Introductory Organic Chemistry

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Lecture – 10

Physical Properties of Alkanes

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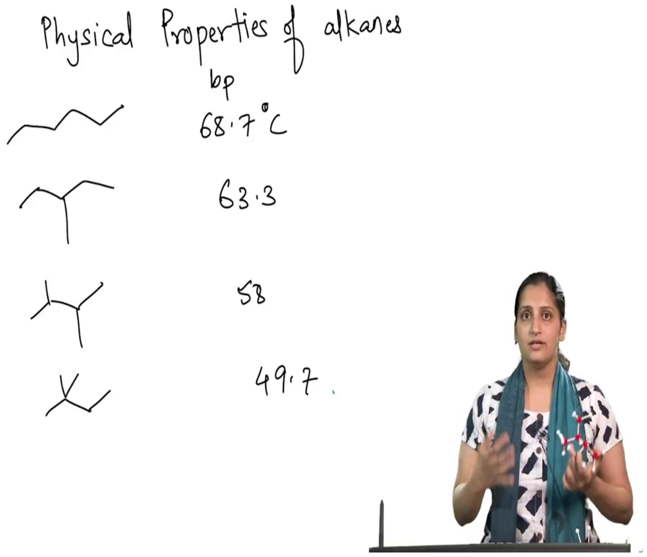

So now, we are going to look at the Physical Properties of Alkanes. The most important physical property of alkanes is their complete lack of polarity. So, this is due to the small difference in electronegativity that exists between carbon and hydrogen. So, if you really look at carbon and hydrogen, they have very similar electronegativities and thus they lack the polarity. So, alkanes are in general non-polar compounds and have only weak interactions existing between the molecules.

So, now, let us look at the physical properties of some of these alkanes. Methane is a gas at room temperature. Methane can be converted to a liquid as you slowly cool it down to around minus 164 degrees. If you go further, you can even convert it to a solid at around minus 182 degree centigrade. The ability of any compound to exist as solid, liquid and gas depends on the temperature of course but it mainly depends upon the inter molecular forces of attraction.

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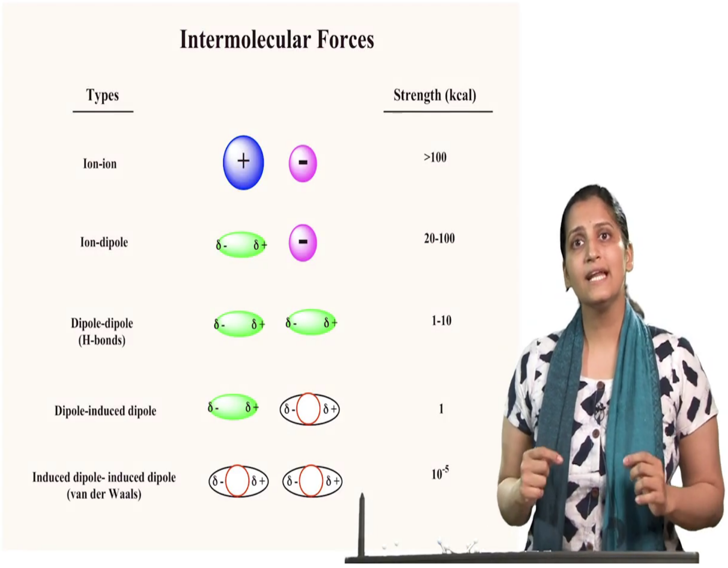

Intermolecular Forces

Types	Strength (kcal)
Ion-ion	>100
Ion-dipole	20-100
Dipole-dipole (H-bonds)	1-10
Dipole-induced dipole	1
Induced dipole- induced dipole (van der Waals)	10^{-5}

So far we have seen the electrostatic forces of attraction. So, like in sodium chloride, we said that they are attracted because of the electrostatic forces of attraction between a cation and anion, and this is really the strongest force of attraction that exist, so which is about 188 kilo calories per mole then comes the dipole-dipole interaction which is about 2 to 10 kilo calories per mole. Dispersion forces are the weakest forces that can exist at the intermolecular level. So, they amount close to like 0.2 to 2 kilo calories per mole.

So, what are these dispersion forces? So, let us imagine a non-polar molecule like hydrogen - H_2. And we said that the electron cloud is equally shared between the two hydrogens such that over time it forms a uniform covalent bond between the two hydrogens. But remember at any point, there exists a nonzero probability that the electron density is slightly polarized towards one of hydrogens, and thus creating a kind of polarity in the molecule

So, overtime they are going to share it equally, but given at an instant there could be polarity created between the two hydrogens. This temporary polarization creates temporary dipole in the molecule. And as a result of which it also creates a temporary dipole in the adjacent molecule. So, let’s say that a temporary dipole is created in one of the hydrogen molecules, because of this dipole an induced dipole is created in another hydrogen molecule and that is the rise of these dispersion forces as we call it. And as you can see because it is a temporary dipole that is created they are very weak in nature.

So, dispersion forces are the only forces that exist inter molecularly amongst alkanes, and because they are so weak the boiling point of alkanes are lower than that of any other type of functional group or any other type of compound with the equal molecule weight. As the number of atoms in any alkane increase, so let’s say as we go from methane to ethane to propane and so on, as the number of atom increase and as the molecular size increases, the molecular weight increases, there is also a higher opportunity for the existence of these dispersion forces between two molecules.

Hence, what we see is as we go on increasing the molecular weight, the boiling point increases. In general, the melting point will also increase as we increase the molecular weight. But remember melting point is a little different phenomena, because what you have to consider when we are looking at melting point is how are these molecules packed in a solid. So, we have to also look at the packing of molecules that matters when we are trying to get them apart as they melt. So, in general, you see a very nice trend in boiling point, the melting point also shows the similar trend, but not so systematically.

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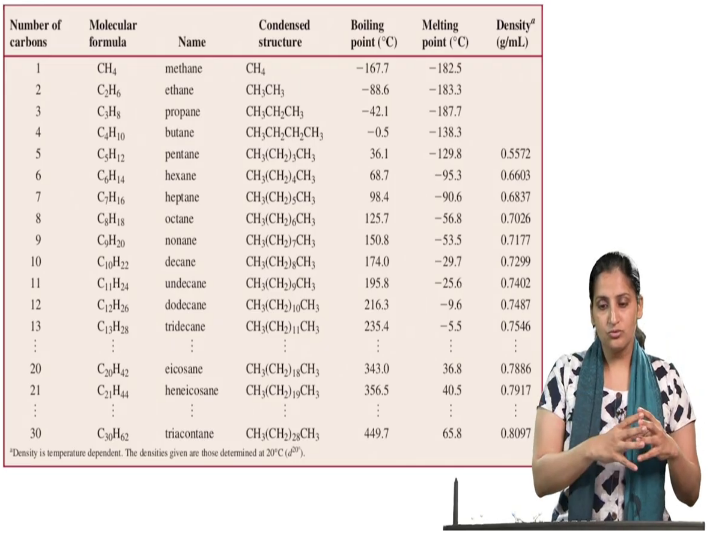

Number of carbons	Molecular formula	Name	Condensed structure	Boiling point (°C)	Melting point (°C)	Density[a] (g/mL)
1	CH_4	methane	CH_4	−167.7	−182.5	
2	C_2H_6	ethane	CH_3CH_3	−88.6	−183.3	
3	C_3H_8	propane	$CH_3CH_2CH_3$	−42.1	−187.7	
4	C_4H_{10}	butane	$CH_3CH_2CH_2CH_3$	−0.5	−138.3	
5	C_5H_{12}	pentane	$CH_3(CH_2)_3CH_3$	36.1	−129.8	0.5572
6	C_6H_{14}	hexane	$CH_3(CH_2)_4CH_3$	68.7	−95.3	0.6603
7	C_7H_{16}	heptane	$CH_3(CH_2)_5CH_3$	98.4	−90.6	0.6837
8	C_8H_{18}	octane	$CH_3(CH_2)_6CH_3$	125.7	−56.8	0.7026
9	C_9H_{20}	nonane	$CH_3(CH_2)_7CH_3$	150.8	−53.5	0.7177
10	$C_{10}H_{22}$	decane	$CH_3(CH_2)_8CH_3$	174.0	−29.7	0.7299
11	$C_{11}H_{24}$	undecane	$CH_3(CH_2)_9CH_3$	195.8	−25.6	0.7402
12	$C_{12}H_{26}$	dodecane	$CH_3(CH_2)_{10}CH_3$	216.3	−9.6	0.7487
13	$C_{13}H_{28}$	tridecane	$CH_3(CH_2)_{11}CH_3$	235.4	−5.5	0.7546
⋮	⋮	⋮	⋮	⋮	⋮	⋮
20	$C_{20}H_{42}$	eicosane	$CH_3(CH_2)_{18}CH_3$	343.0	36.8	0.7886
21	$C_{21}H_{44}$	heneicosane	$CH_3(CH_2)_{19}CH_3$	356.5	40.5	0.7917
⋮	⋮	⋮	⋮	⋮	⋮	⋮
30	$C_{30}H_{62}$	triacontane	$CH_3(CH_2)_{28}CH_3$	449.7	65.8	0.8097

[a] Density is temperature dependent. The densities given are those determined at 20°C ($d^{20°}$).

So, if you see on screen, I have the data of the first few alkanes and their boiling point melting point and density and so on. So, if you closely look at the boiling point as I said as we go on increasing the molecular weight, the boiling point increases. And to summarize the alkanes containing first four carbons, so carbons 1 to 4 are gaseous at room temperature; carbon number 5 to 17 are colourless liquids, and carbon number 18 onwards are these waxy solid that exist in nature. In fact, most of the plant or animal waxes that we obtain from nature are alkanes, and they are higher molecular weight alkanes.

So, for example, the wax in apple skin has the molecular formula of $C_{27}H_{56}$, or you must have heard about paraffin wax which is used in candles, in jellies, etcetera, and that is a very high molecular weight alkane too. So, does the boiling point change with increase in the molecular weight? Yes, so we got that answer. But how does it vary for a compound with the same molecular formula, but different structural formula.

So, now let us look at the following data. So, here in I am going to write different constitutional isomers of hexanes and their boiling points. So, if I take the n-hexane the boiling point is about 68.7 degree centigrade. If I take its structural isomer, the boiling point is about 63.3, goes to 58, then next it goes to 49.7. So, as you can see as I go from a linear chain to a branched chain alkane, what happens is that the bp of each of these branched isomer is lower than the n-hexane. So, you can say that the more the branching, the lower is the boiling point.

So, now let us think why is that, right? So, as we increase the branching what is happening to the shape? So, for example, I have this n-hexane here, and I have one of these derivatives here. So, both of them have the same molecular formula, but different structural formula. So, if you look at this straight chain alkane, it has a large surface area, whereas when you look at this branched chain what you observe is that it is now a compact kind of a molecule. So, it has a lower surface area. As the surface area decreases, the contact amongst adjacent molecule decreases, and the strength of dispersion forces also decrease and so the more the branching, the lower is the boiling point.

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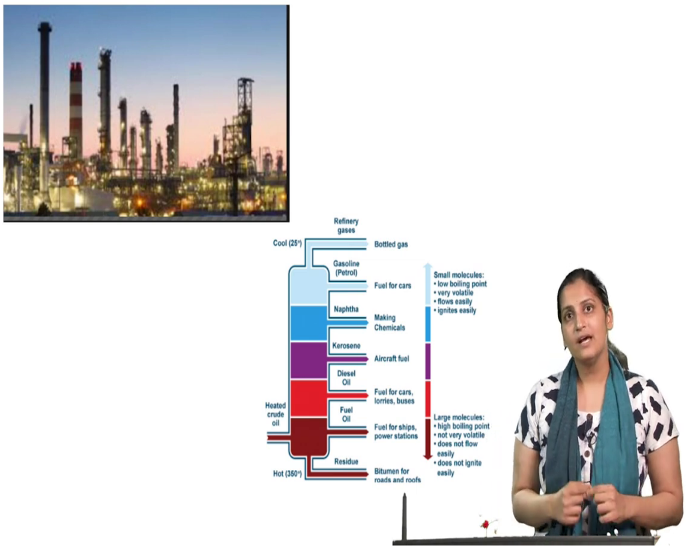

So, now let us talk about our sources of alkanes. Where do we get our alkanes from? The majority of the world’s resources in alkanes really comprise of the fossil fuels that exist. So, fossil fuels meaning natural gas, petroleum reserves and the coal. So, all of these three things together serve as our reservoirs of alkanes for the entire world. These were really the deposits of plants or animal matter that were made eons ago mainly marine matter, that over time because of decomposition have resulted into the current fossil fuels.

So, you must have heard about refineries and mainly natural gas refineries or petroleum refineries. What they are really doing is they are taking a mixture of a lot of alkanes and putting it through fractional distillation, such that you separate these alkanes based on their boiling points. As you can see here in I have a diagram of the refinery. And what you really see is that there you get various fractions.

So, you get gasoline which really works as a fuel for cars, then you have naphtha, kerosene, diesel oil, fuel oil and so on, and all of these really are results of different fractions of the distillation column. Wherein they range from small molecules which are low boiling alkanes towards and slowly go towards large molecules which are high boiling point alkanes, and which are not really very volatile in the sense, they cannot flow easily.

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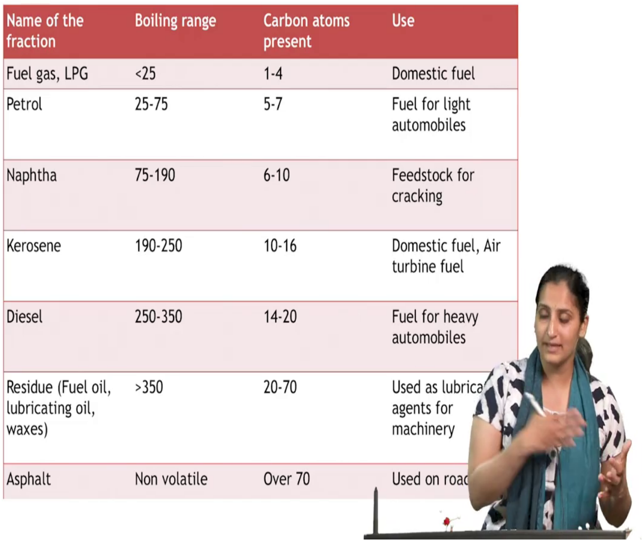

Name of the fraction	Boiling range	Carbon atoms present	Use
Fuel gas, LPG	<25	1-4	Domestic fuel
Petrol	25-75	5-7	Fuel for light automobiles
Naphtha	75-190	6-10	Feedstock for cracking
Kerosene	190-250	10-16	Domestic fuel, Air turbine fuel
Diesel	250-350	14-20	Fuel for heavy automobiles
Residue (Fuel oil, lubricating oil, waxes)	>350	20-70	Used as lubrica agents for machinery
Asphalt	Non volatile	Over 70	Used on roa

So, if you really look at this particular table here, what you will observe is that we get our LPG or fuel gas which has around 1 to 4 carbons present. So, meaning it can range from methane to butane and which we use as a domestic fuel. Wherein if you look at petrol, petrol has the carbon numbers from pentane to heptane, 5 to 7 really you have isooctane as well. So, it should be rather 5 to 8 which really works as a fuel for light automobiles.

If you go further, you have naphtha, you have kerosene, you must have seen that kerosene is used as fuel in most of the small villagers, or you have diesel, you must have heard about fuel oil or lubricating oil or waxes. As you see as we go on increasing the carbon atoms present, the boiling range also increases. And in fact, asphalt which is used for making roads is highly non volatile compounds. So, it’s very very stable and it has over 70 carbons in it, and does not really boil; does not have a boiling range. So, all of these fractions, we get from the refinery of the fossil fuels.

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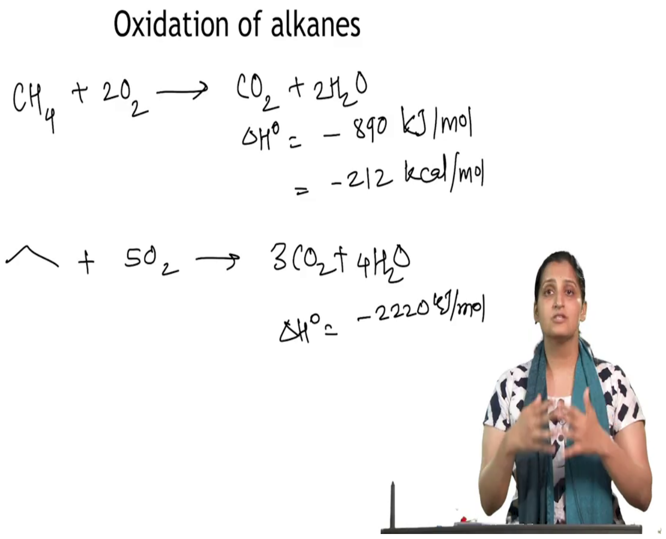

Oxidation of alkanes

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

$\Delta H^\circ = -890\ kJ/mol$

$= -212\ kcal/mol$

$+ 5O_2 \longrightarrow 3CO_2 + 4H_2O$

$\Delta H^\circ = -2220\ kJ/mol$

So, now let us look at some of the reactions of alkanes, because alkanes are very non-polar in nature they do not react very vigorously. So, in the sense, they are kind of unreactive kind of functional groups. So, in fact, we have to only study two reactions of alkanes. One of them is the oxidation of alkanes which is really combustion reaction, and the other one is the conversion of alkanes to alkyl halides.

So, we will go over the second reaction in the chapter of alkyl halides, but for now we are going to study one of the most economically important reactions of alkanes which is oxidation or rather combustion of alkanes to result into energy. So, herein let's look at a reaction, so I have methane, and if I react methane with oxygen as you know we form carbon dioxide and water, right.

Now, the heat of this reaction or the delta H of this reaction, enthalpy of this reaction really, is minus 890 kilo Joules per mole, meaning this particular reaction is going to result into giving out energy right. So, let me write the ΔHº of this reaction this is around minus 890 kilo Joules per mole as I said. Or if you want to talk about in terms of kilo calories, it is minus 212 kilo calories per mole right.

And if you really see in this particular reaction, the energy of the reactants is lower than that of the products. So, what happens is that, you end up releasing energy as this particular reaction happens, so that's why oxidation of alkanes using oxygen is one of the most economically important reactions wherein you release energy as this particular reaction happens.

So, let us look at one more reaction now here. I have propane, and I am going to react it again with five oxygen molecules in order to give 3 CO_2 plus 4 H_2O. Again if you really see the ΔH^o is going to be negative it is about minus 2220 kilo Joules per mole, okay. So, as you go on increasing the number of carbons, the amount of energy that is released also goes on increasing, up to some extent that is true.

So, in these reactions or all of these oxidation reactions of alkanes, the energy of the products is less than that of the reactants, okay. So, this particular reaction in general or the difference of the energy is given by, is called as the heat of combustion. And the heat of combustion is the energy of the products minus the energy of the reactants really. So, the one of the really good uses of this reaction is to give us an idea about the stability of a particular molecule.

Remember that the heat given off is going to be very similar every time. So, in the sense, if I take all the structural isomers of octane or all the structural isomers of heptanes, they all of them are going to result into the same number of CO_2 and water molecules.

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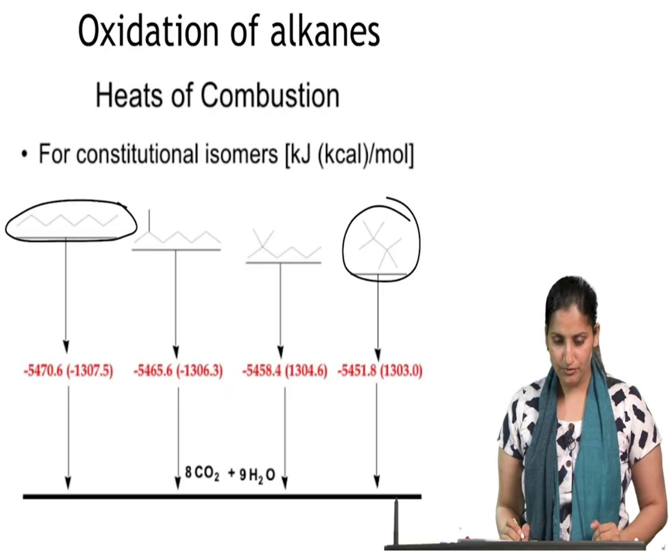

Oxidation of alkanes

Heats of Combustion

- For constitutional isomers [kJ (kcal)/mol]

So, it is like if I take for example in this graph, if you look at this if I take all of these derivatives of octane, the straight chain as well as the branched octane, they are all going to result. If you do the combustion reaction, it results into the formation of 8 CO_2, and 9 H_2O molecules. So, if you really see the n-octane is giving you much more energy than the branched octane here, okay. As you can see as the branching increases, you also go on decreasing the energy that is given off as this particular molecule reacts, or the heat of combustion decreases as the branching increases.

So, as we can see that octane has the largest or the most negative heat of combustion, and the one with the four methyl branches for example here has the lowest heat of combustion. Therefore, what we can conclude is that the branching increases the stability of that particular alkanes, so as we go on creating or as we go on making it more and more branched alkane, it becomes more and more stable. So, you can imagine this particular reaction or this particular phenomena in this way.

Imagine that you and your friend are standing at different levels on the stairs. For example, your friend is standing on level-2, and you are standing on level-5. Both of you are going to jump to get to the ground, right. Now, depending on how much energy you have right, as you jump you are going to give off that much amount of energy. So, as you jump from the fifth level, you are going to release much more energy than when you jump from the second level.

So, you can kind of imagine that the person standing on the second level is a little more stable than the person standing on the fifth level. So, similarly what we see here is that number of branches that are particular alkane has, it is going to be a little more stable than the corresponding straight chain alkane.

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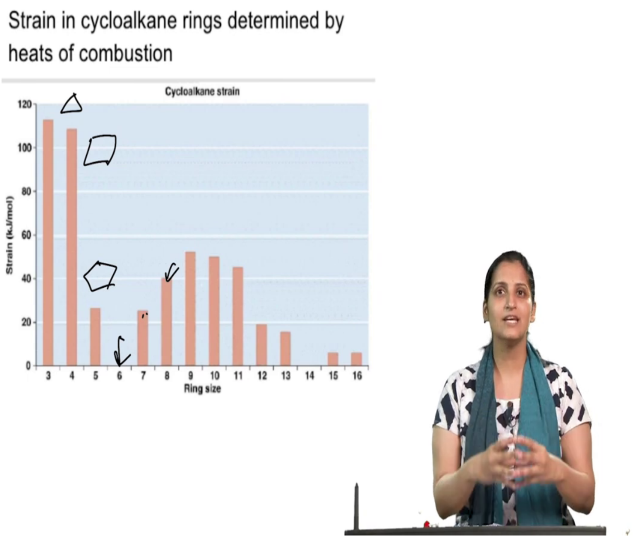

Strain in cycloalkane rings determined by heats of combustion

We can even use the same reactions to judge the stability of cycloalkanes. So, if you remember we talked about how cyclopropane is a much more strained molecule because of the angle strain and the torsional strain in the molecule as compared to cyclobutane as compared to cyclopentane and so on. So, if I now subject all of these cycloalkanes to the combustion reaction and measure what is the energy given off as this molecule undergoes combustion, I can really predict the stability of cyclopropane as compared to cyclobutane and so on.

So, if you really see here, I have the strain in cycloalkane rings which is determined by the heat of combustion. So, cyclopropane gives off the maximum energy when it reacts to form CO_2 and H_2O. So, as you can imagine as the cyclopropane reacts, it's gonna get released from that strained configuration. And it's going to release to form CO_2 and H_2O. So, it is going to get rid of the angle strain, and that strain released is going to be proportional to the energy given off.

So, you can see that the three membered ring and the four membered ring cyclopropane and cyclobutane, right is strained. Cyclopentane is way less strained, but the maximum amount of stability is really achieved for cyclohexane. So, when we studied the chair formula, you saw that how this molecule really does not have much strain in it. And you can see that cyclohexane really gives you the lowest amount of energy released upon combustion.

Whereas, you go on again cycloheptane, octane, cyclooctane, and so on, it goes on increasing. Again as you go closer to the ring having 14 members in it, it goes down again. So, this is because the ring kind of become sloppy and you can kind of fold it to get released of any strain that could be present. So, really small rings have a lot of strain, and then you have a about carbon number 9 or so which have a higher strain. But the strain is least for cyclohexane, and then for carbon number 14 onwards the strain again goes on decreasing. Since, we are talking about combustion reaction, I also thought that we can talk about something that we always see in our daily life is something called as octane rating.

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So, if you go to a petrol pump, and if you want to fill a petrol, you can typically choose a petrol that has a higher octane rating and which will cost you more, but which will also help your engine last longer.

So, what is really octane rating? So let's have a look at that.

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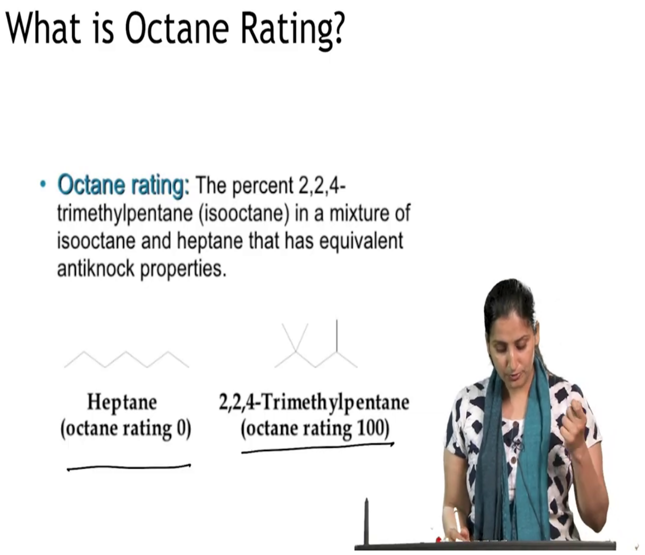

What is Octane Rating?

- **Octane rating:** The percent 2,2,4-trimethylpentane (isooctane) in a mixture of isooctane and heptane that has equivalent antiknock properties.

Heptane (octane rating 0)

2,2,4-Trimethylpentane (octane rating 100)

In a typical four stroke engine, the piston draws a mixture of the fuel and air in its downward stroke and kind of compresses it in its upward stroke. So, just as it is compressing spark plug, it ignites the mixture, and what you have is a combustion reaction happening inside the engine. Not all fuels burn well equally though. For poorer fuels what happens is that the fuel can get ignited even before the spark plug wants to ignite it because of hot surface of the cylinder for example. And this uneven ignition can result into something called as the engine knock. This kind of engine knocks puts unequal pressure in each cycle and really results into damaging the engine over time.

So, of course, we add something called as an anti-knocking agent into the petrol, but different fuels have been tested for their ability to have the least amount of knocking as they burn. So, for example here, the 2, 2, 4-Trimethylpentane here has the octane rating of 100 meaning it knocks very, very less and it is one of the best fuels that can exist. Whereas, heptane has an octane rating of zero meaning it will result into some knocking as the particular fuel or in this case heptane is burned. So, the octane rating overall is the percent of 2, 2, 4-Trimethylpentane or isooctane in a mixture of isooctane and heptane that has equivalent antiknock properties.

So, with that let us end our chapters on alkanes. What we have seen in this chapter is the different structures of these molecules, and what are constitutional isomers, how these structures affect the physical properties, we have also studied one of the reactions of alkanes. But what we have mainly focused on in this chapter is really the conformational analysis, because the conformational analysis tells us about the different energies that a particular molecule can posses based on the conformation that it has. So, with the help of conformational analysis, we have really started building our toolbox to study these molecules, and we will go on making this toolbox more and more rich using newer information or newer knowledge.

So, in the next class, we are going to study about chirality which will give us one more tool to analyze the structures of organic molecules. And then we will begin with the reactivity of these molecules, and really use all of these tools- conformational analysis, different types of isomers, their energies, chirality, all of these tools we will use to study the reactions of carbon compounds.