

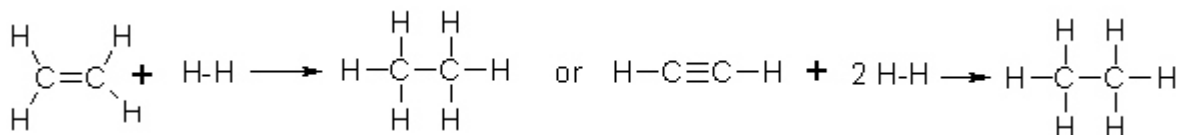
Chapter 22 Organic Chemistry

We have looked at lots of different chemistry up to this point. Now we will concentrate on what is called **Organic** chemistry.

What is Organic chemistry? Organic chemistry is the study of any compound that contains carbon.

22.1 Alkanes: Saturated Hydrocarbons

Hydrocarbons are compounds composed of hydrogen and carbon. A **saturated** hydrocarbon is a compound where all the C-C bonds are single bonds. As you will see in section 22.2 we refer to compounds that have C-C double bonds or triple bonds as **unsaturated** hydrocarbons, since the multiple bond can be reacted in a **addition reaction**.



unsaturated
Ethylene

Saturated
Ethane

Unsaturated
Ethyne

Saturated
Ethane

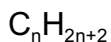
Note that in the unsaturated ethylene each C is bonded to 3 atoms, so if we break the C-C double bond each C can be bonded to 4 atoms.

What kind of bonding should we have in a saturated hydrocarbon? 4 bonds, sp^3 hybridized. How should the atoms be arranged? Tetrahedral, 109° .

We call saturated hydrocarbons **alkanes**. There are literally hundreds of alkanes so we **use a systematic nomenclature to name them. Table 22.1**

| | # C | Formula | MP | BP | # isomers |
|---------|-----|------------------------------|------|------|-----------|
| methane | 1 | CH_4 | -183 | -162 | 1 |
| ethane | 2 | C_2H_6 | -183 | -89 | 1 |
| propane | 3 | C_3H_8 | -187 | -42 | |
| butane | 4 | C_4H_{10} | -138 | 0 | 2 |
| pentane | 5 | C_5H_{12} | -130 | 36 | 3 |
| hexane | 6 | C_6H_{14} | | | |
| heptane | 7 | C_7H_{16} | | | |
| octane | 8 | C_8H_{18} | -57 | 126 | 18 |
| nonane | 9 | C_9H_{20} | | | |
| decane | 10 | $\text{C}_{10}\text{H}_{22}$ | -30 | 174 | 75 |

Also note that since we have only C and H and only single bonds there is a definite relationship between the # of C and the # of H



So if I said octane, this could contain 8 C and $8 \times 2 + 2$ or 18H so



Note in table 22.1 how the MP and BP increase with size why would this be? Will explain in chapter 10 - Larger size, more London dispersion, more attraction

Note also in table 22.1 the column structural isomer. What does this refer to? It refers to the fact that even though you have a compound with the same number of H and C and bonds, the overall arrangement of the atoms can be different. When you have compounds with the same chemical formula but different structures, these compounds are called **structural isomers** of each other.

For example 1 structural isomer for each alkane consists of a long, unbranched string of C. These forms are called **normal, straight-chain, or unbranched hydrocarbons**. Their structure would look like this:

C-C-C-C-C etc.
(Pentane)

How else could we arrange 5 C?

C-C-C-C Note that C-C-C-C is the same, just flipped end-for-end doesn't count
C C

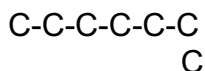
C
C-C-C This is 3 and checks with the table in the book
C

Let's take a closer look at naming these alkanes

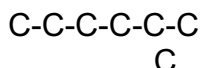
1. Suffix -ane, prefix, methyl, ethyl, propyl, butyl, Greek root for number (penta- etc)
 - a. If branched, always use the **longest** continuous chain of carbons (so our examples above become a butane and a propane)
2. When an alkane is a substituent, drop the -ane and use -yl
Thus in our example we have methylbutane
3. Frequently you will need to number the main chain to tell when the substituent groups are placed. If this happens start numbering the main chain at the end closest to the branching. Also, use a hyphen between the number and the name
Thus 2-methylbutane is correct, not 3-methylbutane

4. The substituent are listed in alphabetical order and di-,tri- may be used to indicate multiple substituents (the di-or tri doesn't count in the alphabetical order).

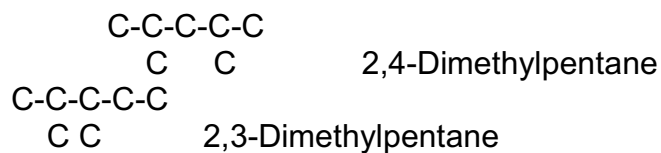
Let's try a few examples Give one or the other to go both ways



Heptane (no branch! I tried to catch you)



2-Methylhexane

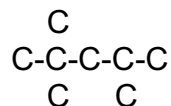


C-C-C-C-C 3-Ethyl-2-methylpentane (note ethyl before methyl)



Try some the other way

2,2,4-Trimethylpentane



Cyclic alkanes

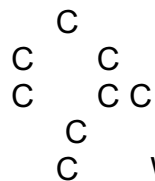
We skipped over one other kind of isomer earlier, cyclic isomers. In cyclic compounds the C chain is linked back to itself. Can be triangle, square or larger. Because they have this link to themselves they have 2 less hydrogens than non-cyclic alkanes, thus this general formula is C_nH_{2n} . But this formula does not mean that it has to be cyclic, could have a double bond - see section 22.2)

Cyclopropane is very unstable while cyclobutane is moderately unstable. Can anybody explain this? Sp^3 hybridization, preferred bond angle 109. In triangle must be 60, in square must be 90, so bonds can't line up with perfect overlap and are **strained**
Check propane Can't you get a non-planar system that works?

5 and larger rings are quite stable because can pucker to relieve strain

Demo boat and chair pucker

The nomenclature for cycloalkanes is the same, just precede with prefix cyclo- and number the ring system so the substituents have the smallest number



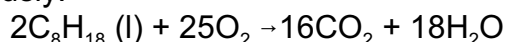
Would be 1,2- dimethylcyclohexane not 2,3 or 5,6 etc.

reaction of alkanes

If you take organic next year you will learn many more reactions of alkanes, but for now let's hit the big ones

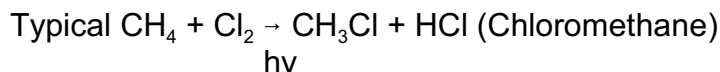
First is the C-H bond stable or unstable. Stable so not very reactive, will not react strong base or strong acid or strong oxidizing agent. In fact not a lot of reactions but there are some important ones

1. Combustion reaction. Hydrocarbons can react with O_2 . Takes a bit of heat to get started., but reaction generates a lot more heat so once it gets started it will go vigorously.



Why did I use this example Octane - gas, etc.

2. Substitution reactions - Substitute one atom for another
Primarily can replace H with Cl



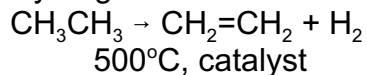
where $h\nu$ is light energy. May be repeated to make Dichloromethane (methylenechloride), trichloromethane (Chloroform) and tetrachloromethane (carbon tetrachloride) the last 3 are commonly used non-polar solvents

This reaction work because the light splits the Cl into 2 Cl[•] Atoms with a free electron. This is a highly reactive species that allows it to react with the alkanes.

Carbons chains that contain both Cl and F are the Freons that are commonly used as refrigerants. (unfortunately so stable that can damage the atmosphere

3. Dehydrogenation reactions

Hydrogen can be removed from alkanes at high temp and catalysts like Cr_2O_3



22.2 Alkenes and Alkynes

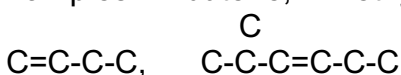
Alkenes

Hydrocarbons that contain C-C double bonds are called alkenes, Formula $C_n H_{2n}$

The simplest alkene is ethylene with 2 sp^2 hybridized carbons and substituents placed at 120° angle and the π bond between the carbon p orbitals

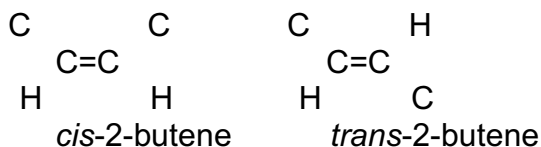
The nomenclature for the alkenes is similar to that of alkanes, you just replace the -ane with a -ene. If there are more than 3 C then the position of the double bond must be specified by indicating the lowest number C involved in the double bond

Examples 1-butene, 2-methyl-3-hexene



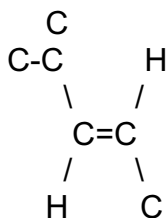
When the pi orbitals line up for the π bond the 2 C involved in the bond are locked in place and cannot rotate. This presents yet another form of isomerization called **cis-trans isomerism**

Note the two butenes shown below



Identical substituents on the **same** side of the double bond are called **cis**, and on **opposite** sides are called **trans**

Let's try one example.



trans-4-methyl-2-pentene
Alkynes

A hydrocarbon that contains a triple bond is called an alkyne. The simplest alkyne is ethyne $H-C \equiv C-H$ (trivial name acetylene)

What is its spatial organization (linear Each C has 2 sp^2 hybridized bonds and 2 π bonds)

The nomenclature is just like that for alkene, just change -ene to -yne

Both alkenes and alkynes can exist in ring structures (cyclohexane)

Reactions of Alkenes and Alkynes

1. Note most alkenes and alkynes contain some C-C single bond so the reaction of this part of the molecule is the same. The double and triple bond of these compounds are more reactive than the C-C single bond. The most common reaction that this bond does is called an **addition** reaction, where atoms are added across the multiple bond. One addition reaction is the addition of H₂ in the **hydrogenation reaction**:

Note the difference in alkanes we had substitution reaction, substitute one atom for another, in alkenes and alkynes have addition, add new atoms

$\text{CH}_2=\text{CHCH}_3 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3$. This reaction requires the presence of a catalyst like platinum or palladium or nickel to occur at room temp.

This reaction is used a lot in the food industry. Does anybody know where?

Ever hear of saturated fats? Or hydrogenated vegetable oil? Vegetable oils frequently contain saturated hydrocarbons. To make them more solid, and because poly unsaturated fats are thought to be unhealthy, these fats and oils are saturated to remove these multiple bonds.

Double bonds can also be **halogenated** in a similar manner using Cl₂ or F₂ etc.

A final reaction, that we will hear more about in a bit is **polymerization** where small molecules are joined together to make larger molecules

22.3 Aromatic Hydrocarbons

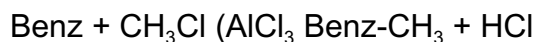
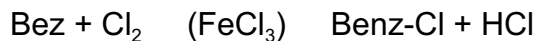
A special class of unsaturated hydrocarbons are known as **aromatic hydrocarbons**. The simplest of these is benzene C₆H₆

Remember when we were doing structure and we found compound that had multiple Lewis structures that were equivalent, and we said that these Lewis structure represented electrons that were smeared out over several different atoms? Well aromatic hydrocarbons are hydrocarbons that contain this kind of linkage. Can you find the two different Lewis structure for benzene? The actual structure has sp² hybridization for each C and the p orbital form large π orbital that delocalize the extra electrons over all 6 Carbons. We usually depict this as a circle within the benzene ring.

The aromatic system is more stable than standard double bonds, so the reactivity of benzene is much different than the reactivity of alkenes.

For instance we just learned about how alkene undergo rapid addition reaction. Benzene will not undergo such reactions.

Benzene instead will undergo substitution reaction (like we saw for C-C single bonds) where the H's are replaced with other atoms with the help of a catalyst



Nomenclature for benzene ring system is the same as for saturated ring systems. If there are constituents you assign them number in a manner that gives the smallest number like
1,2-dichlorobenzene.

There is also a second nomenclature system you will see. In this system substituent adjacent to each other are called ortho or *o*, 1 C between, meta or *m* 2 C between (across from each other) para *p*

Thus 1,2-dimethylbenzene would be *o*-dimethylbenzene

3-Bromonitrobenzene would be *m*- bromonitrobenzene Nitro is NO_2

Note assumed the nitro was 1 and bromo before nitro for alphabetical

Aromatic systems can exist as large fused ring system where the electron can be spread out over many atoms Table 22.3 You may have heard of these referred to as PAH's polycyclic aromatic hydrocarbons

22.4 Hydrocarbon derivatives

Most organic molecules contain other atoms besides C and H. We will view these compounds as hydrocarbon derivatives. That is they are essentially hydrocarbons with various **functional groups** attached

The common function groups are summarized in table 22.4 You are responsible for all of them + one that I will add.

Lets exam class by class

Halohydrocarbons

F, Cl, Br or I substituted into alkanes

CH_3F , CH_2F_2 , C_2F_6 etc.

Alcohols

-have a hydroxyl group present

-replace final -e with -ol

-classified as primary, secondary, or tertiary

if need to number, set up number system so -OH has lowest number

Name CCCC(O)H Propanol

C(C)C(O)H 4-chloro-1-propanol

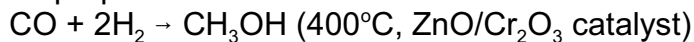
5-chloro-2-methyl-2-hexanol

C
CCCCC
O Cl
H

- usually higher B.P. than expect why? Polar, hydrogen bond interaction

- most important commercial methanol and ethanol

Methanol prep

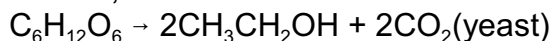


Used to make acetic acid, fibers, plastics, adhesives

Blindness and death if ingested

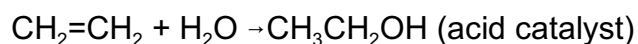
Ethanol

Source, fermentation

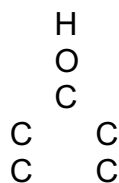


When alcohol reaches about 13% yeast die, that is why wine & beer are 13%. If want anything stronger must distill

Can also be made by reaction



The simplest aromatic alcohol is phenol



C Used in polymers and plastics

Ethers



The ether that will put you to sleep

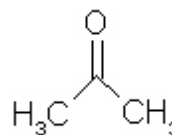
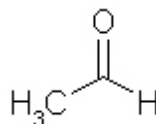
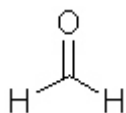
Aldehydes and Ketones

-contain the carbonyl group $\begin{array}{c} \backslash \\ \text{C}=\text{O} \\ / \end{array}$

-in ketones bonded to 2 C Example acetone (dimethylketone)

- in aldehydes at least 1 H

Examples:



Proper name:

Methanal

Ethanal

Propanone

Trivial name:

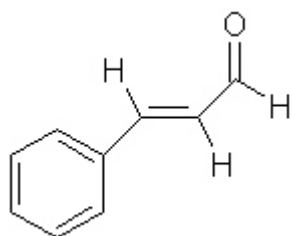
Formaldehyde

Acetaldehyde

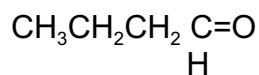
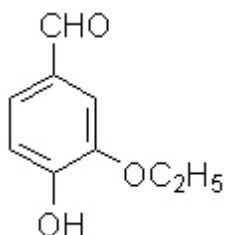
Acetone

- naming replace -e with -al for aldehyde
- replace -e with -one in ketone
- note an aldehyde must always be at one end of a chain, so is always set to 1 in numbering system (proper name for acetaldehyde would be ethanal)
- ketones usually nice solvents

-aldehydes usually av strong odors, vannilla, cinnamon, butyraldehyde



Cinnamaldehyde



Ethyl vanillin
Book has methyl

Butyraldehyde

-Aldehyde prepared commercially from oxidation of primary alcohols
-ketones prepared commercially form secondary alcohols

Carboxylic Acids

-Carboxylic acids have the carboxyl group
-COOH

- typically are weak acids in solutions

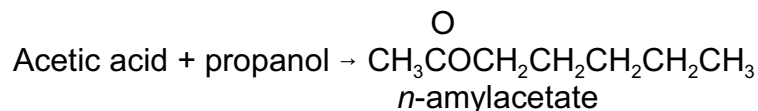
-name from parent alkane drop -e add -oic

Thus acetic acid is more properly called ethanoic acid

-synthesized by using a strong oxidizing agent on a primary alcohol,
typically KMnO_4

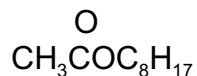
-carboxylic acids react with alcohols to form esters and H_2O

Esters

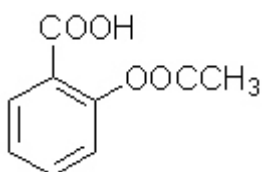


-Esters have sweet, fruit odors. The above is the smell of bananas

N-octyl acetate oranges



-Aspirin is an ester of salicylic acid and acetic acid



Amines

Bases

Like ammonia with N-H replace by 1 or more N-C bonds

primary, secondary, tertiary 1N-C, 2 N-C, 3 N-C

common name are often used

systematic name use amino as a prefix

2-aminohexane

Unpleasant 'fishy' odor or dead animal mater odor

putrecine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$)

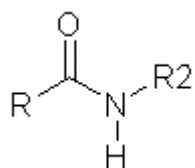
Cadaverine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$)

often used in dyes are also often carcinogenic

Amides

Ester was combination of carboxylic acid and alcohol

amide is combination of carboxylic acid and amine



Even though acid and base combined the amide is not either an acid or a base. This is what holds proteins in your body together

22.5 Polymers

Polymers are large molecules build up from smaller pieces called monomers. They are basis of synthetic fibers, rubbers and plastics

The simplest polymer is *polyethylene*

found in your common recyclables HDPE (High density Poly Ethylene) #2 and LDPE Low Density Polyethylene #4, example?

Constructed from ethylene monomers



used pipes, bottles, insulation

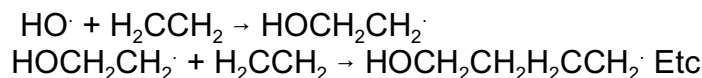
can vary properties by using substituted monomers

use $\text{F}_2\text{C}=\text{CF}_2$ makes Teflon!

Other substituents and uses see table 22.8

Polyethylene is an example of **addition polymerization reaction** that is monomers simply add on to a growing chain to form polymer with no other products

This kind of polymerization is often initiated by a **free radical** (a species with an unpaired electron) The free radical attacks the pi bond of the ethylene to add to it, and to generate a new free radical that can attack another monomer

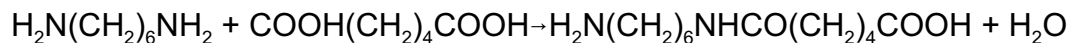


The reaction only stops when 2 radicals react with each other to form a bond

Another type of polymerization reaction is the **condensation polymerization reaction**

In this reaction a small product is formed each time a monomer is added to the polymer

For instance one form of nylon comes from the condensation of hexamethylenediamine and adipic acid



The dimer that can then undergo further condensation

Can I do a demo 22.9? similar to fig 22.17 in class?

22.X Everyday Polymers Not in the chapter, but I may add if I have time

Let's condense this down to a few of the more important points

Thermoset polymer. Heat it up into a form, and then it is set in that shape permanently.

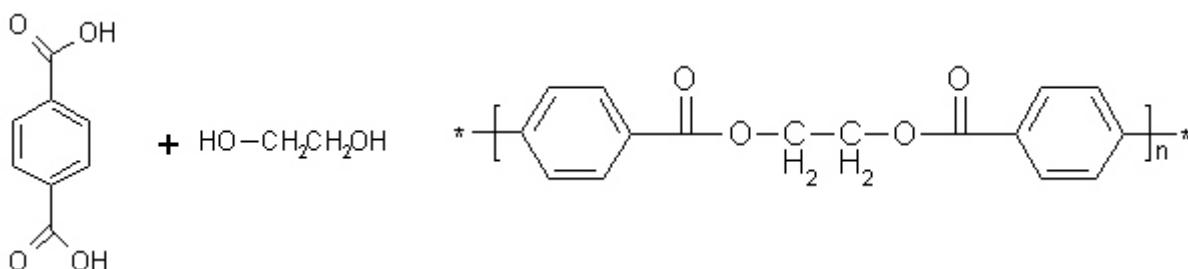
Thermoplastic polymer -Heat it up, you can make it flow into a new shape.

Elastomers -materials that recover their shape after being deformed by a force. first elastomer used natural rubber that was crosslinked with sulfur (Vulcanization, invented by Goodyear)Elastomers are characterized by a highly random structure. When stretched this lines molecules up, want to return to random, so snaps back when released.

- First commercial plastic 1907 Bakelite - Hard brittle black shiny see on many older things is a thermoset

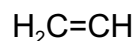
Today you are most familiar with plastics through their recycling number

#1 PETE Polythelene terephthalate - usually clear, rigid bottles



#2 HDPE- milk jugs, oil bottles, A form of polyethylene. Formed at moderate pressure and temperature with a catalyst, so forms long linear chains the fold against each other and give it a high density

#3 PVC



Cl base

Pure PVC very hard and brittle decomposes with just a little heat.

By putting additives can dramatically change properties, make heat stable, can make flexible, can make colorful, etc

Can be clear, put in additives to make opaque also to keep UV light from breaking down. Plumbing pipe

#4 LDPE Plastic squeeze bottle use in lab, bread and food bags

Another polyethylene. However this is made at high pressure and temperature (20,000 psi, 500C) tend to make short branched polymer chain. These don't fold against each other very well, so final material has a lower density than -

#5 PPE polypropylene $\text{H}_2\text{C}=\text{CH}-\text{CH}_3$ monomer. Same kind of reaction arrangement of methyl dramatically change properties most made with a catalyst and this makes methyls line up, so this plastic is harder and stronger than LDPE or HDPE
- Catsup bottles, Yogurt, cottage cheese cartons

#6 Polystyrene
 $\text{H}_2\text{C}=\text{CH}$ -benzene (styrene base)
very brittle all by itself, mix with other to acrylonitrile and butadiene to make ABS plastic (acrylo-butadiene-strene)

22.6 Natural Polymers

Proteins

15% of your body
Molar mass from 6000-over 1,000,000
Not a random polymer, but a highly organized with a distinct 3D structure

2 major classes

Fibrous proteins - make up connective tissue

Globular proteins - water soluble, catalyst that perform virtually all chemical reactions of the cell

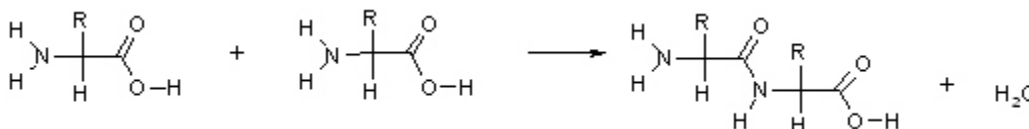
Monomer is called an amino acid

20 different amino acids in nature Figure 22.18

All have same backbone structure

What is different is side chain

Polymer build using a condensation reaction



You should recognize this linkage as the amide given earlier, also called the peptide bond

The linear sequence of amino acids is called the *primary structure*.

Certain sequences of amino acids can fold up into short regular structures like the alpha helix or the beta sheet. These region of regular local structure referred to as the protein's *secondary structure*. These pieces of small structures are then folded

against each other for form exquisitely complex three dimensional structure called the tertiary structure. The protein's function is tied to that 3D structure. Any mistake in the sequence that disrupts the structure kills the protein.

Carbohydrates

Energy source for most organisms
Source of structure for plants

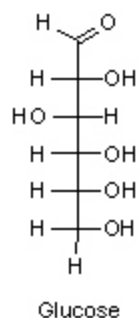
Monomer is called a monosaccharide or simple sugar

General formula is $C_nH_{2n}O_n$

For most simple sugars $n=6$ (Hexoses) or $n=5$ (pentoses)

But there are others

Sugars are frequently drawn in a linear structure



Note that sugars are composed of lots of alcohols, and usually one aldehyde or ketone functional group. That makes them very polar, and strongly attracted to water

Whether the OH in the above structure points to the right or the left is yet another important kind of structural isomerism, but one we won't worry about in this class

Finally while chemists like to write linear structure as shown above it is easy, these linear structures usually undergo an internal cyclization reaction to form cyclic structures [Figure 22.30](#)

This is the monomer, what about the polymer?

In the polymer we start to link sugars together in condensation reaction between the OH groups

Formation of sucrose (Table sugar) from glucose and fructose is an example of [such a reaction Figure 22.31](#)

Different polymers of glucose are used to make starch, (for plant energy storage) Glycogen (for animal energy storage) and cellulose (plant structural material)

These polymers tend to have a random sequence and poorly defined 3D structure.

Nucleic Acids

There are two types of nucleic acids
deoxyribonucleic acids (DNA)
Ribonucleic Acid (RNA)

The monomer unit here is a mix of 3 things
A 5 carbon sugar (ribose in RNA or deoxyribose in DNA)
A nitrogen containing base (A, T, G, C, or U) Figure 22.34
You do not need to memorize these bases in this class
A phosphoric acid molecule (H_3PO_4)

Linked together to form a nucleotide Figure 22.35

In polymer, phosphate of one nucleotide is linked to sugar of next. Bases are stuck out and don't do anything Figure 22.36

Using the base complementarity a second strand is made that fits perfectly with the first, with the bases buried inside Figure 22.37

In this polymer the 3D structure is a simple long extended floppy rod. It is the exact sequence or primary structure of the bases that encodes your genetic information, and allows a cell to pass this information from one generation of cells to the next.

22.Y The petrochemical industry

This was a section in a previous edition of the text, I have not used since 2005

Since much of what we work with in our everyday world, from plastics to petroleum derives from oil, and indeed, most organic chemical , come from oil let's take a brief look at how oil is precessed to get these compounds

Chemical from refineries

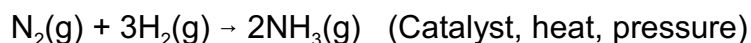
The composition of oil is fairly variable but is roughly given in table 22.4

You can see that if all we did was to simply distill oil only 15-30 % of the oil would give us useful gasoline. Thus we need to process the various components of the oil.

Large molecules are broken down into smaller, more useful components in a process called **cracking**. This can be done by exposing the substance to high temp (pyrolysis or thermal cracking) or by using a catalysts and lower temp (catalytic cracking) The later is what is usually done now days because it takes less energy.

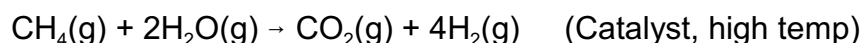
Alkanes can be reformed into aromatic compounds plus H₂ gas in a process called **catalytic reforming**. Aromatic compounds are a key ingredients in gasoline because it increases the octane rating of the gas. Aromatic compounds made in this was are also useful in making plastic and other chemical

Interestingly one product of catalytic reforming is hydrogen gas. Rather than simply burning this product to get rid of it, Petroleum companies combined it with N₂ in the air for form ammonia in a reaction called the Haber process



The petrochemical industries then had to convince the farmers that this was better than cow dung on their fields, and the practice of using chemicals to fertilize field was born

Today there is so much demand for ammonia that the processing of oil doesn't provide enough H₂, so another process had to be discovered to convert natural gas (methane) to hydrogen



Other refining process that are used include alkylation, polymerization, and isomerization

About 10% of the petroleum processed in the US is used make other chemical called **feedstocks**. Feedstocks are chemical that are in turn used to make other chemicals.

The operation of a refinery demand a wide range of flexibility. You must be able to vary your refining, both to accommodate the type of oil that is coming in, and you need to vary the output depending on the environment, make more gas in spring and summer when people travel, more heavier heating oils in winter. As well as which feedstocks are most profitable at a given time.

