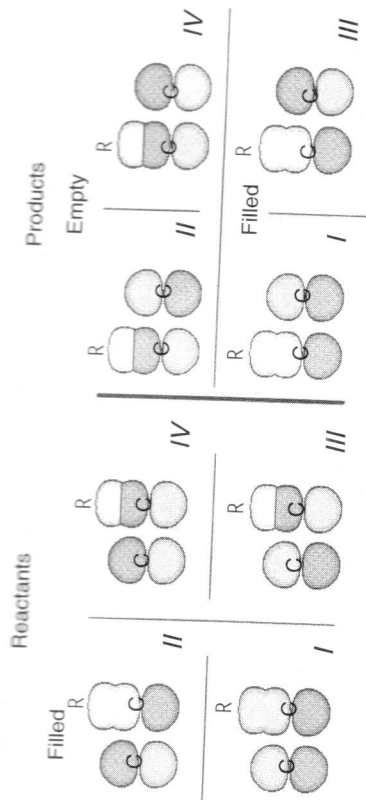


Figure 12.23 A rough diagram of the key MOs during reaction (12.101).

During reaction (12.101) the system starts out with the orbitals in the left of Figure 12.23. There are four MOs labeled I, II, III, and IV. In the diagram, we have arbitrarily assigned the lobe on the *R* group to have a positive sign, and then considered all possible signs on the *p* hybrids on the carbon. In MO I, both the *p*'s are positive; in MO II, the left *p* is negative, while the right *p* is positive. In the MO III the right *p* is negative and the left *p* is positive, while in MO IV, both *p*'s are negative. In MOs I and II, the π group has a bonding interaction with the carbon, while in III and IV, there is a sign change in moving from *R* to *C* and so the interaction is antibonding. As a result, orbitals I and II are bonding orbitals while orbitals III and IV are antibonding orbitals. In contrast, at the end of the reaction, the *R* group migrates from the right to the left of the molecule. In this case, orbitals I and III are bonding while orbitals II and IV are antibonding.

Now consider moving the *R* group. Notice that the *R* group needs to move across the molecule for reaction to occur. However, in order to move the positive orbital on the *R* group in orbital II, it will need to displace the negative nonbonding orbital on the carbon. In Chapter 10 we found that such orbital displacements have large barriers. The net effect is that 1,2 displacements have large barriers with neutral radicals.

Notice that the repulsion occurs only because the electrons in the *R* group are pushing up against the nonbonding orbital in the molecule. If one modifies the charges on the molecule, one can remove the electrons from the nonbonding orbital. If one puts a +1 charge on the molecule, there will be no repulsions.

Well, again on **superacid catalysts** the charge is nearly +1. That promotes easy isomerization. The net result is that the superacid catalyst is able to promote reaction (12.101). These results show that catalysts can modify the intrinsic barriers to reaction. These modifications allow very selective reactions to occur.

These results show that catalysts can be designed to modify the changes on the reactants in a way that facilitates reaction.

12.12 CATALYSTS CAN BE DESIGNED TO BLOCK SIDE REACTIONS

Another thing that catalysts can do is to block side reactions. The idea is simple. You design the catalyst so that it is shaped in such a way that the reactants can get together