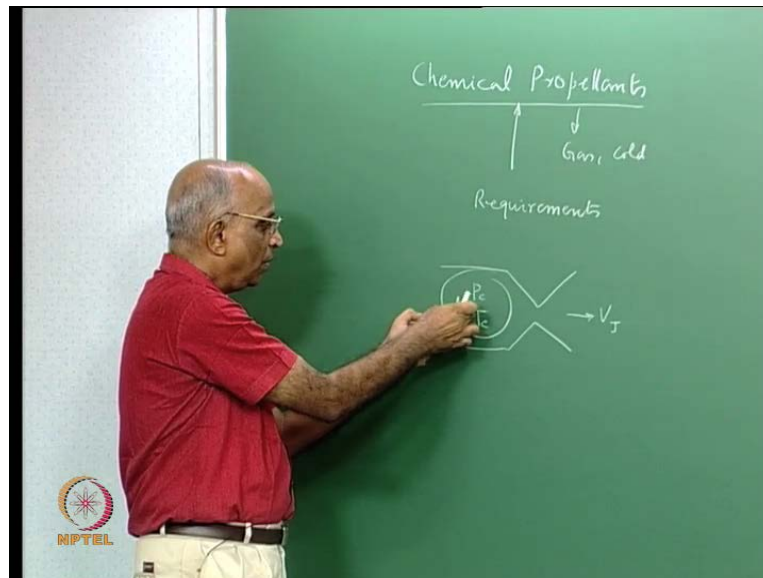


**Rocket Propulsion**  
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**Module No. # 01**  
**Lecture No. # 15**  
**Criterion for Choice of Chemical Propellants**

Good morning, today we will start a new topic on chemical propellants.

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Let us first be clear what we mean by a propellant, we told ourselves any substance which is used for propulsion of a rocket is known as a propellant. It could be anything, it could be something like a gas, the gas could be cold at high pressure the gas could be hot. Therefore, it is a propellant may be we even considered these boys throwing stones and stones were the propellant. It could be anything it could be a charged particle, it could be a plasma, it could be anything, but what we consider in the next 3 classes is what constitutes chemical propellants.

And then we go to chemical rockets and chemical rockets are solid propellant rockets, liquid propellant rockets, hybrid rockets and so on. Therefore, let us see what are the

requirements before we study anything we must know what are the requirements. What is the requirement of a propellant? I think that is the basic with which we should get started and we have studied in nozzles that, when we look at any rocket chamber, let us say that this is a chamber you have a nozzle which is coming, our aim is to get as high as a jet velocity as possible. And to get a high jet velocity we told ourselves in the chamber I would require a high value of the chamber pressure and a high value of the chamber temperature.

We also told ourselves we require a small molecular mass of the gases which are being expanded out. In which case I will get a higher jet velocity and what was the term that we used to determine in all these. We use the term  $c^*$  which is a transfer function between what is generated or what is sent into the combustion chamber and the high pressure, high temperature, low molecular mass combustion gases which are generated. And what was the expression for  $c^*$  we had the expression,  $\sqrt{R}$  into temperature of the hot gases divided by the specific heat ratio  $\gamma$ .

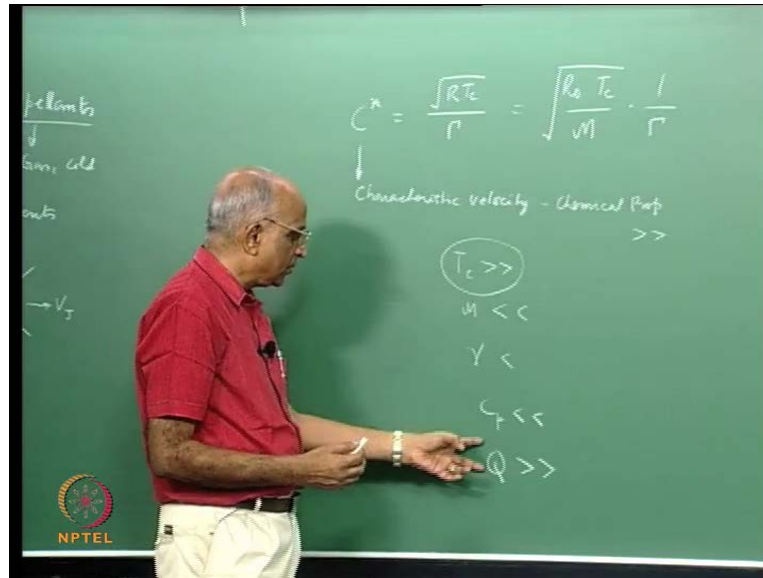
And this was the specific gas constant which in terms of the universal gas constant, we could write it as  $R_u / M$  by the molecular mass of the gases which are sent out through the nozzle. And this is again  $\sqrt{R_u / M}$  we have  $1/\gamma$  which is a function of  $\gamma$  therefore, this should tell us what we really require in a propellant to do. What we require is this transfer function which tells the capacity of this particular chamber to generate high pressure gases must be high or rather this characteristic velocity. Which was a transfer function (no voice 03:07 to 03:14) of the propellant of the chemical propellant any propellant say chemical propellant must be large.

If it has to be large obviously we have told ourselves well  $c^*$  is equal to  $\sqrt{T_c}$  rather  $T_c$  must be large or the molecular mass of the gases which are escaping through the nozzle must be small. Anything else see we have the combination of  $\gamma$  we told  $\gamma$  must be small because  $c^*$  was equal to  $\sqrt{R_u / M}$ , to  $1/\gamma$  plus 1 to the power  $\gamma + 1$  divided by  $2\gamma - 1$  the requirement was also that  $\gamma$  should be small.

It is not as sensitive as  $T_c$  and  $M$  therefore, basically we are looking at the following may be I would require  $T_c$  to be large the molecular mass of the gases to be small, may be the specific heat ratio also to be a small number. If I can have propellants which could

generate gases such that the temperature of the hot gases the pressure of the gases should be large. The molecular mass of the gases should be small and the specific heat ratio of the gases must be small. This is what a propellant should do, how do you get it?

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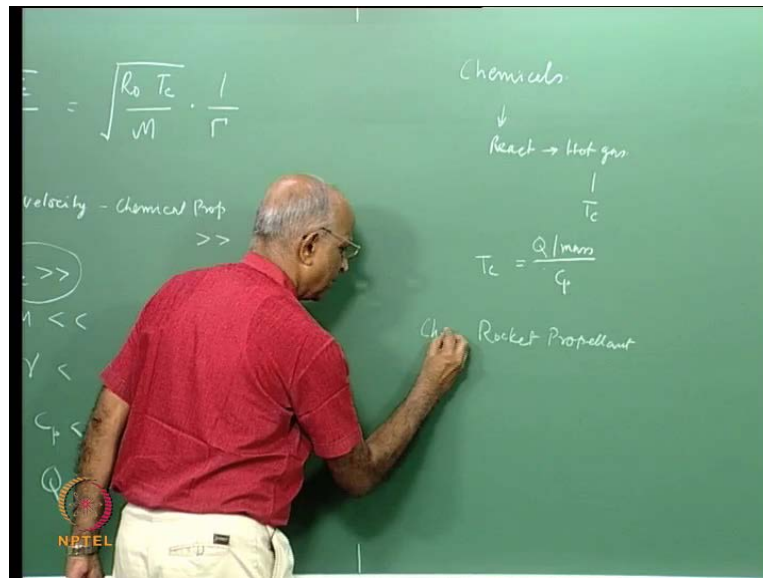


Let us take a look at  $T_c$ , What will give me a high value of  $T_c$ ? If I have a chemical propellant and now we must say I am talking of chemicals, there are a large number of chemicals available I cannot use all these chemicals. And why do we use a chemical? Maybe I want the chemicals to react with each other or react and generate hot gases. Why hot gases? If I have hot gas I have  $T_c$  which could be a higher number. Therefore, basically I am looking at chemicals because I am looking at chemical propellants, substances which are chemicals which could react generate hot gases and these hot gases could be at a high temperature. To generate a high temperature gases the heat release in the chemical reactions should be large.

And therefore, if heat release is large divided by that is heat release per unit mass is large mass unit mass of the propellant is large divided by let us say that the specific heat of the gases may be I am burning at constant pressure. Therefore, the heat at constant pressure is small I can have let us say a large value of  $T_c$ . I have introduced one more word all what I am saying is I have chemicals these chemicals react generate hot gases at high temperature. When do I get high temperature? If the heat release per unit mass is a large number and if I take  $C_p$  because  $C_p$  into  $\Delta t$  is a heat release.

If I have the small value of the specific heat ratio then I can get a high value of temperature. Therefore, How what? do I say now I put another number here may be I say the specific heat of the gas is let us say specific heat at constant pressure must be also a small number. Well these are the requirements I am looking, at well in terms of this may be  $q$  must also be large the heat release must be large number. These are the basic requirements of a chemical and I am looking at what are the requirements of the chemicals which can do the job. The chemicals should have a large value of heat release a small value of specific heat release may be a small molecular mass of the product gases which are generated a high value of the temperature and perhaps a small value of gamma.

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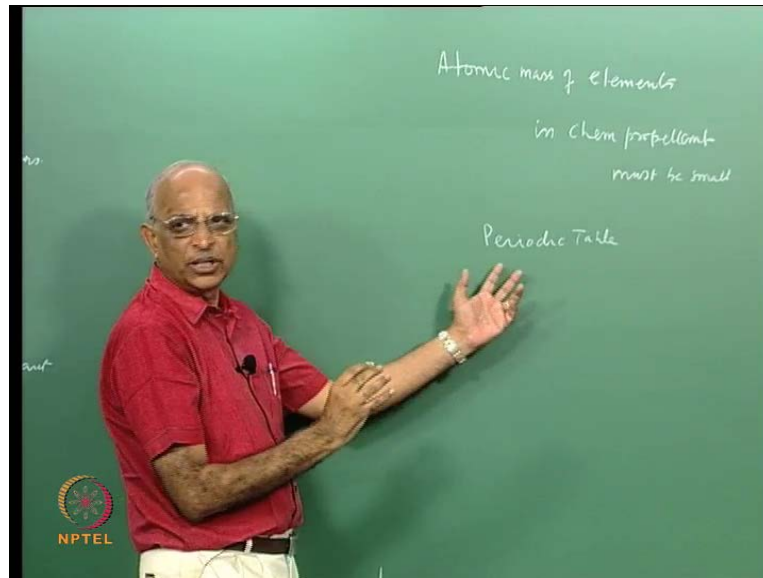


If we can address all these points together, maybe I can find a chemical or a few chemicals out of the millions of chemicals that are available I can find one or two which can be used as chemical rocket propellant or rocket propellants. Which are maybe chemical or chemicals, chemical rocket propellant let us say. And this is what I am going to do in this class therefore, let us ask ourselves well to have to determine temperature I need heat release and also specific heat. Let me start with something simple, under what conditions will I get a low molecular mass of the gases which are generated.

Let us say I have a chemical and the chemical by reaction generate it is hot gas or gases. Therefore, basically I must take a look at the atomic mass or the mass of the elements

atomic mass of elements in the chemical propellant must be small. Why should it be small?

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If the atomic mass is small the product gases will also have low atomic mass. First let us take a look in chemistry we have, what is known as periodic table and what does periodic table do? It arranges all the elements in terms of its atomic number and this is what we will first take a look at it. Let us say this is the periodic table over here given we have elements starting with an atomic number of 1 the atomic mass of hydrogen whose atomic number is 1. The next is helium the atomic number is 2 the atomic mass is 4. Next is lithium number 3 the mass of lithium atom is 6.9. Beryllium 4 atomic mass is 9. Boron 5 the atomic mass is 10 and so on carbon 6, 12 and so on.

Equal to oxygen nitrogen fluorine then I have neon is for lighting it is an inert gas, when I have sodium, magnesium, aluminum, silicon, phosphorous, sulphur and chlorine. I stop at 17 because already the atomic number has increased to 17 and as you see the atomic mass is increased from 1 to almost 36, the values of the atomic mass which I have shown here are with respect to hydrogen. Beyond this, if I go the atomic mass is so, large that any product which is formed will become very heavy. What does this table tell us? Let us take a particular case may be hydrogen as a low atomic mass and even if I take a hydrogen molecule  $H_2$  whose molecular mass is 2.

It is lower than anything else therefore, it is a very viable propellant from the molecular mass point of view. I next go to helium, helium is inert it can be used as a cold gas cannot be used as a chemical propellant I would not consider it. Lithium is used in solid propellants because of its low atomic mass, we will have to take a look at it when we study solid propellants beryllium, boron are used the masses are still small at atomic mass of 9 and 10. Carbon is a part of any hydrocarbon, carbon and hydrogen together well we cannot escape fortunately for us carbon has an atomic mass of 12. Which is still not very bad nitrogen is inert, but most of the substances in nature are associated with nitrogen.

We find that the atomic mass of nitrogen is 14, oxygen is a powerful oxidizer may be its used for oxidizing any fuel it has its atomic mass as 16 molecular mass is 32. Fluorine is a very reactive oxidizer, much more reactive than oxygen very near to oxygen itself it is atomic mass is 19. Neon is inert I cannot consider it. Sodium is very reactive metal I drop sodium in water it just explodes I cannot use it. Magnesium you know you would have seen magnesium ribbon being used as a for diwali function, you will light it and it glows it is a reactive metal very reactive therefore, it is going to be difficult to use magnesium as it is.

Aluminum is a light metal atomic mass is 27, it tells us supposing I have to use a metal better I use aluminum rather than iron which is going to be much heavier. Only aluminum is used compared to iron is never used. Silicon is something which is a light material, but it is not reactive. I will not consider phosphorous is very reactive, I cannot consider sulphur has a molecular atomic mass of 32. Fluorine has is again an oxidizer with atomic mass of 35.


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**PERIODIC TABLE**

| ELEMENT     | H | He | Li  | Be | Bo | C  | N  | O  | F  | Ne |
|-------------|---|----|-----|----|----|----|----|----|----|----|
| AT. NO.     | 1 | 2  | 3   | 4  | 5  | 6  | 7  | 8  | 9  | 10 |
| ATOMIC MASS | 1 | 4  | 6.9 | 9  | 10 | 12 | 14 | 16 | 19 | 20 |

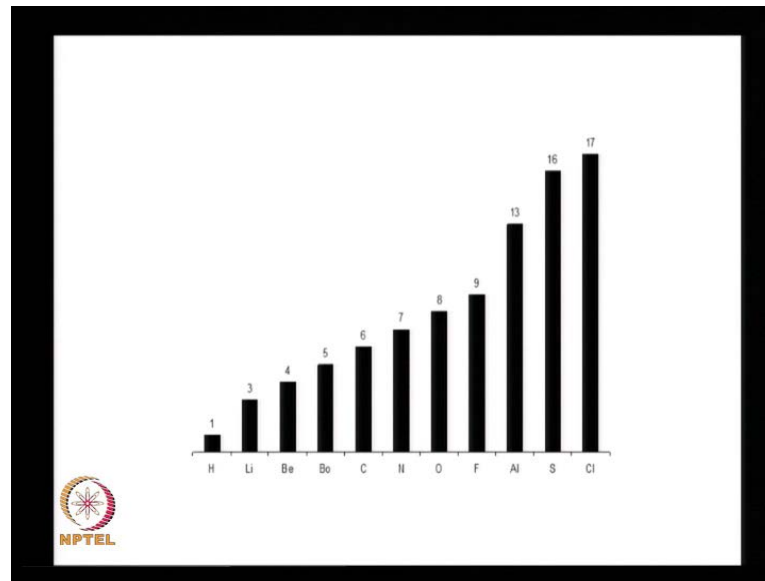
| Na | Mg | Al | Si | P  | S  | Cl   |
|----|----|----|----|----|----|------|
| 11 | 12 | 13 | 14 | 15 | 16 | 17   |
| 23 | 24 | 27 | 28 | 31 | 32 | 35.5 |



Beyond this you know you go to argon and other elements and they become progressively more and more heavier and they cannot be used. Therefore, all that we say is out of all the chemicals I can now isolate something like up to Cl which has an atomic number of 17. Which are little favorable from the molecular mass point of view, we know yes better to select some of the lighter elements. I show this again in the next slide where in I now choose my hydrogen, lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, aluminum, sulphur and chlorine.

And I say well these are the elements which I use in my chemicals it will be better for me to get a low value of molecular mass and hence it is more desirable. Therefore, we address the first point namely the molecular mass point of view. When will my molecular mass of my products be small? When the atomic mass of the element of what I consider should be small and therefore, I localize myself in to something saying, these are my things which I should be using fluorine is very reactive it is more reactive than oxygen. And in fact liquid flow in fluorine they did try to use for rockets, it used to just corrode the tanks itself.

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And therefore, it was used in 1 of the delta machines, but subsequently I do not find it being used, anyway we will keep it here we will see under what conditions fluorine can be used. Oxygen, fluorine, chlorine are oxidizers may be hydrogen is a fuel. Lithium, beryllium, boron, carbon and aluminum are fuels. Aluminum is a metal which can burn you know something which is interesting, see during Diwali function you all would have seen this sparkler. What is a sparkler? It consists of a composition which is known as a black powder composition and it is coated in a on a rod may be a steel rod or something.

You could have had it either as a composition or could have it the same sparkler you could have it some metals which are embedded sparkling. When the sparkler the metal gives violent energy because, the metal is so, strong that means it is so, dense that it can produce much more energy. Therefore, metals such as aluminum may be, boron may be, beryllium can also be used as fuel. Therefore, now we tell ourselves I have looked at 1 step of it may be from molecular mass point of view. Let me take a look at the next step may be from the temperature point of view, what whether I should have a some of these elements or what should be the composition of gases such that I get a high value of temperature.

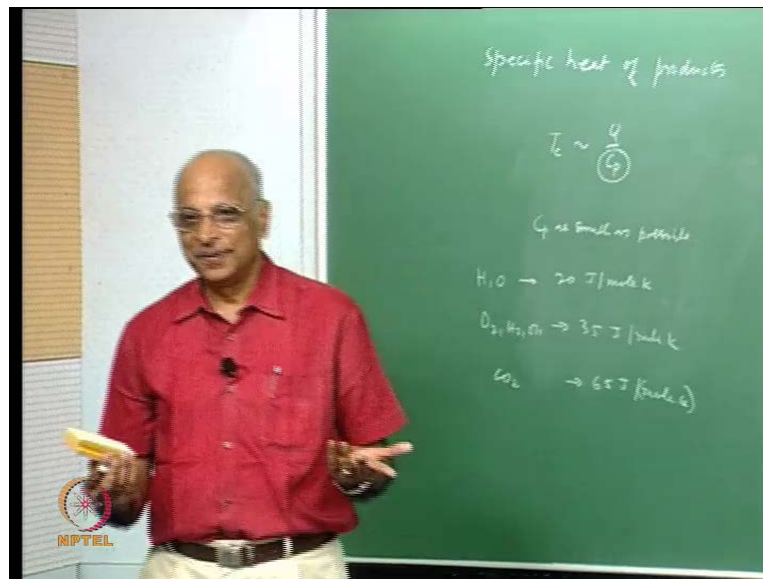
May be if you go through this may be half of our work in choosing a propellant will be over. Let me come to the second part therefore, let us take a look at the specific heat(no voice 15:30 to 15:50)



Of may be the products of burning or of chemical reaction which are escaping through the nozzle. We tell ourselves well  $T_c$  goes as heat released divided by the specific heat I would like to have  $C_p$  as small as possible. This is thermal all of us know it all of us know that single atom like hydrogen oxygen atom, hydrogen atom that is mono atomic has a specific heat of the order of something like 20 joule per mole Kelvin. Unit of specific heat per mole per Kelvin my unit of measure is mole joule per mole Kelvin. If I have di atomic molecule like  $O_2$ , hydrogen or  $OH$  that is 2, 2 of them together it increases to something like 35 joule per mole Kelvin. If I still have more complicated things like  $CO_2$ , 3 of them together it increases to almost like 62 or 63.

Let us say 65 joule per mole Kelvin. Why should specific heat increase as the molecule changes from mono atomic to di atomic to tri atomic and all that why should it go, what is, what will be your reaction, why should it increase? Mind you the unit is per mole Kelvin.

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Why should go up? what happens? let us take simple molecule, let us say like oxygen atom it is just  $O$ , if I take  $O_2$  well it is  $O_2$  over here or let us say we are not bothered about double bond single bond it is all bonded together. Let us say (( )) now when I heat this the degrees of freedom are smaller it absorbs less amount of energy. This will absorb little more energy because I have more degrees of freedom, it is more complex absorbs. If I have  $CO$  like this  $CO_2$  it can still have more bonds, more energy it can absorb and

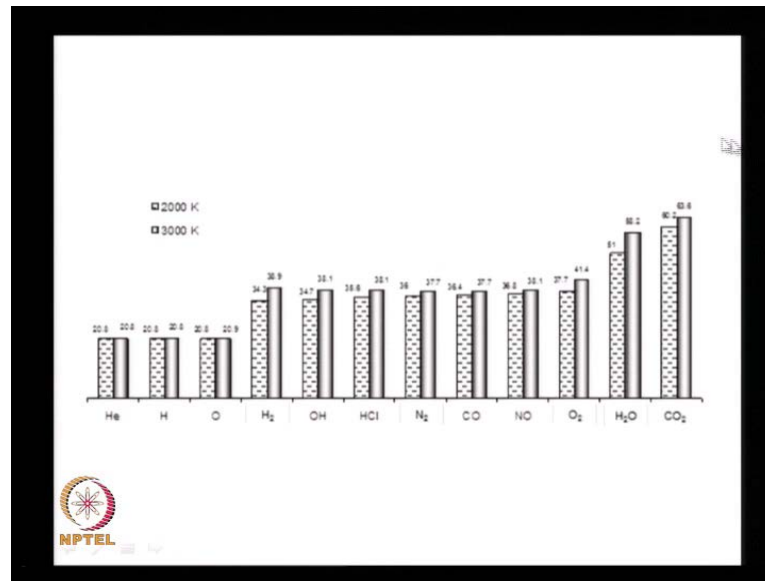
therefore, the energy absorbed per mole of a mono atomic substance is less, di atomic is more, tri atomic is more and so on it increases.

Therefore, let us see some values of them we say well mono atomic has the lowest, di atomic has higher value, tri atomic has still has a high value and as I go on the molecular the specific heat keeps increasing. Therefore, from this point of view I should say if my product gases are all mono atomic, I am better off it is better off di atomic I can tolerate it is still high and so on. You know that means the product of combustion must be what do we say must be simple not complex, in which case I can have a smaller value.

I put down some of the values of  $C_p$  in the next slide over here you know this say here helium which is mono atomic at 2 temperatures of 2000 Kelvin and 3000 Kelvin the change in temperature there is hardly any change. Therefore, irrespective of temperature for the mono atomic may be helium, hydrogen atom, oxygen atom the value is around 20. If I go 2 di atomic gases hydrogen O H may be H C 1 may be N 2 may be CO, N O see all have a ball park number of around 35 and change in temperature is not that profound therefore, I say I have an average value here.

When I say a tri atomic gas well its even higher well of the order of 60 to 65 to something like 60 here water is around 51 to 58 this CO<sub>2</sub> is between 60 and 63 may be around 63 64 is what is the average value I find mono atomic has around 20, this is around 35 to 36, this is around 60 to 65. Therefore, this is the range I would still like to get according to this specific heat point of view, if my product gas is were all differentiated in hydrogen and oxygen atoms or di atomic its better.

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If I keep on increasing my specific heat keeps increasing and I will not be able to get a high temperature and therefore, I say specific heat must be small. We have looked at 2 criterion namely we looked at the criterion of molecular mass we say well that the atomic mass must be small or atomic number must be low. Second we say  $C_p$  means the product gases which come out of the chemical reactions of the chemicals must be somewhat simple or disassociated. Let us go to the next before I come back to the temperature and heat release let us take a look at gamma, we say gamma should also be small.

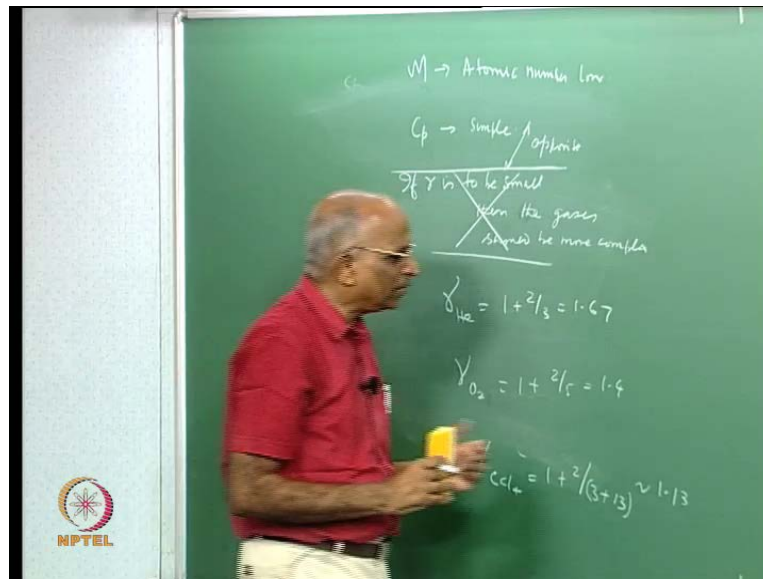
What does this imply gamma should also be small. If we go through thermodynamics and the kinetic theory of gases, we say gamma we defined as  $C_p$  by  $C_v$  which in terms of the degree of freedom of the molecule can be written as  $1 + \frac{2}{n + 3}$ . Where n shows the degrees of freedom of the gas over and above the translational modes. Let me call qualify suppose I am having an oxygen atom this being an just an atom, it can either move in this direction, in this direction or in this direction that means it has 3 degrees of freedom. If I have an oxygen molecule well it has it is now in addition to translation in the 3 directions it could also vibrate it could also rotate.

Therefore, it has a degree of freedom of 2, compared to the atom which only translates. I could also have atoms in which we have may be C<sub>3</sub>H<sub>8</sub> which becomes more complicated it could have lot of freedom compared to a simple translation. And for

instance if I take CCl<sub>4</sub> carbon tetrachloride, the degrees of freedom are almost something like this 13 or 14. Because it has so much the molecule becomes more complex it has more degrees of freedom. Therefore, for gamma value for a mono atomic gas, for which the number of degrees of freedom are only 3. And n shows more than 3 that means we say for mono atomic gases like let us say gamma for helium sorry gamma for helium is equal to 1 plus 2 by 3 which is equal to 1.67.

For di atomic gases like oxygen, hydrogen, nitrogen and all that you have 1 plus 2 by 5 which is 1.4. May be as it becomes very complex like gamma for CCl<sub>4</sub> carbon tetrachloride is going to be something like 1 plus 2 divided by 5 that is 3 plus something like I think like almost 13 or so, 12.5 or something in case it becomes something like 1.3 or 1.12. That means more complex molecule has a lower value of gamma and therefore, now I tell myself gamma is to be small, then the gases which are passing through the nozzle which should have should be then the gases through the nozzle should have should be more complex.

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Gamma requires to be small the gases must be more complex, but for C<sub>p</sub> to be small the gases must be simple it is just opposite of what we want. Similarly, if you want the atomic mass to be small well we are also thinking of simple product gases therefore, we find that gamma requirement is somewhat contrary to the requirements of C<sub>p</sub> and also molecular mass. Therefore there is a problem and we also know based on what we have

studied so far namely nozzle theory and  $\beta_j$  that  $\gamma$  is not very sensitive. and therefore, we will not give very much importance to  $\gamma$ , what is it I have done.

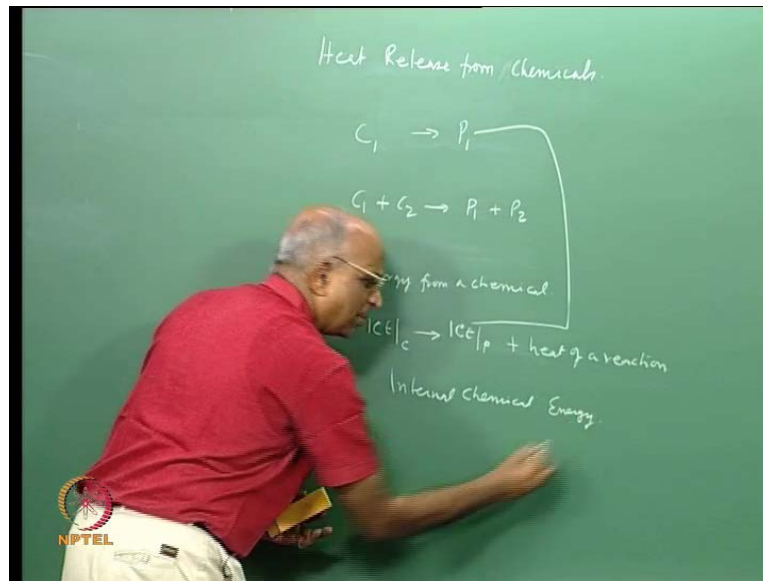
We say yes I have a handle on there the  $C_p$  should be small,  $\gamma$  decreases as the complexity of the gas increases. I cannot have the same trend coming out from and this together therefore, I will give less weight to this because  $C_p$  directly gets into temperature. Now, what is I am left with I am left with heat release and for able to determine the value of  $T_c$  less. Let us take a look at heat release and  $q$  in chemical reaction last point which I am doing is some chemical substance.

Let us have a chemical we call it as may be chemical  $C_1$  this chemical gets converted to gas like a product let us say  $P_1$ . We are just looking may be this chemical by itself reacts within itself and gives  $P_1$  or else I have  $C_1$  plus  $C_2$  reacts to give me  $P_1$  product 1, product 2. The question is how do I get the heat released in these reaction? these are all chemical reactions of a component of a chemical, giving the products or chemical reaction between 2 chemical which give me some products. And to be able to do that how do we say when will I get energy from a reaction from a chemical reaction.

All of us have studied both in combustion course and in the course on explosions. And how do we say any substance any chemical will have its own internal energy? I call it as chemical internal energy of the substance. Now, if it gets converted to product and it will also have some energy like chemical energy of the products. Instead I here also use the same notation internal chemical energy of the chemical as it is, the chemical gets converted to products. If you have more energy here of the chemical compared to the products which have less energy the deficit of energy is what we have as heat of a reaction.

What is it I am telling? Suppose I have some chemicals over here chemicals have some energy, this duster has some energy. Where does the energy come? I have all these bonds together it has some energy over here, now I burn it and I get carbon di oxide carbon, mono oxide whatever I get. If my if the energy which is available here is more than the energy of the final thing, then the energy cannot get destroyed. It manifests itself as heat and that is the heat of a reaction.

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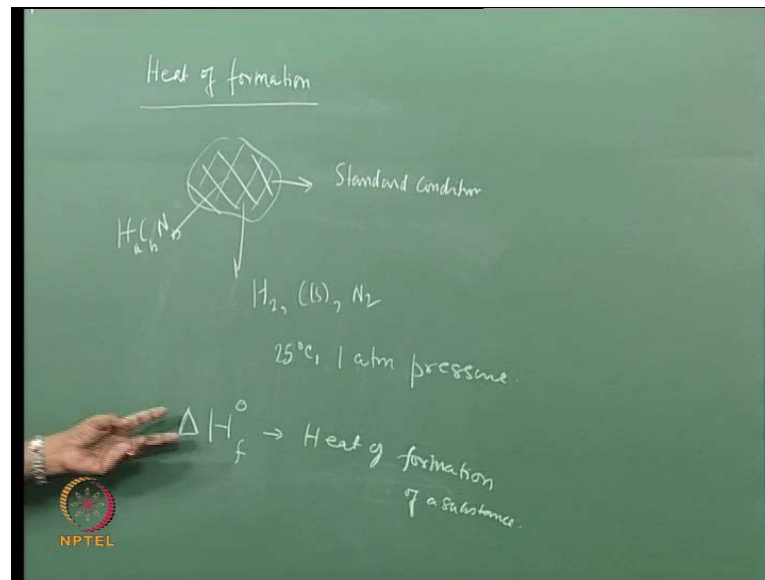
Therefore, basically I need to find out what this internal chemical energy or what is the energy available as the chemical with which I call as internal chemical energy. You know the word given to be able to describe this internal chemical energy is what all of you know very well is what we call as heat of formation. And how is it defined the heat of formation? The heat requires to form a substance any substance at standard state from its elements again at standard state let us put it down together. We need to be able to describe what is the energy available in a given chemical and to be able to find this we need some domain some standards.

We say well I say a standard condition what is the energy available with the chemical. And how do I define? Let this substance could be let us say hydrogen, carbon, nitrogen some substance like  $H_2$ ,  $C$ ,  $N_2$  this solid substance over here. What are the elements which constitute this? They are again hydrogen, carbon as a solid, gain nitrogen as a gas and mind you these are all substances. Hydrogen is a gas under standard conditions, carbon is a solid under standard conditions, nitrogen is a solid again at standard conditions, I am sorry nitrogen is a gas under standard conditions.

And the standard condition is taken as 25 degree centigrade and one atmosphere pressure. In other words if I want to form a substance at the standard condition from its elements again at the same standard condition the energy what is required to form the substance is known as heat of formation. The notation is well I have to give some heat

which is enthalpy, I have to give some more heat over the elements that are an increment in heating I need to form the substance I will form it at the standard condition. Therefore,  $\Delta H^{\circ}$  is defined as heat formation of any substance of any chemical is the heat of formation of a substance.

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If we know the heat of formation of a substance then all what we know is the heat of formation. This is the internal energy of the substance  $C_1$  which is the chemical is known the product formation is known and if there is a minus that means if the heat of formation decreases. I get energy the heat of reaction is exothermic I get some heat from the chemical reaction. This is all about the finding out of a heat of a reaction let us put it together. Let us say I have now I say expand myself see I have a fuel F, I have an oxygen O this gives me products. Fuel could be any fuel may be I take wood as a fuel or oxygen as or oxygen itself from the air as oxidizer and I get something like may be some product it is like  $CO_2$  may be CO.

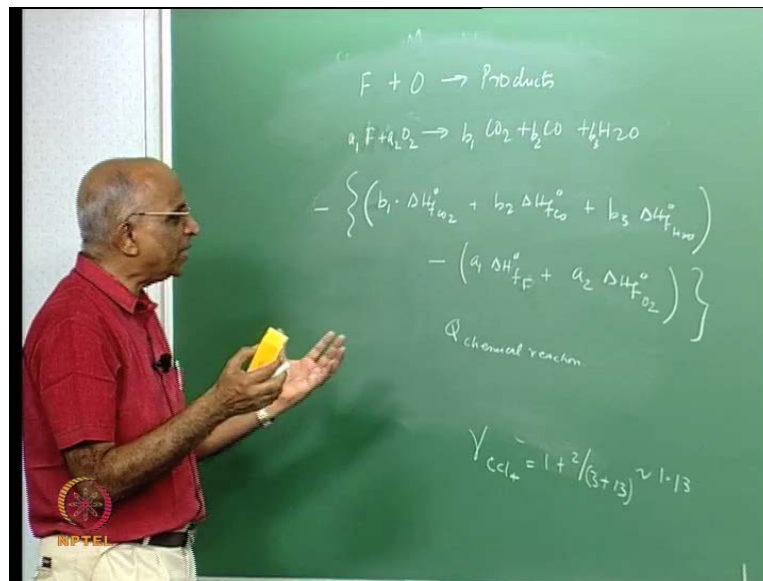
May be something some more of the substances therefore, now I say my reaction my chemical reaction is fuel plus oxygen gives me let us say  $CO_2$  plus CO. I am not bothered may be I just say this is contains hydrogen also may be  $H_2O$  also composition of the fuel is known. Let us say I take a 1 moles of the fuel, I take a 2 moles of the oxidizer and then I get b 1 moles of 1 product. I get b 2 of second product I get b 3 of the third. Therefore, what is the energy released in this particular reaction? I tell myself there

should be a decrease that means the heat of formation of the products is b 1 into heat of formation of CO<sub>2</sub>.

Mind you, heat of formation is the heat required to form 1 mole to the heat required to form 1 mole of the substance at standard condition from its elements again from standard conditions. Heat of formation unit is joule per mole and this is the mole, this is the joule over here plus b 2 into delta H f for CO plus b 3 into delta H f for H<sub>2</sub>O. This is the value of the total heat of formation of the products over here. What is the heat of formation of the reactants? It is equal to over here a 1 into heat required to form fuel f plus a 2 moles of this into heat of formation.

I should have put this standard all over here all at the standard conditions into oxygen over here and now I say the changes is like this, but only there is a decrease. The heat energy which is given is equal to minus of heat of formation of the products divided by the heat of formation of (( )).

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Is it you know you all would have studied this is in your combustion course, but any way we need to go through this. Because what is it I am trying to look at I am trying to see what are those chemicals which will give me maximum q? That is why I am trying again ask myself these questions. Are there some particular properties of these chemicals which make q to be larger and from there make it comfortably to other cases. Now let us take an example let us I have formed carbon di oxide, let us say I have I do an



experiment I do an standard state may be a take carbon. Which is a solid at 1 atmosphere pressure at initial temperature of 25 degree centigrade.

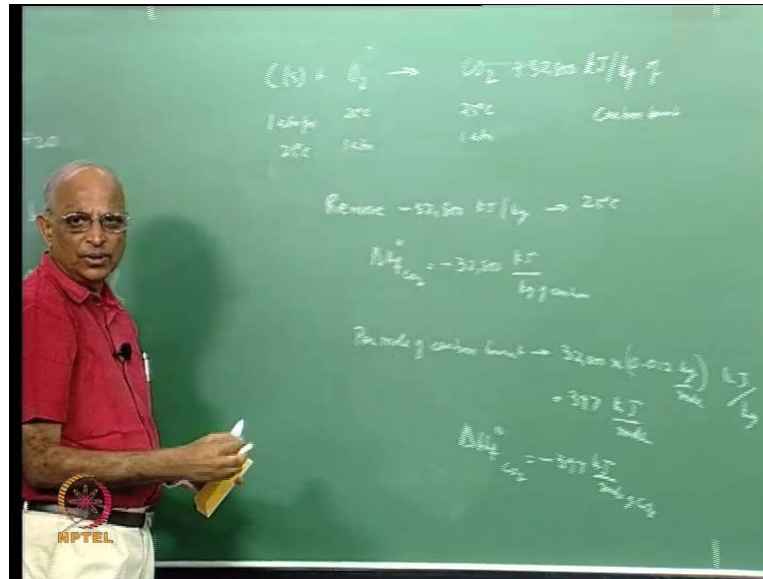
I react it with oxygen which is a gas this is again at 25 degree centigrade and one atmosphere pressure and I form carbon di oxide. Again I form it at 25 degree centigrade and at one atmosphere pressure then I say the energy required to form carbon di oxide its elements C s and O 2 will give me the heat of formation. But all of u know, if I take carbon and burn it gives out some amount of energy large amount of energy. And the energy which I get from burning 1 kilogram of carbon is something like is 32800 joules no kilo joules per kilo gram carbon.

That means when I burn carbon with oxygen per kilogram of carbon which I burn I get something like 32800 kilogram joules of energy. Now, what is going to happen? This 32800 kilo joules of energy is not going to form carbon at 25 degrees rather the temp of carbon will go up. If my products carbon di oxide has to be at 25 degrees centigrade. What is it I have to do? I have to remove some heat from this reaction, that means I have to remove minus 32800 kilo joule per kg of carbon burnt so, that the products can gain be at 25 degree centigrade.

Now therefore, the heat of formation of this should have something like minus when the reaction is exothermic the heat of formation of at standard state of carbon di oxide should be something like minus 32800 kilo joules per kg of carbon burnt. But this unit is something wrong we cannot of kilogram of carbon here and when I am looking at this therefore, better I refer it to kilogram joules per mole of carbon di oxide. Let us try to remedy the situation what I say is maybe per mole of carbon the energy, which is released is equal to 1 mole of carbon has a mass of 12 gram and the heat released is equal to 32800 into 0.012 kilogram which is something like something like 397.(no voice 38:30 to 38:44)

What is it I have to do I have to remove the heat and that the heat of formation at standard state of carbon di oxide is equal to something like minus 397 kilo joules of mole of carbon or per mole of carbon di oxide. Because 1 mole of carbon gives me 1 mole of carbon di oxide per mole of carbon di oxide, the heat of formation of carbon di oxide is minus 397 kilo joule per mole. And this is how we calculate the heat of energy.

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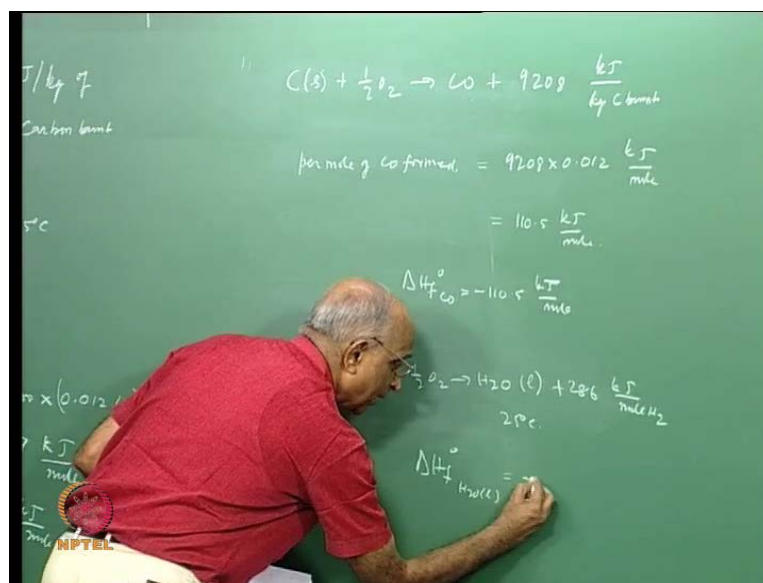


You know any reaction which is exothermic will result in the product which have a slightly a negative value of heat of formation. Let us take 1 or 2 small examples because this is something which is basic we will just spend another 2 minutes with 2 or 3 more reactions. Let us take the reaction of carbon as a solid at element level with half oxygen forming carbon mono oxide. Now what is going to happen I have carbon mono oxide here I have carbon di oxide, here it is not fully oxidized the heat which I get something over here is something like 9 2 0 8 kilo joules per kilogram of carbon burnt.

Therefore, I quickly do it for per mole of CO formed to form one mole CO I need to burn 0.012 kilogram of carbon for me to get 9 2 0 8 into 0. 0 1 2 so much kilo joules per mole of CO and this is equal to something like 100 and 10.5 kilo joule per mole. And what is happening is heat is getting generated and CO is heat I have to bring it back to the same standard condition of 25 degrees of oxygen element of 25 degrees of carbon element and heat of formation of CO this is minus 100 and 10.5 kilo joule per mole.

You know this is how to hydrogen and oxygen to form water, we have hydrogen plus half oxygen giving H<sub>2</sub>O. Why I take this example is? Hydrogen is an element gas at 25 degree, oxygen is a gas at 25 degree, but water should be a liquid at 25 degrees same standard condition. I can say that the heat of formation water as a liquid at standard condition should be equal to the negative of the heat releases of hydrogen, which is I think 286 that is plus 286 joule per mole of hydrogen.

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Now I am putting in terms of mole therefore, heat of formation of water as a liquid is equal to minus 286 kilo joule per mole. Because 1 mole of hydrogen forms 1 mole therefore, this is how we determine the heat of formation of the difference substance. Please let us not forget that since the heat of formation of a substance is defined with respect to the elements. The heats of formation of the elements themselves are therefore, 0 at the standard state. One last substance I should take because that has a positive heat of formation. And that is again important let us take the formation of hydrogen as an atom we have H<sub>2</sub> forming disassociating 2 H.

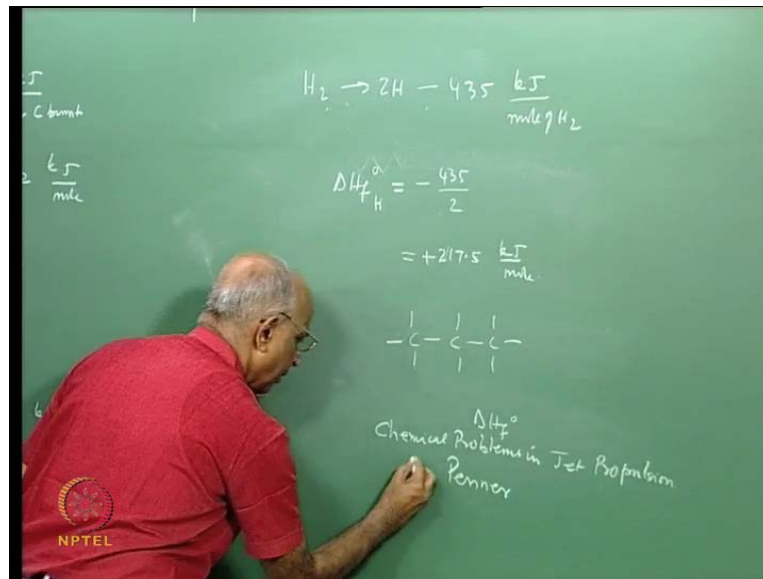
What we do in this case? We have to supply heat to be able to form hydrogen atom and the amount of heat required to disassociate 1 mole of hydrogen is something like I have the value something like F C minus 435 kilo joules per mole of hydrogen. And therefore, this means that there the reaction I have to supply heat, that means the reaction is endothermic. Therefore, heat of formation f of H is equal to minus 435 for 2 moles of hydrogen for each mole of hydrogen. Therefore two moles of hydrogen atom per mole of hydrogen molecule and therefore, the value is minus 100 and 17 to 2 1 7.5 kilo joule per mole. And this is plus n sorry because what is happening is endothermic I have to supply heat to element hydrogen and it is plus 2 1. 5 kilo joules per mole.

Therefore this is how heat of formation of different substances are done, but you know basically one need not even do an experiment. If I have all the let us say hydrocarbon I

have the bonds which are known I know the energy of each of the bonds then I know the energy of the basic elements. I subtract the bond energy of the product or the substance from that of this element I will get the value of delta heat of formation. But there are certain problems which come in a product or a substance does not only have energy of the bonds, it could have some resonance mode also it could act it could exist in different forms.

It could have resonance energy, it is necessary to have bond energy plus resonance energy of the substance minus the bond energy of the elements which will give me this is the way of theoretically calculating. I think one should look at a book by penar chemical problems in jet propulsion

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Where in he gives a good treatment of heat of formation the name of the book is it is a beautiful book chemical problems in jet propulsion by S. S. Penar. If we now know about heat of formation may be now we can make some recommendations let us see what are the recommendations.


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FUELS

| FUELS                         | METHANE | ETHANE | PROPANE | BUTANE | KEROSENE | HYDROGEN | POLYMER |
|-------------------------------|---------|--------|---------|--------|----------|----------|---------|
| kJ/MOLE<br>$\Delta H_f^\circ$ | -74.9   | -84.7  | -103.9  | -124.7 | -292.9   | 0        | -60     |

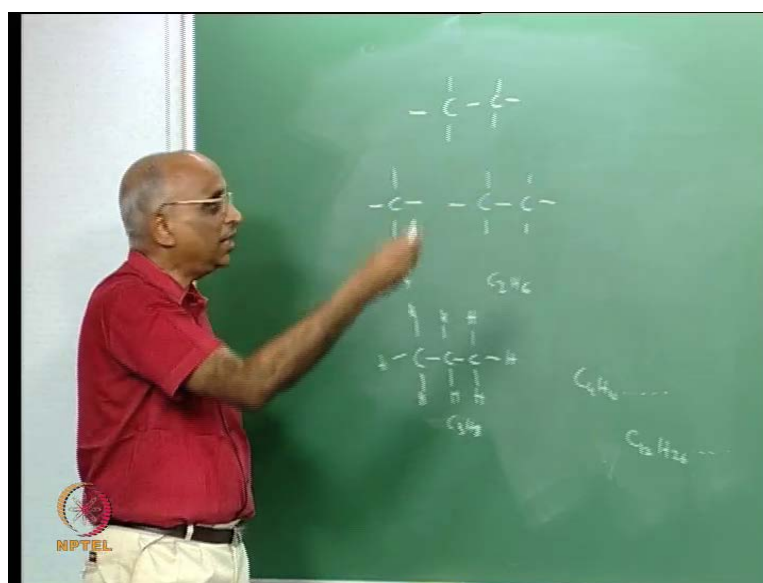
EXPLOSIVES

|           |                   |                |
|-----------|-------------------|----------------|
| HYDRAZINE | HYDROGEN PEROXIDE | NITROGLYCERINE |
| +50.3     | -187.8            | -370           |



I will quickly go through heat of formation of some of the substances over here we have fuel and why not I put on the board first. You know when I have a hydrocarbon we say well a hydrocarbon could be saturated, it could be unsaturated, it could be aliphatic, it could be aromatic, What do we mean by all this? All what we mean is if the carbon atom in the hydrocarbon are fully saturated that means all are single bonds. We say it is an aliphatic substance, if you say aromatic well you have something like a change a benzene change something like C C C and C may be a series of double bonds coming over here.

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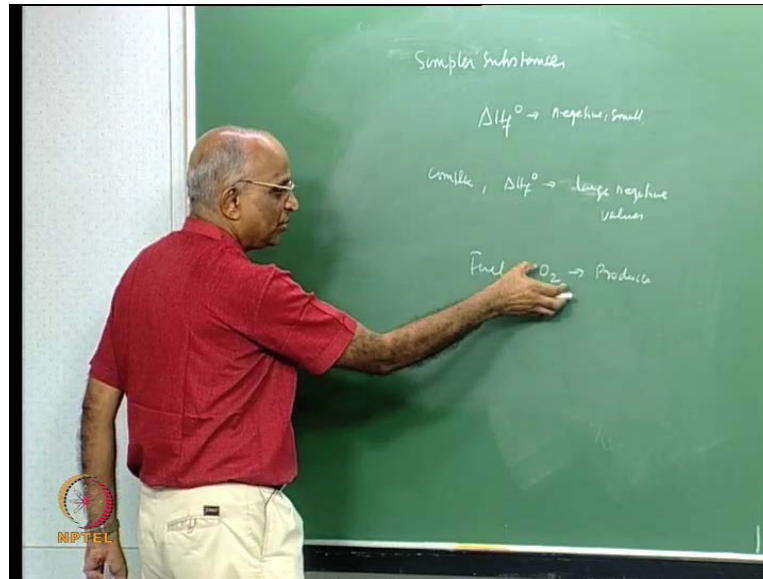
These substances which have this typical benzene structure are known as aromatic these are known as straight forward hydrocarbon or saturated hydrocarbon. Now if we want to take a look at hydrocarbon well the simplest hydrocarbon is methane the next one is ethane that is  $C_2H_6$  May be next is propane next is  $C_3H_8$  all are H over here. Next is butane  $C_4H_{10}$  and so on the chain goes may be by the time it comes to kerosene it is little more longer in chain kerosene is do Decane  $C_{12}H_{26}$  and if you have lubricating oil it is still higher and so on. The saturated hydrocarbon goes now if I want to do an experiment to determine the heat of formation of these things.

I find that the value of the heat of formation of let us say methane is something like minus 74.9 kilo joule per mole ethane is minus 84.7. Propane which is  $C_3H_8$  is minus 100 red and 73. 9, butane minus 24 and it keeps on increasing to kerosene. Which is minus 292 which means a fuel as it becomes more and more complicated or more and more longer in chain becomes has a higher value higher negative value of heat of formation. If I go to a polymer what is a polymer it consists of a chain of carbon and hydrogen the heat of formation is something like 60 kilo joule per mole. But it does not come in this particular family of may the saturated hydrocarbons.

It consists of unsaturated bonds double bonds we will be dealing with it when we get into something like solid propellants when we consider solid propellants as it were. Therefore, let us let us now tell ourselves well we find that for simple substances the heat of formation is smaller and negative that is for smaller or simpler substances. The value of heat of formation is negative and small as the substance becomes more and more complex the value of  $\Delta H_f$  becomes more negative becomes negative, but larger. That means can I write it as large negative values this is just based on methane ethane propane and all that up to kerosene and all that.

If you take a substance like hydrogen which is again shown here hydrogen is an element and therefore, at the standard condition it is 0. Because we are defining heat of formation the increment Of energy from the elements to the substance therefore, it has to be 0 for all the elements standard elements it has to be 0. There are certain substances which are known as explosives and explosives are substances which have in built oxygen in it that. Means it contains both fuel and oxygen within it in other words compared to a fuel whenever I have a fuel I react it with an oxidizer it gives me products that means, what does the fuel do it goes searches out for oxygen and then it burns

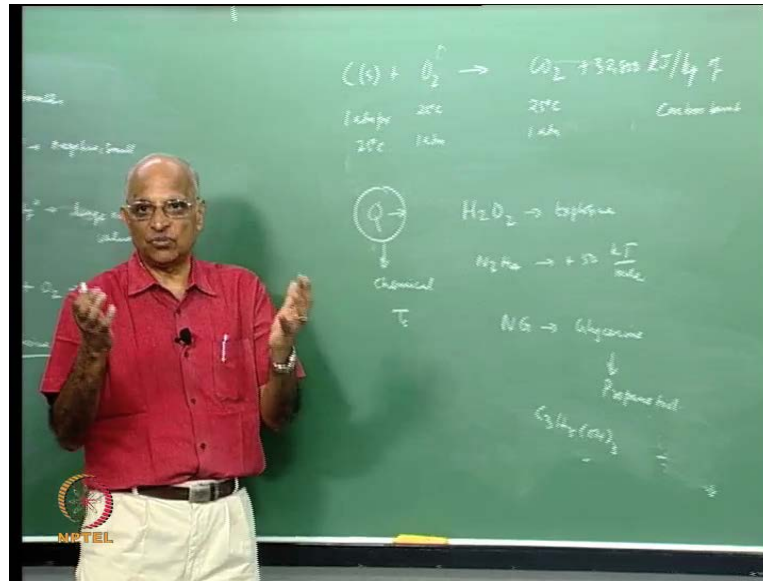
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And explosive is a substance which contains fuel plus oxygen such substances are known as explosives. Plus typical cases considering hydrogen and oxygen it could be integrated together we could have a substance like H<sub>2</sub>O<sub>2</sub> hydrogen peroxide you have oxygen you have hydrogen and it consist of more oxygen than. What is required to form water and therefore, this becomes an explosive. Similarly, you have substances like let us say nitrogen N<sub>2</sub> and hydrazine and this is again is an explosive because by itself it could react or it could also have some amount of it could it could by itself react to form products.

Therefore such substances are explosives and if you take some of the substances like say hydrogen peroxide has a heat of formation of minus 187.8 what is hydrazine. Hydrazine is what I wrote here N<sub>2</sub>H<sub>4</sub> it has a small positive value of heat of formation. Something like plus 50 and if I were to consider some other explosive like let us say consider nitro glycerin. What is nitro glycerin? Nitro glycerin is something like glycerin and glycerin is something like propane Tyrol and propane Tyrol means I am looking at C<sub>3</sub>H<sub>5</sub>OH<sub>3</sub> in which I replace h by NO<sub>2</sub> or NO it gives me nitro glycerin and this again gives me heat of formation.

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Which is something like this is given as minus 370 we are looking at the heat of formation of the different substances. And based on this heat of formation of the different substances we would like to find out, which chemical when it reacts gives maximum heat. And therefore, under what conditions can I have chemicals which will give me a high value of temperature. I will continue with this in the next class what I will do I will go through the heat of formation of some more substances. And find out what are the chemicals which are most viable for rockets? And we will 0 down the number of chemicals which can use for rockets to something like 7 or 8 of them so that we are very clear what to do for chemical propellants well thank you then.