Section 17.1

Oil Refineries

Petroleum is one of our most versatile natural resources. In the past century and a half, petroleum has developed from a replacement for animal and vegetable oils in lighting and lubrication into one of the foundations of our economy. In addition to providing energy for transportation, petroleum is the source material for much of the chemical industry. Petroleum and petroleum products are so important to our society that they warrant a little more attention than the occasional trip to the gasoline pump.

Questions to Think About: *Why don't oil and water mix? What distinguishes gasoline from kerosene from diesel fuel? What is actually different between regular and premium gasolines? Why are winter gasoline formulations different from summer formulations? Why does gasoline get "old," so that it doesn't work well in an engine after a few months? Why does motor oil lose its viscosity when it overheats?*

Experiments To Think About: *One of the first problems faced by a refinery is removing water and salt from the crude oil. You can look at this problem yourself by mixing some salad oil, water, and salt in a jar. The water dissolves the salt and sinks to the bottom of the jar. But if you put only a small amount of water into the oil and shake the mixture vigorously, you will find that the water breaks up into tiny droplets and has a great deal of trouble falling to the bottom of the jar. Similarly, the salt grains may find themselves suspended in the oil for a considerable length of time. The first step in refining real crude oil is in merging the water droplets together and washing the salt out of the oil.*

What is Petroleum?

To understand petroleum refining, you must first understand what petroleum is. It's a complicated mixture of chemicals, thought to have formed from the decay of ancient marine organisms. Most of the constituents of petroleum are hydrocarbon molecules—molecules composed exclusively of carbon and hydrogen atoms. However some of the organic molecules in petroleum also include oxygen, nitrogen, and sulfur atoms. Moreover, petroleum contains various metal salts as well.

Petroleum is found trapped in porous rocks beneath domes of impermeable rock. Because petroleum is less dense than water, it floats on water and becomes caught between the water below it and the impermeable surface above it. Sometimes the uppermost portion of the petroleum under a dome is natural gas. The water beneath the petroleum is *saline* (salt water) and probably came from the ancient sea in which the decaying organic matter was originally deposited.

With time and pressure, petroleum's chemical structure evolved into its present form and it migrated into the porous rocks in which it's now found. The mechanisms for its chemical evolution and its migration aren't well understood. But despite the uncertainties in its origins, petroleum exists and our society is now consuming it at a furious pace.

But what are the constituents of petroleum actually like? To answer that question, we must look at their molecular structures. The hydrocarbon molecules take principally four different forms: *paraffins*, *olefins*, *cycloparaffins*, and *aromatics*. These names, and a variety of equivalent names, describe the ways in which the carbon atoms bind to one another and to the hydrogen atoms.

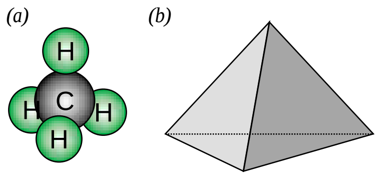


Fig. 17.1.1 - The covalent bonds that hold organic molecules together are directional. When a carbon atom binds to four hydrogen atoms (*a*), the hydrogen atoms arrange themselves at the corners of a tetrahedron (*b*).

In all four cases, the atoms are held together by covalent bonds. In a basic covalent bond, two adjacent atoms share a pair of electrons and become bound together at an equilibrium spacing. By letting the electrons move back and forth between and around their nuclei, these two atoms manage to reduce their overall energy so that it takes work to separate them.

This energy reduction is partly due to electrostatic effects and partly due to quantum physics. Locating the electrons between the two nuclei creates stronger attractive forces than repulsive ones, reducing the overall electrostatic potential energy and helping to hold the two atoms together.

But the shared electrons also have a larger domain in which to move. They are suddenly able to orbit two atoms rather than one. An electron has a wavelike character and the longer its wavelength, the smaller its kinetic energy. When allowed to spread out between two atoms, the electrons can increase their wavelengths and reduce their kinetic energies. Overall, a covalent bond lowers both potential and kinetic energies, and makes it quite difficult to separate the atoms involved.

The most important atom in both petroleum and organic chemistry is carbon. A carbon atom has four valence electrons and needs four more to complete its electronic shell of eight electrons. This shell structure is a consequence of quantum physics and, when completed, is a nearly uniform, spherical ball of electrons. Completing the shell minimizes the energy of the atom and makes the molecule it resides in more chemically stable. To complete its electronic shell and achieve this stability, a carbon atom typically shares valence electrons with four adjacent atoms. It ends up with four pairs of shared electrons and a completed shell.

But those adjacent atoms can't be just anywhere. The sharing scheme only completes the carbon atom's electronic shell if the shared electrons end up uniformly distributed around the atom. The best way to achieve this uniform distribution of electrons is to arrange the adjacent atoms on the four points of a tetrahedron (Fig. 17.1.1). A tetrahedron is an equilateral pyramid with a triangular base. This tetrahedral arrangement places the four atoms as far apart as possible and allows the electrons to complete the electronic shell properly.

So a carbon atom's neighbors must be in the right places. In general, covalent bonds only work when the atoms involved are correctly oriented relative to one another. This directionality of covalent bonds gives organic molecules specific shapes and these shapes are important to the properties of petroleum. They are also critical to the functioning of biological systems, so that life couldn't exist without the directionality of covalent bonds. Since most atoms need four pairs of electrons to complete their electronic shells, tetrahedral arrangements of atoms are common in organic molecules.

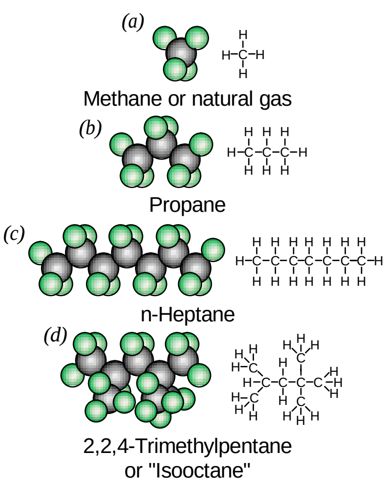


Fig. 17.1.2 - Paraffins are chain-like hydrocarbons with single bonds between carbons. These molecules can be linear, as in (*a*) methane, (*b*) propane, and (*c*) heptane, or they can have branches as in (*d*) 2,2,4-trimethylpentane ("isooctane" or simply "octane").

To see how covalent bonds contribute to the characteristics of petroleum, let's look at the structures of the four different hydrocarbons listed above. The simplest case is the **paraffins**—chain-like molecules in which strings of carbon atoms are decorated with hydrogen atoms (Fig. 17.1.2). As you might expect, the four atoms surrounding each carbon atom in a paraffin molecule are located on the points of a tetrahedron. This arrangement gives the paraffins a zigzag structure. Some paraffin molecules have only a single chain (Fig. 17.1.2*c*) while others branch extensively (Fig. 17.1.2*d*). The branching is important for gasoline and diesel fuel.

Branching allows the carbon atoms in a paraffin molecule to arrange themselves in a variety of different ways. The 2,2,4-trimethylpentane molecule shown in Fig. 17.1.2*d* is just one of eighteen ways in which 8 carbon atoms and 18 hydrogen atoms can join together to form a molecule. Two molecules that contain the same assortment of atoms but differ in the exact arrangements of those atoms are called **isomers**. Petroleum contains vast assortments of these different isomers.

While the paraffin molecules in Fig. 17.1.2 appear to be rigid, orderly structures, they actually have some freedom of motion left. The covalent bond between each pair of atoms allows those atoms to turn freely about the bond (Fig. 17.1.3). The atoms in a paraffin molecule can and do swivel about the bonds between them. As a result, paraffin molecules are quite floppy.

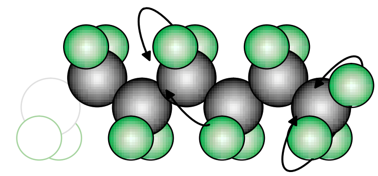
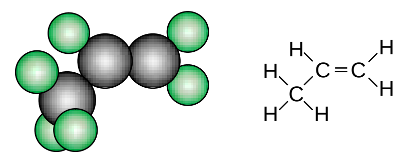


Fig. 17.1.3 - Paraffin molecules aren't rigid because carbon atoms can rotate around the covalent bonds between them. The rightmost carbon atom in this paraffin molecule can swivel, just like the knob of a water faucet.

Olefins are similar to paraffins except that they contain one or more double bonds between carbon atoms (Fig. 17.1.4). Instead of sharing one pair of valence electrons, the two carbon atoms in a double bond share two separate pairs of valence electrons. One pair of electrons orbits both nuclei through a path that takes them directly between the atoms but the second pair follows a path that is located on either side of a line between the atoms.

The Pauli exclusion principle prevents two indistinguishable electrons from following identical paths in the covalent bonds. With the first pair of electrons orbiting directly between the two carbon atoms in the double bond of Fig. 17.1.4, the second pair of electrons must orbit in a path that takes them in front of and behind those two atoms. This broader arrangement of electrons helps to complete the spherical electronic shells of both atoms, but it prevents the atoms from rotating about the double bond. The rightmost carbon atom in Fig. 17.1.4 can't swivel about the double bond. Because of their rigid double bonds, olefin molecules are stiffer than paraffin molecules.



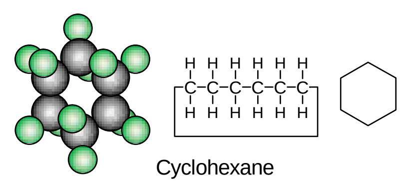
Propene

Fig. 17.1.4 - Olefins have one or more double bonds between carbon atoms. Here the rightmost pair of carbon atoms in a propene molecule are connected by a double bond. One pair of valence electrons lies between the two carbon atoms, while the second pair of electrons orbits in front of and behind the line between the atoms.

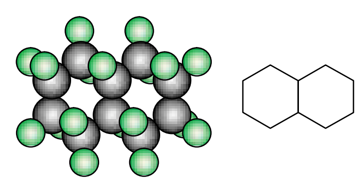
The double bonds in olefin molecules make them susceptible to chemical attack. A double bond is particularly vulnerable to a free radical—an incomplete molecule containing an atom with an unpaired valence electron. This unpaired valence electron seeks out valence electrons on other atoms, attempting to form a new covalent bond to complete its electronic shell. While a free radical's best option for partnership is the unpaired electron on another free radical, it will sometimes attack an electron in an existing covalent bond, particularly a double covalent bond. This sort of attack changes the natures of the molecules involved.

A free radical attacks a double bond by grabbing one electron from the second pair, the pair that's not directly between the two atoms. The free radical forms a new covalent bond with one of the two carbon atoms. The former double bond becomes a single bond, leaving the second carbon atom with an unpaired electron. That second atom becomes a free radical itself.

Their double bonds make olefin molecules reactive and they tend to stick to one another permanently. Automobiles can tolerate olefin molecules in their gasolines as long as the olefins have only one double bond. But olefins with more than one double bond per molecule, *polyolefins*, can form gummy deposits in your car and are unsuitable for gasoline. While olefin molecules are rare in crude oil, they're created during the refining process. Part of the finishing work in a refinery is to remove polyolefin molecules to make the gasoline more stable against gum formation. Aircraft, which burn fuel in thin, high altitude air, run into gum problems even with olefins containing only one double bond. Aviation fuels avoid olefins entirely.



Cyclohexane



Decalin

Fig. 17.1.5 - Cycloparaffins contain chains that close on themselves to form rings. Adjacent carbons bind to one another in a zigzag pattern so that these molecules aren't flat. The rings are often represented by polygons, in which each vertex corresponds to a carbon atom holding as many hydrogen atoms as it can.

In addition to the chain-like paraffin molecules, petroleum also contains ring-like molecules called **cycloparaffins**. Cycloparaffins occur because chain-like paraffins are floppy and can form loops and coils. The two ends of a typical chain-like paraffin molecule can touch one another and will bind together to form a ring if you remove two hydrogen atoms (Fig. 17.1.5). While the most commonly occurring rings contain five or six carbon atoms, rings with three, four, seven, or more carbon atoms are also found in petroleum. Molecules with more than one ring are also common.

The last important group of hydrocarbons found in petroleum are the **aromatics**. These molecules include a special type of six-carbon-atom ring—an **aro-**

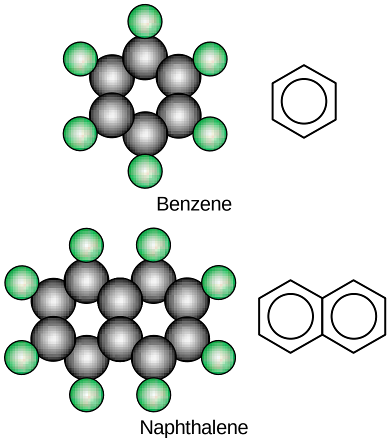


Fig. 17.1.6 - Aromatic molecules include one or more special six-carbon-atom rings. The atoms in an aromatic ring are held together by one and a half covalent bonds, with the half bond referring to six electrons that circulate about the ring above and below the lines between atoms. Aromatic rings are represented as hexagons with circles inside.

matic ring. The simplest molecule containing an aromatic ring is the benzene molecule (Fig. 17.1.6). In this ring, two adjacent carbon atoms are held together by sharing one and a half pairs of electrons. The first pair of electrons orbits between the two carbon atoms and forms a typical covalent bond. But the extra half pair of electrons is shared around the entire ring to form an extra half bond between each pair of carbon atoms. Each carbon atom contributes one electron to this special bonding arrangement, yielding six electrons overall. These six electrons orbit all the way around the ring, above and below the atoms themselves, and help to hold the six atoms together. With lots of room to move, these electrons have long wavelengths and low kinetic energies.

Aromatic rings are naturally flat. The tetrahedral structures that give paraffin and cycloparaffin molecules their zigzag shapes are absent in the aromatics. The carbon atoms in an aromatic ring still act to fill their electronic shells but the ring electrons occupy the tops and bottoms of those shells. As a result, the carbon atoms don't bond to atoms above or below the ring. Instead, each carbon atom bonds to three atoms at the points of an equilateral triangle and thus completes its electronic shell. Two of these atoms are other carbons in the ring. The third is typically a hydrogen atom. Because they are built out of equilateral triangles, the aromatic hydrocarbons are basically flat (Fig. 17.1.6).

These four types of hydrocarbons account for most of the molecules in petroleum. However, petroleum also contains molecules that mix two or more of these types together. Such molecules include rings with side chains and aromatic rings attached to cycloparaffin rings. Systematic studies of crude oil have shown that it contains almost any hydrocarbon molecule you can imagine.

Some petroleum molecules also contain oxygen, sulfur, and / or nitrogen atoms. These three atoms, along with carbon and hydrogen, account for most of the organic chemicals in living organisms and presumably entered petroleum during its formation from decaying biological material. Like carbon and hydrogen, oxygen, sulfur, and nitrogen atoms form covalent bonds with their neighbors. However they are closer to completing their electronic shells and don't need to form as many covalent bonds as do carbon atoms.

Oxygen and sulfur atoms both have six valence electrons and need only two more to complete their electronic shells. These atoms normally form two covalent bonds with adjacent atoms, bringing in two additional shared electrons and completing a shell of eight electrons. Nitrogen atoms have five valence electrons and need three more to complete their electronic shells. They normally form three covalent bonds with adjacent atoms, bringing in three additional shared electrons and again completing a shell of eight.

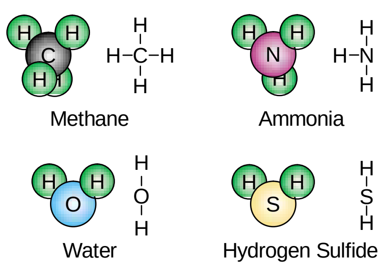


Fig. 17.1.7 - Carbon, nitrogen, oxygen, and sulfur atoms can all form covalent bonds. A carbon atom can form four covalent bonds, a nitrogen atom three, and an oxygen or sulfur atom two. When these atoms bond to hydrogen atoms, they form four familiar molecules.

Oxygen, sulfur, and nitrogen often substitute for carbon atoms in organic molecules but bind to fewer atoms (Fig. 17.1.7). While a carbon atom can bind to four hydrogen atoms to form methane, a nitrogen atom can bind to only three hydrogen atoms to form ammonia. Oxygen and sulfur can bind to only two hydrogen atoms, forming water and hydrogen sulfide (rotten egg gas) respectively.

Substitutions of oxygen, sulfur, and nitrogen atoms in the molecules of crude oil are generally undesirable in finished petroleum products. Sulfur is particular bad because of its unpleasant smell and contribution to acid rain. Crude oil that contains substantial amounts of sulfur is called "sour crude" while that without much sulfur is referred to as "sweet crude." Oxygen, nitrogen, and sulfur atoms are often removed from petroleum molecules during the refining process by reacting them with hydrogen gas in a process called *hydrotreating*.

CHECK YOUR UNDERSTANDING #1: Sometimes It's Good to be Rigid

The protein molecules that carry out most of the chemical tasks in living organisms have complicated but well-defined shapes. These proteins are composed principally of carbon, hydrogen, oxygen, nitrogen, and sulfur atoms. How does a protein molecule maintain its well-defined structure?

What are Petroleum Products?

Unfortunately, crude oil isn't very useful in its raw form and must be processed extensively before it's marketable. This processing is the job of an oil refinery. But before we examine how oil refineries work, we must first consider the products they're trying to produce. Each petroleum product is an assortment of different molecules, selected and blended so that the finished mixture has the appropriate physical and chemical properties for the task it must perform. Here are some of the petroleum products made at refineries.

Let's start with gasoline for automobiles. To make gasoline, the refinery blends molecules that tend to be liquid at room temperature but gaseous at temperatures above about 200 °C, that burn easily and completely in the presence of sufficient air, and that are resistant to knocking. As we saw in Section 7.2, knocking is premature ignition that occurs when fuel and air are compressed in an automobile engine cylinder. Work done on the gaseous mixture of fuel and air during compression raises its temperature, so the mixture is in danger of igniting spontaneously before the spark plug fires. A properly formulated gasoline avoids this spontaneous ignition.

While gasoline should remain a liquid at room temperature to stay in the tank, it must become a gas in a hot engine to burn efficiently. Not every hydrocarbon molecule can meet these two requirements. Some hydrocarbon molecules are more **volatile** than others—converting easily into a gas. A hydrocarbon molecule's volatility is determined mostly by its size. Small hydrocarbon molecules evaporate more easily than large hydrocarbon molecules.

The size-dependence of volatility is related to the force holding the hydrocarbon molecules together as a liquid: the van der Waals force. This force is the result of tiny electric charge fluctuations that are present in all molecules. As electrons in two nearby molecules move about, they tend to arrange themselves so that the molecules attract one another (Fig. 17.1.8). At any given moment, the two molecules have small electrical dipoles that pull them toward one another. These dipoles come and go but they're still able to hold the molecules together.

The van der Waals forces between two molecules depend on their sizes and shapes. The larger the molecules are, the more electrons they contain and the more electrically polarizable they are. Large molecules experience stronger van der Waals forces than small molecules, which is why most small molecules are gases at room temperature while most large molecules are liquids or solids.

With gasoline, the van der Waals forces must be strong enough to keep it mostly liquid at room temperature, but weak enough to allow it to become mostly gaseous at about 200 °C. These requirements limit the sizes and shapes of the hydrocarbon molecules that gasoline can contain. The size of a hydrocarbon molecule is determined mostly by the number of carbon atoms it contains. For gasoline, the appropriate hydrocarbon molecules range from about 4 carbon atoms on the small end to about 12 carbon atoms on the large end.

Refineries adjust the precise balance of large and small molecules to give the gasoline just the right volatility over the normal range of operating temperatures. The large molecules bind together rather strongly and help to keep the gasoline liquid during storage. The small molecules are easily separated into a gas and quickly evaporate from an open container of gasoline. Butane molecules, which have only 4 carbon atoms, are included in the gasoline to make starting easy, even in a cold engine. This volatile chemical evaporates readily and is soon

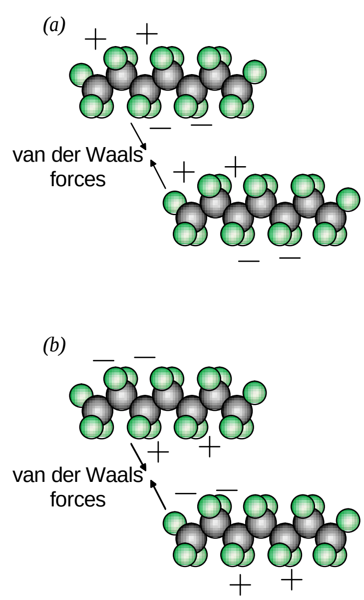


Fig. 17.1.8 - Two nearby hydrocarbon molecules attract one another with van der Waals forces that are caused by tiny fluctuations in the distributions of electric charge. At one moment (*a*), the charges on the two molecules are arranged so that the molecules attract one another ever so slightly. At another moment (*b*), the charges have rearranged, but the molecules still experience a weak attraction.

lost from stored gasoline. A car or lawnmower with an old tank of gas may not start because its gasoline has no more butane in it.

Because gasoline's ideal volatility depends on the outdoor temperature, the oil refineries adjust their blends according to season and climate. In winter, they reduce the average molecule size so that the gasoline vaporizes more easily in cold weather. In summer, they increase the average molecule size so that the gasoline is less prone to unwanted boiling.

But volatility isn't the only criterion for the molecules in gasoline. The other critical issue for gasoline is its resistance to knocking. Unfortunately the unbranched paraffin molecules that are common in crude oil ignite much too easily to be the major components of gasoline. Instead, most gasoline molecules are highly branched paraffins, olefins, or aromatics that are difficult to ignite.

Resistance to knocking is normally characterized by a gasoline's **octane number**. The higher the octane number, the harder it is to make the gasoline knock. 2,2,4-Trimethylpentane (also called "isooctane" or simply "octane")—a highly branched paraffin molecule with 8 carbon atoms (Fig. 17.1.2*d*)—is particularly resistant to knocking and is the standard by which all other molecules are measured. Its octane number is defined as 100. *n*-heptane, an unbranched paraffin molecule with 7 carbon atoms (Fig. 17.1.2*c*), knocks very easily and is the other standard. Its octane number is defined as 0.

These two hydrocarbons and their mixtures are used to assign octane numbers to gasolines. Each gasoline is compared to various mixtures of "octane" and *n*-heptane until a match is found. The percentage of "octane" in the matching mixture is then the octane number of the gasoline. For example, a gasoline that has the same knock resistance as a mixture of 90% "octane" and 10% *n*-heptane is given an octane number of 90. However, a gasoline's octane rating depends slightly on the conditions in which this comparison is made. The two standard conditions are *research*, corresponding to hard acceleration at low speeds, and *motor*, corresponding to zero acceleration at high-speeds. Any gasoline has two different octane numbers, its **research octane number** (R) and its **motor octane number** (M). These two octane numbers are averaged, (R+M)/2, to give the octane number that appears on the pump.

In formulating a gasoline, the refinery blends various hydrocarbons to achieve an overall octane number of about 87 for regular or 93 for premium. Since octane number only measures resistance to knocking, two different gasolines with identical octane numbers may contain very different assortments of hydrocarbon molecules. Often **antiknock compounds** are added to a gasoline to increase its octane number. These chemicals interfere with ignition. Tetraethyl lead was the antiknock compound of choice until concerns about lead pollution sent it into disuse. Modern antiknock additives include tert-butyl alcohol and methyl tert-butyl ether.

Kerosene is less volatile than gasoline and consists of molecules with between 10 and 15 carbon atoms. Since kerosene is often used inside houses in lamps and space heaters, it must burn easily and cleanly, without soot or noxious odors. It's normally made from unbranched paraffins and cycloparaffins. Olefins and aromatics are difficult to burn and tend to form soot. Aromatics also tend to have strong odors.

Diesel fuel, jet fuel, and heating oil are very similar. They are even less volatile than kerosene and contain hydrocarbons with between 12 and 20 carbon atoms. While heating oil can contain just about any hydrocarbon, diesel fuel and jet fuel have to be prepared with a little more care.

In a diesel engine, liquid fuel is injected into a cylinder filled with very hot, high pressure air (see Section 7.2). The fuel must ignite easily and spontaneously and burn completely in a very short period of time. The same easy and rapid combustion is important in a jet engine. This requirement of easy ignition is just the opposite of that in a gasoline engine. The ideal diesel and jet fuel molecules are unbranched paraffin molecules such as *n*-cetane, which contains 16 carbon atoms. Diesel fuels are rated according to their **cetane number**; the extent to which the fuel resembles the easy to burn *n*-cetane and not the hard to burn heptamethylnonane, a highly branched paraffin molecule that also has 16 carbon atoms.

Lubricating oils and waxes are even less volatile than fuel oils and contain molecules of between 20 and 50 carbon atoms. Pure hydrocarbons with molecules this large are normally solids at room temperature. However, lubricating oils contain so many different molecules that they're unable to find the orderly arrangements needed to form crystals. The molecules don't fit together well enough to form a rigid structure and remain a thick, viscous liquid.

Only the longer unbranched paraffin molecules are able to join together to form crystalline solids. These solids are called *paraffin waxes*. With time, paraffin waxes settle out of lubricating oils and are usually removed. At lower temperatures, shorter unbranched paraffin molecules also settle out of lubricating oil. The semi-solid material that forms in cold lubricating oil is *petrolatum* or *petroleum jelly*.

The remaining fluid is lubricating oil. Inserted between two movable surfaces, lubricating oil prevents those surfaces from experiencing sliding friction and wear as they slide across one another. The oil molecules cling to the surfaces and to one another with van der Waals forces and keep the two surfaces from touching. While outside forces may try to push the two surfaces together, pressure in the oil pushes back and keeps the two surfaces apart.

Oil's slipperiness comes from the nature of the forces between molecules. A pair of oil molecules is drawn together by van der Waals forces and by whatever pressure is present in the oil. However, if the molecules approach one another too closely, they begin to repel. This repulsion appears when the electron orbits of the two molecules begin to overlap. The Pauli exclusion principle doesn't allow identical electrons from both molecules to follow identical paths so it keeps the two molecules separated at an equilibrium distance.

But these forces depend only on the distance separating the two molecules and don't prevent the two molecules from sliding across one another. In fact, the molecules in oil do slide across one another quite easily and it is this mobility that makes oil such a good lubricant (Fig. 17.1.9). The van der Waals forces are virtually unaffected by sideways motion in the oil molecules.

However, when two surfaces are pushed together by outside forces, they

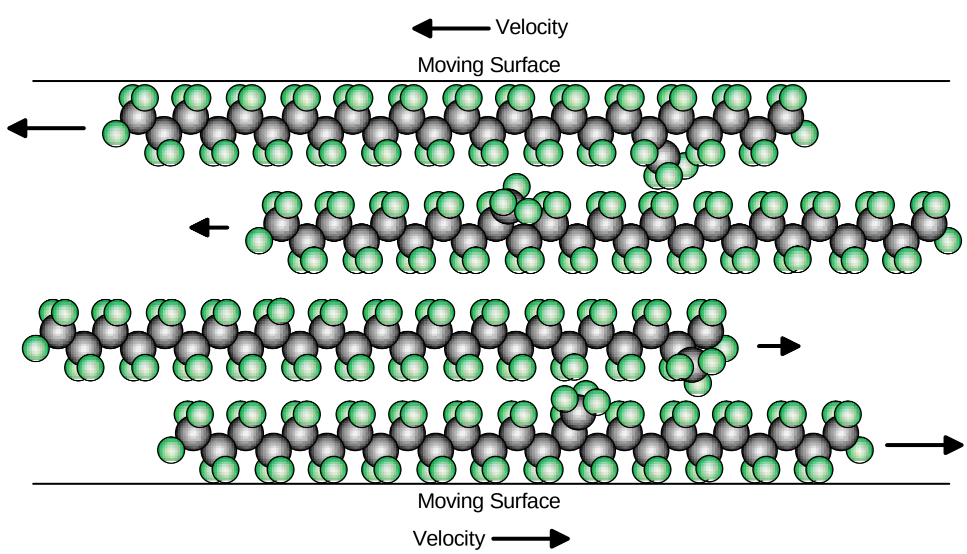


Fig. 17.1.9 - Lubricating oil molecules cling to one another with non-directional van der Waals forces and slide across one another easily. They prevent two surfaces from touching and dramatically reduce the amount of sliding friction between those surfaces.

create pressure in the oil. In a completely sealed environment, this rise in oil pressure wouldn't matter. But most lubricated surfaces have openings to the outside, where the pressure is lower. Since fluids always accelerate toward lower pressure, lubricating oil accelerates toward openings. The only thing preventing oil from squirting out from between two lubricated surfaces is the oil's viscosity—its difficulty flowing past itself. The more viscous the oil, the more it tends to remain between two surfaces to protect them from wear.

Using a lubricating oil with the right viscosity is important in many applications. If the oil isn't viscous enough, it will escape and will not protect the surfaces. If it's too viscous, energy will be wasted doing work against viscous forces, which turn that work into thermal energy.

An oil's viscosity depends strongly on the sizes of its molecules. The larger the molecules, the more viscous the oil. But molecular structure and temperature are also important. Some molecules, particularly cycloparaffins and aromatics, change their viscosities significantly as their temperatures change. Since most situations call for oils that don't change with temperature, most lubricating oils are composed primarily of branched paraffin molecules (Fig. 17.1.9).

Motor oils frequently contain additives to maintain their viscosities at higher temperatures. These additives are long molecules that roll up into compact balls at low temperatures but open up at high temperatures. In their open forms, these molecules thicken the oil and help it do its job. At very high temperatures, these additives and the oil itself fragment into smaller molecules and permanently lose much of their viscosity. That's why it mustn't be overheated.

The largest hydrocarbon molecules that leave an oil refinery are found in asphalt. Asphalt is what's left over when all of the other hydrocarbon molecules have been separated from crude oil. Asphalt molecules may have long paraffin chains or a number of interlocking rings, and frequently include atoms other than carbon and hydrogen. This crazy mixture of giant molecules is used mostly to pave roads. Asphalt molecules are large enough that the van der Waals forces between them prevent their motion at room temperatures. They form a stiff, structureless material that clings to surfaces and makes an excellent binder for the gravel in pavement.

The last major product of oil refineries is gases. These hydrocarbon molecules are so small that van der Waals forces can't keep them together at room temperature and atmospheric pressure, and they evaporate into gas. While many of these gaseous molecules are formed during the refining process, methane, with only 1 carbon atom (Fig. 17.1.2*a*), occurs naturally in underground reservoirs. Methane extracted from the ground is sent through pipelines and is sold as natural gas. It's a colorless, odorless, non-toxic gas that is significantly lighter than air. Breathing it is dangerous only because it contains no oxygen. Methane is very flammable, however, so a small amount of a sulfur-based odorant is added to it to help point out leaks.

Methane can only be liquefied by cooling it to very low temperature. This limitation makes natural gas difficult to store. However propane, with 3 carbon atoms (Fig. 17.1.2*b*), becomes liquid under pressure. Liquefied propane gas is stored in pressurized tanks and is used for heating and cooking. Liquefied petroleum gas (LP gas) contains both propane and butane.

Pressurizing the propane gas increases its density enough to sustain a liquid phase in a tank. Individual propane molecules continue to move back and forth between the liquid phase and the gaseous phase, but there's no net change in the amounts of liquid and gas. When you remove some of the propane gas from a tank to cook your food, some of the liquid evaporates to replace the missing gas molecules. This automatic replacement of the removed gas makes propane a very convenient fuel.

CHECK YOUR UNDERSTANDING #2: Easy Come, Easy Go?
The carbon dioxide molecules in dry ice are nonpolar and vanish into the air at a temperature of only –78.5 °C. What holds these molecules together as a solid?

Oil Refining: Removing Water and Salts

After that long introduction, it's time to look at how an oil refinery works. The refinery must separate the various components of crude oil into specific petroleum products such as gasoline or lubricating oil. Unfortunately, the crude oil that arrives at the refinery rarely contains the right assortment of molecules for the products the refinery wants to produce. Thus the refinery must usually modify the molecules it receives so that they fit its products. This purification and modification is an enormous task and requires a large facility.

The refinery's first job is to remove water and salt from the crude oil. These contaminants are of no use to the refinery. Fortunately, water and hydrocarbons don't mix well because their molecules don't bind to one another strongly. The molecules in water cling to one another with hydrogen bonds, while the molecules in oil hold onto one another only with weaker van der Waals forces. When you put the two liquids together, the water molecules stay bound to water molecules and the oil molecules stay bound to oil molecules. They don't mix.

What ultimately makes oil and water so **immiscible** is the strength of the hydrogen bonds between water molecules. It takes far too much energy to separate water molecules for them to mix with the oil molecules. If you pour water and oil into a glass, the less dense oil floats on top of the water and a sharply defined interface forms between the oil and the water.

The water molecules at this interface are special. While the water molecules below them can form hydrogen bonds with neighbors in all directions, the water molecules at the interface have only oil molecules above them. These surface water molecules cling particularly tightly to one another and they create an inward tension along the water's surface. A **surface tension** of this type appears whenever one material ends and another begins. Surface tension is particularly strong in water because water molecules attract one another so strongly.

Surface tension always acts to minimize a liquid's surface area. The surface of the liquid behaves like an elastic membrane, stretching when you exert forces on it but always snapping back to a taut, smooth shape. Surface tension squeezes raindrops into tiny spheres and turns the surface of a calm lake into a trampoline for water bugs.

Surface tension minimizes the surface area between the water and the oil by making the interface flat and level. But if you cover the glass and shake it hard, the interface will stop being flat. Instead, the glass will become filled with droplets of oil in water and water in oil. You will have formed an **emulsion**, a situation in which droplets of one liquid are suspended in another.

Surface tension will quickly minimize the surface area of each droplet by making it spherical. But the emulsion will contain more surface area overall than it did before you shook the glass. Because it can further reduce the surface area by reducing the number of droplets, you will see the droplets touch and coalesce. Each time two droplets merge, their combined surface area goes down. Eventually all of the droplets will have joined together and the oil and water in the glass will have separated completely.

But the smallest droplets don't merge together easily. They experience large drag forces as they try to move through the surrounding liquid and travel extremely slowly. It takes a long time for them to find other droplets with which to

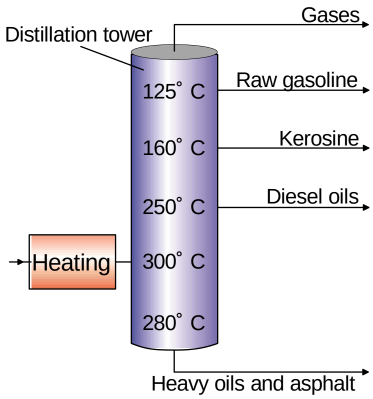


Fig. 17.1.10 - The temperature in a distillation tower decreases from the crude oil inlet to the top of the tower. Liquid extracted from trays at various heights and temperatures contain different mixtures of molecules, and are appropriate for different petroleum products.

coalesce. In thick, gooey crude oil, tiny water droplets form an emulsion that takes almost forever to settle. In fact, various chemical impurities in the petroleum actually surround the water droplets, so that they can't touch and coalesce. As a result, getting the water out of crude oil is quite difficult.

Oil refineries usually break the emulsions by heating the oil and passing it through settling tanks or filter columns. At elevated temperatures (90 to 150 °C), water's surface tension decreases and the water droplets are able to merge together more easily. In fact, the energetic water molecules bounce around so vigorously that they have trouble staying together at all. To keep molecules of water or oil from becoming gaseous, the hot crude oil must be kept under pressure. Heat also reduces the crude oil's viscosity and the water molecules are able to settle more easily.

As it settles, the water collects the salt molecules in the crude oil. Since salts are composed of electrically charged ions, they only dissolve in liquids that bind well with charged particles. Water molecules are polar and do a good job of dissolving most salts. Because hydrocarbon molecules are **nonpolar**—they have no electrically charged ends—they rarely dissolve salts. So the salts accumulate in the water as it settles to the bottom of a tank or filter column.

The smallest water droplets still have trouble settling out of the crude oil. Gravity and buoyant forces are sometimes just too weak to overcome drag forces. Many refineries use electrostatic precipitators to pull the water droplets through the oil. Since oil doesn't conduct electricity, it behaves like very thick air. Charged particles injected into the crude oil quickly attach themselves to water droplets and these electrically charged water droplets are pulled through the oil by electric fields.

CHECK YOUR UNDERSTANDING #3: I'm All Shook Up
Why must you shake most clear salad dressings before you serve them?

Distilling the Crude Oil

Once water and salts have been removed from the crude oil, the refinery is ready to begin sorting its molecules. The principal sorting technique is distillation. Distillation is described in the supplement on water purification, but here the job is somewhat different. In water purification, the goal is to separate a volatile chemical (water) from a non-volatile chemical (salt) and the only molecule that becomes a gas at reasonable temperatures is water. But in petroleum distillation, almost all of the molecules can become gaseous in the right circumstances. So the refinery must carefully adjust those circumstances in order to collect particular groups of molecules from the mixture.

The crude oil leaving the water separator is heated and then injected near the bottom of a tall distillation tower (Fig. 17.1.10). This tower contains a series of collecting trays, one above the other (Fig. 17.1.11). The temperature inside the tower is carefully controlled so that it's highest where the crude oil enters the tower and gradually decreases from the bottom to the top of tower. Thus each collecting tray is a little cooler than the one beneath it.

As the hot oil enters the tower, all but the largest molecules evaporate and become gas. This gas gradually ascends the tower and its temperature decreases (Fig. 17.1.10). With each decrease in temperature, the molecules in the gas find it more difficult to stay apart. The larger molecules in the gas begin to stick to one another and form liquid in the tower's trays. Some of this liquid drips down from each tray to the tray below. Overall, gas moves up the tower from below and liquid drips down the tower from above.

Each tray tends to accumulate those molecules that can be *either* gas or liquid at the tray's temperature of the. Any molecules that tend to be gaseous at that temperature will move up the tower to the trays above. Any molecules that tend to be liquid at that temperature will drip down the tower to the trays beneath. Thus each tray concentrates a particular group of molecules.

However this concentrating process doesn't produce pure chemicals. The liquid in a particular tray still contains a number of different molecules. While one range of sizes is most likely to accumulate in that tray, it will also contain some smaller and larger molecules that manage to find their way into the liquid. In general, nature always tries to maximize the randomness of a liquid. The same statistical rules that govern the flow of heat and are responsible for the laws of thermodynamics also make it very difficult to purify chemicals completely.

Unlike oil and water, these hydrocarbon molecules mix easily with one another. They all stick together with van der Waals forces, regardless of how large their molecules are. Chemical such as these that dissolve freely in one another are said to be **miscible**. While the smaller molecules will tend to evaporate from the liquid more easily than the larger molecules, they are all pretty much equal in the liquid itself.

Crude oil's first trip through a distillation tower separates it into several parts, including diesel oil, kerosene, and raw gasoline (Fig. 17.1.10). The diesel oil and kerosene are basically ready for consumer products, but the raw gasoline is not. It has a very low octane number and must be reformed and blended before it's ready for automobiles. Molecules that are too small to become liquid even at room temperature reach the top of the tower and are processed into propane and LP gases.

The largest molecules that enter the distillation tower rarely become gaseous below 300 °C and drip as a liquid to the bottom tray. It might seem reasonable to heat this **residual liquid** to a higher temperature to separate its molecules from one another. Unfortunately, temperatures above about 360 °C cause hydrocarbon molecules to decompose into fragments, a phenomenon called **cracking**. These fragments can then recombine to form gums that plug up the distillation equipment. To avoid cracking, the distillation columns must avoid excessive temperatures.

While the molecules in the residual liquid can still be separated by distillation, that distillation must be performed at very low pressures in a vacuum distillation tower (Fig. 17.1.12). The residual liquid from an atmospheric pressure tower is reheated to 350 °C and fed into a vacuum tower near its base. Gases move upward while liquid moves downward and each tray accumulates those molecules that can be either gaseous or liquid at its particular temperature.

Because the pressure and density of the gas are reduced in the vacuum tower, molecules don't have to be very volatile to become a gas. Since forming a thin, low pressure gas of lubricating oil molecules is much easier than forming a dense, high pressure gas of those same molecules, it occurs at a much lower temperature. Thus the vacuum distillation column is able to separate various lubricating oils and waxes from molecules that simply aren't volatile. The residual liquid leaving the bottom of the vacuum column is asphalt.

The hydrocarbon gases that reach the top of the atmospheric pressure distillation column must still be separated according to molecular size. As usual, this separation involves distillation, but this time the distillation is done at high pressures and relatively low temperatures. By squeezing the gas molecules close together, the refinery encourages them to spend time as a liquid and they drift upward as gas and downward as liquid. Trays near the bottom of the high pressure tower accumulate liquid butane, those near the middle of the tower accu-

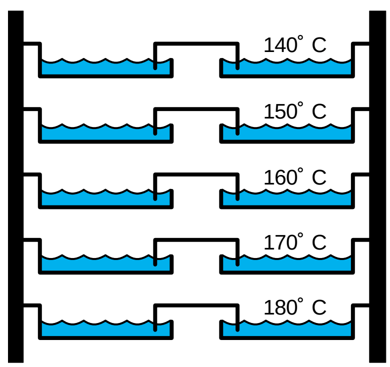


Fig. 17.1.11 - Inside a distillation tower is a series of trays, each one cooler than one below it. Gaseous oil molecules bubble up through each tray from below. As they do, the larger molecules condense into liquid. The liquid in each tray is different, with lower trays containing larger molecules than upper trays.

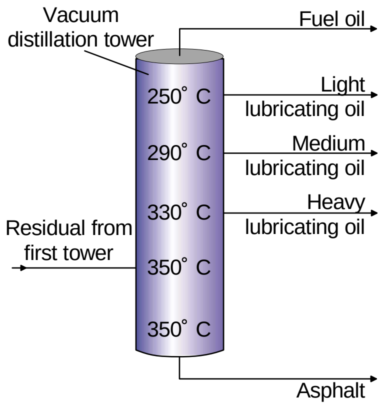


Fig. 17.1.12 - In a vacuum distillation tower, the reduced pressure allows even relatively non-volatile lubricating oils to become gaseous.

tower accumulate liquid butane, those near the middle of the tower accumulate liquid propane, and ethane and methane drift to the top of the tower.

CHECK YOUR UNDERSTANDING #4: Too High To Climb?
Why will very few large molecules be found in a tray near the top of the first distillation tower?

Thermal and Catalytic Cracking

Unfortunately, just sorting the molecules in crude oil isn't good enough for most refineries. The principal outputs of these refineries are transportation fuels and there is comparatively little market for the other molecules in crude oil. Since less than half of the molecules in crude oil are suitable for transportation fuels, the refinery has a problem. Moreover, it can't store the unmarketable molecules indefinitely. While the refinery burns some of the less useful molecules to provide its own power, it must sell everything else to make room for incoming crude oil. So large integrated refineries have facilities for converting the less useful molecules in crude oil into ones it can sell.

The original method for converting larger molecules into smaller molecules is thermal cracking. Above about 360 °C, hydrocarbon molecules decompose into fragments. At that temperature, the random thermal energy in a hydrocarbon molecule is occasionally large enough to break that molecule into two pieces. After a short time as a free radical, each fragment rearranges into something that's chemically stable. Most of the time the new molecules are smaller than the old molecules.

The higher the temperature, the more often such decompositions occur and the faster the petroleum cracks. While thermal cracking is a nuisance to be avoided in distillation, it's valuable when done in a controlled manner in a cracking tank. The big molecules that aren't suitable for gasoline generally decompose into smaller ones that are.

Moreover, thermal cracking produces many olefin molecules that have higher octane numbers than the usual contents of crude oil. These olefin molecules are made when the free radical fragments of original hydrocarbon molecules rearrange internally to form double bonds. If the last carbon atom in a chain has only three neighbors, it can complete its electronic shell by forming a double bond with the carbon atom next to it. This rearrangement causes the neighboring carbon to abandon a hydrogen atom, which immediately becomes part of a hydrogen molecule. So thermal cracking creates many smaller molecules, with double bonds at their ends, and hydrogen molecules.

But thermal cracking is difficult to control and also creates many large and useless molecules. As a rule, the higher the temperature in the cracking tank, the higher the octane of the gasoline it produces but the smaller the yield. To make premium gasoline by thermal cracking, the refinery might have to waste all but 20% of the hydrocarbons it feeds to the cracking tank. Because this waste is intolerable, thermal cracking has been replaced almost completely by fluid catalytic cracking and reforming.

In these processes, hot hydrocarbon molecules are brought into contact with silica-alumina catalysts. Like all catalysts, these materials facilitate chemical reactions by reducing the activation energies needed to complete them. When a hydrocarbon molecule attaches to the surface of the catalyst, the catalyst helps it rearrange (Fig. 17.1.13). The catalyst reduces the potential energies of the par-

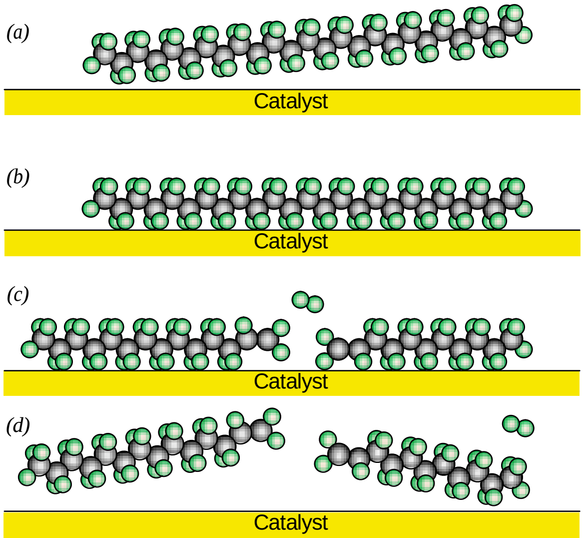


Fig. 17.1.13 - A catalyst provides a special surface (*a*) to which a long unbranched paraffin molecule can attach (*b*). The catalyst helps the molecule crack into two parts (*c*)—the final pair of carbon atoms in each of the new chains is joined by a double bond and a hydrogen molecule is released. Once the rearrangement has occurred, the new molecules leave and the catalyst is left unchanged (*d*).

tially rearranged molecules so that less overall energy is needed to complete the rearrangement. Catalyzed rearrangements thus proceed at lower temperatures.

These catalysts also help to control the rearrangements. A particular catalyst will assist certain rearrangements more than others. Catalysts are particularly helpful in cracking larger molecules into smaller ones so that yields of gasoline molecules are much higher with catalysts than without.

Because all of the catalyst's work is done by its surface, most commercial catalysts are designed to have lots of surface area. The silica-alumina catalysts used in fluid catalytic cracking are actually small particles of porous materials. These particles are only about 50 microns in diameter and they swirl around with the fluid they are cracking.

The reactions take only a few seconds to complete, after which the catalyst particles must be separated from the fluid. The mixture passes through a *cyclone separator*, where it moves very rapidly around in a circle. The acceleration causes the denser catalyst particles to migrate to the outside of the separator and the clear fluid can then be extracted from the middle of the device.

Unfortunately, the catalyst particles quickly accumulate a coating of very large molecules that don't react and can't be removed easily. Like most catalysts, they lose their catalytic activity when their surfaces become dirty. The only effective way to clean the surfaces of these particles is to burn the residue off them. That's just what the oil refinery does. This burning regenerates the catalyst particles and prepares them for their next trip through the fluid.

CHECK YOUR UNDERSTANDING #5: It's All On the Surface

Which would make the more effective catalyst, a 1 kg cube of silica-alumina or 0.1 kg of silica-alumina particles?

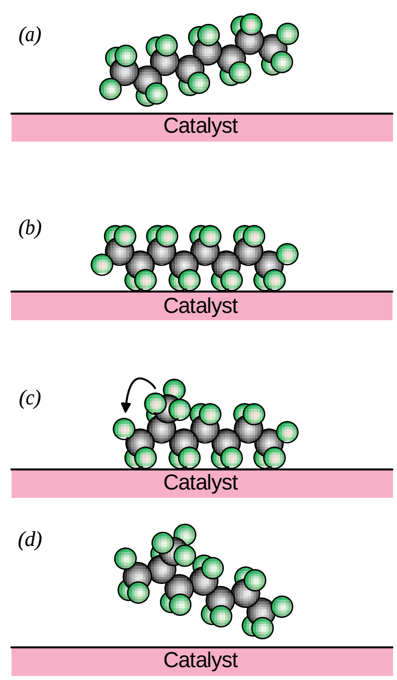


Fig. 17.1.14 - An unbranched paraffin molecule (*a*) attaches to the surface of an isomerizing catalyst (*b*). This catalyst helps a carbon atom and a hydrogen atom exchange places (*c*) by stabilizing the pieces during the exchange. The branched paraffin molecule leaves and the catalyst is left unchanged (*d*).

Improving the Quality of Petroleum Products

Catalysts also help individual hydrocarbon molecules to change their structures, processes called *isomerization* and *reforming*. Long unbranched paraffin molecules and cycloparaffins aren't useful in gasoline because they cause knocking. **Isomerizing** catalysts, usually platinum, help the unbranched molecules to rearrange into highly branched molecules (Fig. 17.1.14). **Reforming** catalysts, usually plati-

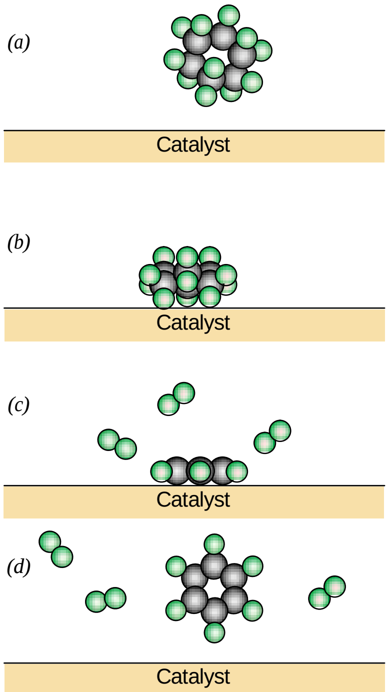


Fig. 17.1.15 - A cycloparaffin (*a*) attached to the surface of a reforming catalyst (*b*). This catalyst helps in the removal of hydrogen molecules from the ring (*c*) and creates an aromatic molecule. This molecule leaves the surface and the catalyst is left unchanged (*d*).

num and rhenium, assist in converting cycloparaffins into aromatics. In both cases, the octane numbers increase substantially. Much of the low octane, raw gasoline obtained from the first distillation tower is subsequently sent through catalytic isomerizing and reforming facilities to increase its octane number.

The goal of isomerization is to add more branches to a paraffin molecule by interchanging hydrogen atoms and carbon atoms. On the isomerizing catalyst's surface, one carbon atom and one hydrogen temporarily let go of the hydrocarbon molecule and exchange places. Several such interchanges turn the molecule into a highly branched paraffin with a high octane number.

Without a catalyst, this isomerizing process requires a great deal of energy. Two separate covalent bonds must break completely so that the pieces become free radicals. The carbon and hydrogen atoms must then exchange places and reattach to the main portion of the molecule. This complicated process is unlikely to happen, even at high temperatures.

The isomerizing catalyst facilitates the process by binding temporarily to the molecule and its fragments. The various pieces never become free radicals. Instead, they migrate along the surface of the catalyst and eventually reattach to one another without ever being completely free. The catalyst even helps the fragments stay close enough together to exchange places. What would otherwise be an almost impossible event becomes rather likely.

A reforming catalyst helps cycloparaffin molecules get rid of hydrogen atoms and become aromatics (Fig. 17.1.15). Aromatics have higher octane numbers than cycloparaffins, so this reforming is important for gasoline. Although catalysts ease the removal of the hydrogen atoms as hydrogen molecules, the final product molecules have more chemical potential energy than the original molecules. Because this reaction converts a significant amount of thermal energy into chemical potential energy, heat must be added to keep it going.

In addition to isomerization and reforming, oil refineries also use catalysts to attach smaller molecules together to form larger molecules. Catalytic alkylation and polymerization are used to form gasoline molecules from smaller molecules that would otherwise be difficult to use. Both processes start with olefin molecules produced in thermal or catalytic cracking. The olefin molecules have reactive double bonds, and catalysts encourage them to stick to one another or to other molecules. These reactions produce highly branched, high octane gasoline.

CHECK YOUR UNDERSTANDING #6: Don't Get Involved

Many of the catalytic processes performed in oil refineries use precious metals such as platinum and rhenium. Why don't these metals end up in the petroleum products?