Introduction to Explosions and Explosion Safety
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Lecture - 19
Role of Chain Carriers in an Explosion

Good morning, you know we have done the lump mass system for modelling an explosion. And as per the theory what we developed, we found that there are two parameters which govern whether an explosion is possible or not.

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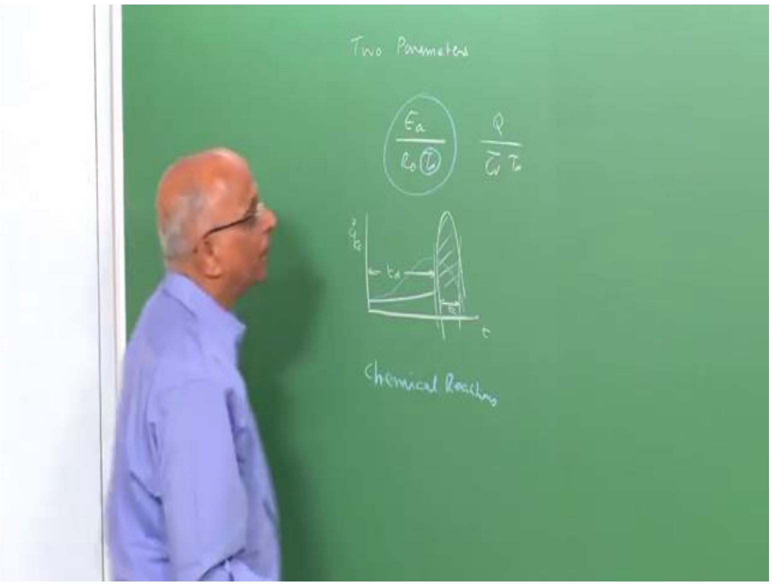

The first one is the ratio of the activation energy, divided by the value of, let us say the initial temperature that means, this so much joules per mole. This is also the ambient temperature T ambient into the universal gas constant.

And the other parameter is the ratio of the heat released kg per mole divided by, we can say the specific heat per mole that means, joule per mole Kelvin into T ambient. We said if both these parameters are large an explosion is more likely. We said based on this the activation energy must be large, or the ambient temperature must be small. What does this non-dimensional term represent?

It represented the tendency for spurting that means, a small value of the chemical energy release time. Rather we said if I represent the chemical energy by the value of Qc dot that is dQ by dT. And if I put the time over here, well initially the reaction takes some time to take place, but by the time the actual energy gets liberated, it is in the form of a spurt. And this happens when the value of the activation energy is large. Equivalently, when I say well if the activation energy is large, I have this spurting technique and, the actual time of chemical reaction is therefore, a small value, well I say this is the chemical reaction time, this is the induction time td.

And therefore, any explosion is associated with a small value of the chemical reaction time, compared to the heat released time which we have seen in detail in the last class. Therefore, what is this therefore, activation energy must be large, we said for most explosives the value is around 80000 to 160,000 joules per mole. The second point is, if the ambient temperature is high what is going to happen? If the ambient temperature is high well, the reaction starts off because the ambient temperature is high, the reaction starts off at a fast rate. And therefore, the spurting tendency gets diminished therefore, an explosive is, explosion is more likely when the ambient temperature is small.

Now, this is the non-dimensional parameter, which characterises the spurt in chemical reactions, or spurt in heat release, after induction time. This term just tells you what is the magnitude of heat release visa vies, the initial internal energy of the medium. If I have more energy release, well an explosion is capable of forming a strong blast wave, these are the 2 parameters. What I do in the class today is, maybe we will try to apply it for different chemical reactions. One or two typical cases or maybe one typical case such that we know how to apply. Like for instance let us, let us go back to our starting point.

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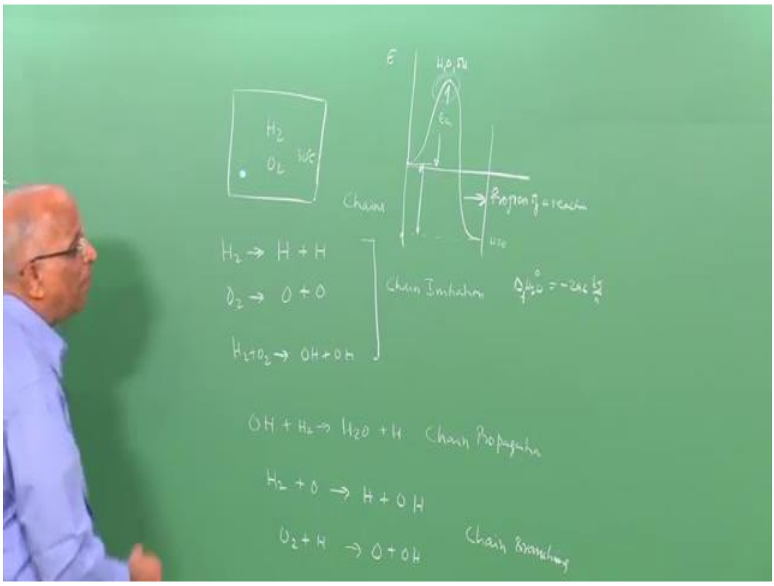

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You know we always took this example we said well I have a container, in this container I have hydrogen gas, I have oxygen gas, which are mixed together. We told well hydrogen and oxygen can be in the container for years together, let us say it is at room temperature, it is at let us say 30 degree centigrade, which is the room temperature. It can be there at 30 degrees, let us say 1 atmosphere pressure for years together nothing is going to happen.

But if I want to start a reaction, we said well, I must put an electric spark in it that means, I deposit some energy at some point and maybe the reaction takes place. I am still within the confinement of overall what we said is uniform temperature, uniform concentration therefore, I am still looking at the lump parameter approach. I put some energy release, and what does the energy release do? It takes the hydrogen, maybe the hydrogen is takes place. It decomposes the hydrogen or it breaks the hydrogen into H and H atoms point 1.

It could, because I am releasing some energy and hydrogen and oxygen maybe it breaks it up into H and H atoms, we will, we will see what this is. It also takes the oxygen molecules and break it, breaks it up into O and O atoms and also maybe the hydrogen and oxygen since they are mixed together, it could also break it up into hydroxyl OH and OH atoms. Now, the H atom, O atom, OH atom, are all active you know, see this is something which is nascent stage therefore, these are all active radicals and these are known as chains.

That means, what do you do is the active chains therefore, what we do is, the act of putting some energy release in it activates the hydrogen molecule into hydrogen chain H chain, O chain, and OH chains. And therefore, these three reactions I can call as let us say the chain initiation or active radical. That is, I say well I have chain initiation which takes place when some energy is released into the medium. I have let us say OH being formed, it could react with H 2 and what could happen, I could form H 2 O. And H 2 O and one H that means, for every chain of OH, another chain of H is being formed, we call this as chain propagation.

That means, the chain continues to propagate. It is still possible, that I can have maybe the hydrogen molecule which is available, when it, when one of the chains like O comes and reacts with it, I could form H and OH. And similarly, I could also have maybe the O 2, which reacts with the hydrogen chain which is formed here, to form let us say, OH and O plus OH. Therefore, in this case what happens, one chain, or one O radical, or one chain forms 2 chains over here therefore, we call it as chain branching.

Therefore what has happened? The act of releasing some energy starts these reactions, maybe the chain initiation reaction, chain propagation reaction, chain branching reactions. And what it does, it produces a lot of these chains, and you will recall, we also talked in terms of maybe that this axis represents the progress of a reaction. We said that the energy could be plotted on the y axis, well initially hydrogen and oxygen maybe at 25 degrees, it is at almost 0 maybe at 30 degrees, the energy content is over here. And what happens, the act I want to initiate the reaction.

Therefore, I put some energy it gives some activation energy, takes it up to a transient stage over here. And then what happens it reacts and forms the products, and forms the products which is H 2 O, and we know the heat of reaction of products H 2 O. We will recall, we had delta H 2 O, heat of formation, and standard condition was something like minus 296 kilo joule per mole.

Therefore, this corresponds to the product maybe lower energy level and therefore, this is the heat of reaction which is given and therefore, and this is the activation energy. Therefore, what did activation energy do? When you want to activate a radical, or a reaction, what we do is, we are essentially forming these chain carriers and therefore, what happens is, I form all these chain which are in the transient stage over here.

That means, I form H, I form O, I form OH, because of this is form, this is all not stable it is all chains, all are active radicals.

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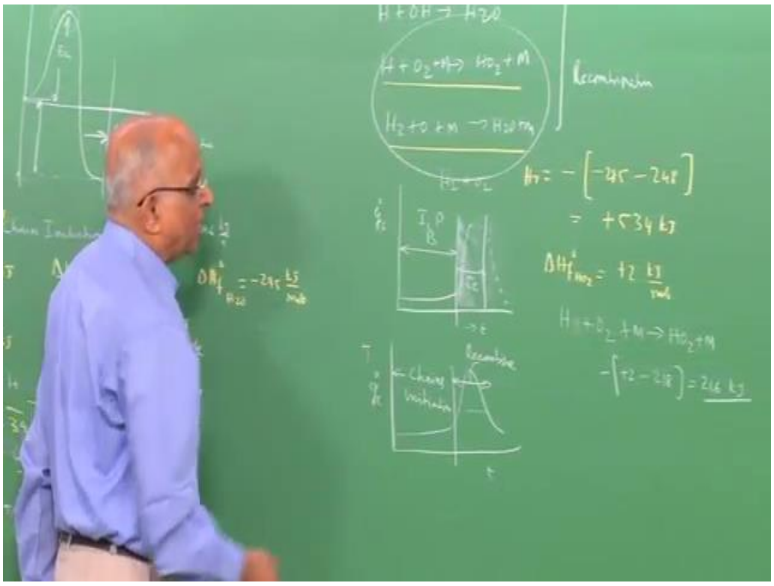

Let us put this maybe H plus O let us say H may combine with OH to form maybe H 2 O, or let us say H plus OH. You know whenever it combines like this maybe some times the third radical also influences this. But let us say well H and OH can combine to form a stable molecule, or rather I can also form H plus O 2, also can combine let us say HO 2, but since these are all helped by the molecules which are available that means, molecules which help such a reaction to take place.

Mind you, whenever we say chemical reactions, the H atom, and O 2 atom must hit against each other. If there are neighbouring atoms which are also our neighbouring molecules, which also help this hitting and breaking the structure, we call it as a third body, I can also write it as HO 2 plus M.

Similarly, here H plus OH giving H 2 O, I can write it as M giving H 2 O plus M, I can form H 2 O by different means H 2 plus O plus M, that is a third body. It could be OH, it could H, it could be H 2, it could be O 2, which facilitates this reaction give me H 2 O plus M. Well these are the recombination reactions, I say these are the recombination reactions.

And when recombination reactions takes place, well the H, O and OH which are formed here come back to the products and I get the completed products of combustion. Therefore, we say well the reaction takes place through something like a chain initiation step, followed by chain propagation, and chain branching, and ultimately the energy is released in the recombination. Why did I say energy being released in the recombination?

Maybe I have to look at these reactions a little more closely. Let us say what is the heat generated in this reaction because ultimately, let us not forget this, and what is it that I am working towards? We want to find out, whether this reaction between H 2 and O 2, I do not know the proportion, I presume it goes through these steps of reaction. As a function of tan, if I were to plot the heat release, I for an explosion to occur I should have something like a phase during which not much energy is liberated in an induction period, followed by a spike, and this is what I expect in a chemical reaction to take place.

And therefore, let us keep our tendency for this spiking and therefore, maybe it spikes and then it drops up over here. Therefore, is it possible, how do I calculate this? Let us go back and see what is the heat release in these reactions, to be able to get the heat released. It is necessary for me to know the heat of formation of the reactants, and heat of formation of the products. We tell ourselves, well I go back to the literature and look at heat of formation, I find that the heat of formation under standard condition for H is equal to, the value of heat of formation for H is equal to plus 218 kilo joule per mole.

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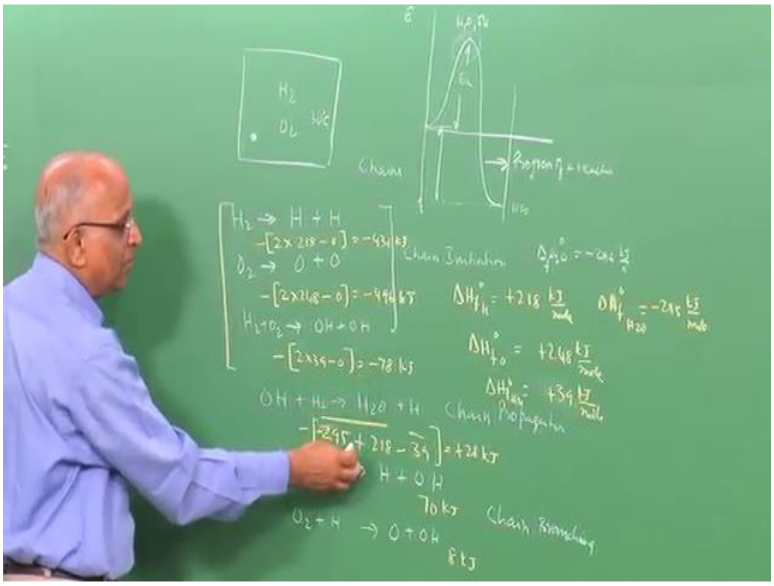

The heat of formation of oxygen atoms, heat of formation standard for oxygen is equal to plus 248, and the heat of formation of OH is equal to plus 2, no it is plus 39 kilo joule per mole. In other words to form H, I have to supply heat that means H 2 has to be heated to form this therefore, the heat of formation of H atom, O atom, and OH over here, H f of OH are all positive, this being 39 and this. Using this I can calculate the energy released in this reaction. If I were to put it just below this, what is the net value minus of heat of formation of H, well heat of formation of H is 218, I have 1 plus 1 2 radicals, 2 into plus 218 minus H is a naturally occurring element that means, H occurs and it is at standard state minus 0 therefore, the heat of formation of this is minus 436 kilo joules for the reaction.

So, all so, for the reaction O 2 is equal to O plus O, we have heat of formation of O is plus 248 therefore, it is minus, of heat of formation of products I have 2 of O, 2 into plus 248 minus. Anyway O 2 is 0 therefore, this is equal to minus 496 kilo joules. If I take a look at this reaction, these are stable things I have OH here, heat of formation is minus 2 into 39 minus 0 which is equal to minus that is, minus 78 in other words, kilo joules. In other words, the heat of reaction over here is minus 436 kilo joules. Heat of the reaction O 2 dissociating into O is minus 496. The heat of reactions is minus 78 that means, these reactions are endothermic.

That means, they absorb energy no heat is being liberated in the three chain initiation reactions. If we take a look at the heat of reaction, corresponding to OH plus H 2 giving H 2 O plus H, what is it I get? Minus of H 2 O well, these we know by now, yes heat of formation H 2 O let us say heat of formation at standard condition, for water as a liquid is equal to minus 295 kilo joules 295, 296 kilo joules per mole.

Therefore, I put the value I have one mole of this therefore, 295 and the value of H is, but mind you know 295 it is minus, that means, minus 295 plus H that means H is positive plus 218, that is the value of the 2 products H 2 O and H, this is the heat. And for OH, well OH is minus 39, minus of plus 39. This is for the products, and if I add these up, the heat of reaction of this particular propagation reaction, comes out to be equal to plus 28 kilo joules. Similarly, I can calculate the energy for the chain branching reactions now, I know the heat of formation of H, I know the heat of formation of OH, I know this, I put together.

Similarly, I get the value for the chain branching reaction as H 2 plus O giving me something like 70 kilo joules in a similar manner, and for the last one O 2 plus H giving O plus H, the energy released in this reaction is 8 kilo joules. Well we find yes these 2 reactions and this one, these three, the chain propagation, and the chain branching reactions are exothermic, but the exothermicity is small. How do I say it is small? Let us work out one or 2 cases. Let us find out the exothermicity of let us say a reaction like H 2 plus O plus M is equal to H 2 O plus M.

If I take this, well the heat of this particular reaction is equal to minus of H 2 O that is, minus 285, and I have O over here. We know heat of formation of water is plus 248 therefore, I have minus 1 into 248. Therefore, the heat of this recombination reaction H 2 O plus H 2 plus O plus M is equal to H 2 O plus M comes out to be something like plus 534 kilo joules. Similarly, if I were to write the heat of formation of this maybe H plus O 2 plus some HO 2 plus M. We said well the heat of formation of HO 2, if I go to the standard literature tables and plot it out, well HO 2 has a value of plus 2 kilo joule per mole.

And therefore, the energy liberated in the reaction H 2 plus H plus O 2 plus M is equal to HO 2 plus M is equal to we are talking of maybe minus of plus 2. That is the product we have to M and M is the same over here, minus I have H over here, the value of heat of formation of H is equal to plus 218 minus 218 which is equal to something like 216 plus therefore, because this is the small positive value over here, it is plus 216 kilo joules.

Therefore, these recombination reactions have high value of exothermic heat release whereas, the chain propagation, and the chain branching reactions have very small values 8 or 28 and all this. Whereas, the chain initiation reactions have hardly, they absorb energy, they are endothermic.

Therefore, you know what is going to happen let us say, I dump some energy I start these chain initiation, chain propagation, and chain branching reactions, and as more chains and more chains are being formed, I have the recombination reactions taking place. And what is it I find? I find well the energy is essentially liberated in the recombination reactions.

And hardly any worthwhile energy gets liberated here with the result, what I can now tell is, well during the initial phase of the reaction when I activate the reactions that means, I look at maybe the temperature gain, what is going to happen? The temperature hardly changes, it just is endothermic which is balanced by the energy release, and once the recombination reactions take place the temperature increases, and I have a signature like this.

In other words initially, there is hardly any value of chemical heat release. And which is followed by a spurt therefore, in this period I have chains which are being formed, chains being initiated, followed by a period, in which the chains recombine to give heat. Therefore, we tell ourselves well during the initial phase, I have chain initiation, chain propagation, and chain branching reactions that means, initiation, propagation and branching reactions, for the chains and the chains combine in the period later on to give energy that means, T c corresponds to recombination.

And during the initial phase I just do not get much energy release. Well this matches with whatever we were telling for high activation energy, and this is how a reaction progresses in practice. Having studied this, you know why I am, why are we going into these details? See tomorrow we want to control a reaction, or control an explosion. If you want to control a, control an explosion, it is necessary, that I do not allow this to happen.

Maybe I should somehow absorb the chains during the reaction, and this is what I will do subsequently, but to be able to be clear on what little we have been doing so far.

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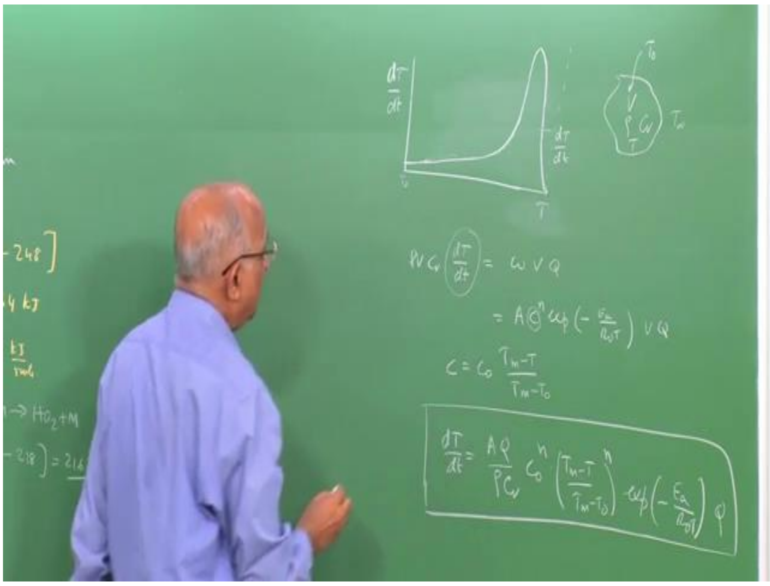

Let us put it together in a plot of let us say the last plot could be maybe as a function of dT by dt. That is the rate of temperature rise as, can I work it out as a function of time, which means as a function of the temperature itself. Because, we said as time increases, the temperature increases therefore, as a function of time I could be able to do this I want to take a look at this.

Therefore, we again say well my constraints are the following. I also have a lump mass system, I have a volume, I have a density of the explosive which is rho. The Cv of the explosive that is, the specific heat of the explosive is Cv. I have the ambient temperature T ambient. The temperature at any time is T, the initial temperature could have been T 0. Well, what did we tell ourselves well. I have the mass of the system rho v into the specific heat that is, the thermal mass of the system, into I have dT by dt, which is…and this gives me the rate in so much kilo grams or kilo joules per second or joules per second. And where does this come from?

It comes from the rate of the reaction, that is so much moles per c c second into the value of volume that means, moles per second multiplied by Q so much joules per mole. It also give me joule per second and this is what I am balancing. I want to see how the value of dT by dt that is d capital T by d small t changes. And therefore, now I write the value for the reaction I say well, reaction given by AC n exponential minus activation energy by R 0 T into I have V and Q over here. And you know, you will also recall we had an expression for C, we derived one expression for C. We said well, I can write the expression for C is equal to C 0 into temperature maximum minus temperature at any point in time when the concentration is C divided by T m minus the initial temperature.

We plug this in and then we say, we can get the value of dT by dt is equal to well, in this particular expression V need not be taken into account. I have AQ, A, Q over here, well I have divided by rho Cv and then, we have taken these terms over here therefore, now we have only the value of C n.

Therefore, I can write C naught raised to the power n, where we are still considering an n th order reaction, or we say the rate of a reaction is proportional to C to the power n, n could be 1, it could be, it could be even 0, it could be 2 for a second order reaction, and we say most of the reactions are n is equal to 2. And we said is equal to Tm minus T divided by Tm minus T 0 to the power n. AC 0 into we have the exponential term coming over here, minus Ea by R 0 into T into the value of Q over here. And this gives me the expression for the rate of temperature increase. And if I look at the rate of temperature increase and let us say, I first plotted with respect to temperature that means, on the x axis I have temperature, what is it I get?

Well, when the temperature is initially let us say, the ambient temperature, I have Tm minus T 0, Tm minus T 0 well, this is a strong term well it is a small number over here. And as temperature increases and reaches the final maximum value it becomes 0 that means, ultimately it becomes 0 over here. And in between if my activation energy is large, like what we have been talking earlier well, that temperature increases like this. It goes, it goes after a long induction time let us, let us put it down more reasonably. We tell ourselves initially, the temperature increase is small because the activation energy Ea controls it.

After some time well it peaks like this, and it comes down to 0 over here. This is the type of dT over d time curve, and what is the temperature, how does it change? Well, initially the temperature is T naught over here that is, and it reaches the value. And therefore, if I were to know change this x axis instead of temperature, I plot the time, what is the type of relation what I get? Let us put everything together such that we can now, interpret the reaction taking place and the rate at which the temperature build up takes place.

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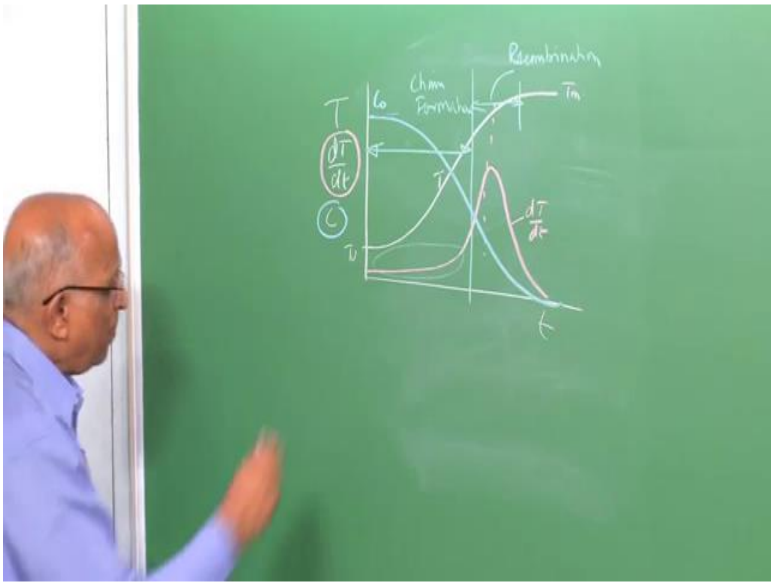

I have temperature versus time, I have dT by dt, I want to plot it on the axis again, I also want to plot C as a function of time. Well, let us first plot this well it starts with a temperature T naught, and it goes to a maximum value Tm.

This is the value of T, let us now, plot the value of the rate of temperature increase well it is, it starts at the low value. Maybe somewhere over here the peak occurs, well it goes like this peak occurs and comes back over here. This is the value of dT by dt. If I were to plot the concentration, and if I denote the concentration C at any time, well initially the concentration is C naught.

The final value of concentration is 0 because, all the fuel is consumed and therefore, maybe this is initial value, it starts like this and comes over here. Well, these are the concentration plots, the temperature increase plots, the rate of temperature increase plots, and we tell ourselves well, based on whatever we have discussed for hydrogen, oxygen and it is true for any hydrocarbon or most of the substances. We can tell ourselves it is during this period that, the chain initiation, chain propagation, and the chain branching reactions are there, an avalanche of chains are being formed.

And these, during this period recombination reactions take place during the actual time of heat release that is, recombination of chains to give me the heat, and these are essentially the chain formation stage. We should know, what must I do to control? Supposing, I do not want an explosion and all of us are looking at ways to control an explosion, or to stop an explosion. What must I do to stop the chains being formed? Maybe I should add something such that the chains do not get formed, but before I do this let us quickly take a look to the chain initiation reactions.

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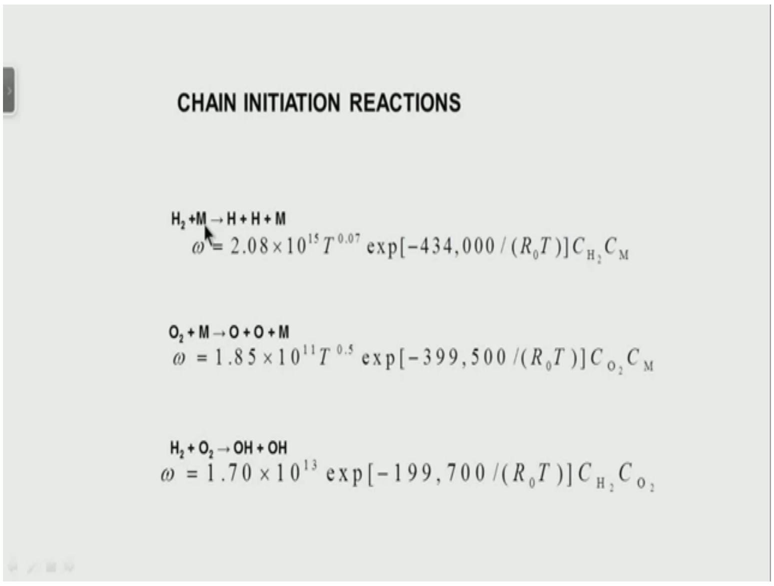

CHAIN INITIATION REACTIONS

$H_2 + M \rightarrow H + H + M$

$$\omega = 2.08 \times 10^{15} T^{0.07} \exp[-434{,}000/(R_0 T)] C_{H_2} C_M$$

$O_2 + M \rightarrow O + O + M$

$$\omega = 1.85 \times 10^{11} T^{0.5} \exp[-399{,}500/(R_0 T)] C_{O_2} C_M$$

$H_2 + O_2 \rightarrow OH + OH$

$$\omega = 1.70 \times 10^{13} \exp[-199{,}700/(R_0 T)] C_{H_2} C_{O_2}$$

We told ourselves well H 2 forms H plus H. You know the formation of chains is sort of facilitated, when I have other molecules. Maybe I have something like maybe a wall, maybe I have something like an energetic wall which can help in the reaction or I have maybe, the oxygen molecule also provides a collision. Therefore, we say the third body helps in the reaction. And this third body does not take part in a reaction, it helps in the reaction, but it is available to me after the reaction as the third body itself.

Therefore, we say H 2 plus M is equal to H plus H plus M. And the rate of a reaction we called as omega so much moles per c c second, and that is equal to 2.08 into 10 to the power 15 exponential the way we have been telling second order reaction. Therefore, concentration of hydrogen into concentration of whatever is available as a third body over here.

We also find that there is a weak dependence on temperature coming over here. You will recall when I got the value of omega, I did stay well it could be a small function of temperature. And when we do experiments, we do find it is a weak function of temperature in addition to temperature coming in the exponential term we do have temperature coming over here.

Similarly, the chain initiation reaction of O 2 forming, O plus O chains, is also helped by a third molecule and the rate of reaction is given by. In this case again temperature is quite weak over here explicitly, a combination of the oxygen and the third molecule over here. This is the reaction rate over here similarly, for the chain, you also could have chain initiation reaction in which I have H 2 plus O 2 forming OH plus H, this is also chain initiation. Well in this case the temperature effect is not there, the rate of reaction is given by this.

I can, I knowing the rate at which the chains are there, I can write the value of omega is equal to d H d of H 2 by dT is equal to omega into using the law of mass action as concentration of H into concentration of the third body. I can solve for the rate at which the chains are being formed that means, the rate at which H 2 is getting depleted or dH by dT is equal to omega into H 2 plus M over here. And of course, I have 2 of them therefore, 2 of dH by dT is equal to this and therefore, I can find out the rate at which the chains are being formed. This is for the chain initiation reactions.

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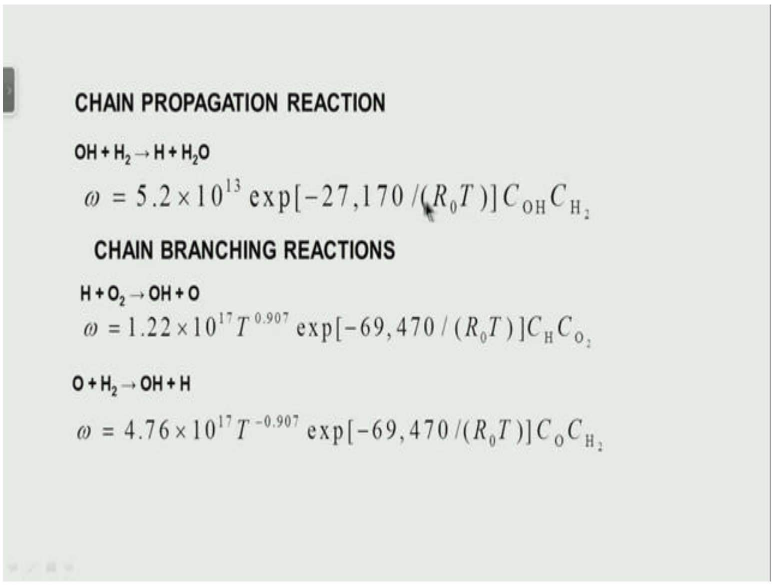

CHAIN PROPAGATION REACTION

$OH + H_2 \rightarrow H + H_2O$

$$\omega = 5.2 \times 10^{13} \exp[-27,170/(R_0 T)] C_{OH} C_{H_2}$$

CHAIN BRANCHING REACTIONS

$H + O_2 \rightarrow OH + O$

$$\omega = 1.22 \times 10^{17} T^{0.907} \exp[-69,470/(R_0 T)] C_H C_{O_2}$$

$O + H_2 \rightarrow OH + H$

$$\omega = 4.76 \times 10^{17} T^{-0.907} \exp[-69,470/(R_0 T)] C_O C_{H_2}$$

I get a similar one for the chain propagation reaction OH plus H 2 is equal to H plus H 2 O. The rate of a reaction is given in terms of the concentration of OH and H 2, and we have the rate of a reaction is there. Similarly, the chain branching reactions H plus O 2 OH plus O and, the chain branching reaction that means, for each chain I form 2 more chains or O plus H 2 forming 2 more chains. The reaction rates given by this, these are somewhat temperature dependent reactions in addition to temperature coming under the exponential sign over here. Therefore, we have the chain initiation, chain propagation, chain branching reactions, and when we talk in terms of chain termination reactions, I write these two.

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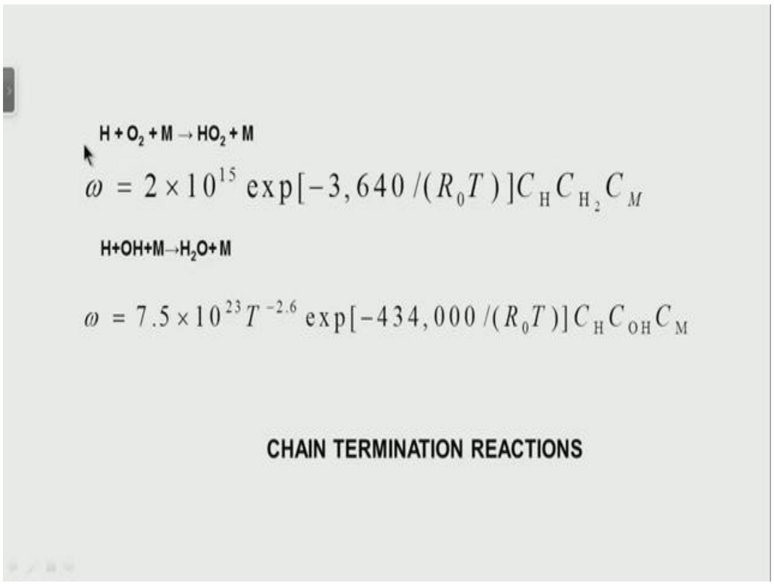

$H + O_2 + M \rightarrow HO_2 + M$

$$\omega = 2\times 10^{15}\ \exp[-3,640/(R_0 T)]C_H C_{H_2} C_M$$

$H{+}OH{+}M \rightarrow H_2O{+}M$

$$\omega = 7.5\times 10^{23} T^{-2.6}\ \exp[-434,000/(R_0 T)]C_H C_{OH} C_M$$

CHAIN TERMINATION REACTIONS

H plus O2 plus a third body mind you, you know when we talk of these recombinations and a third body over here, you know the collisions you need number of H number of O 2 because three bodies are reacting together at a point. This happens essentially at high pressures because at low pressures you know, you do not have the feasibility of three molecules colliding with each other.

Therefore, these three body reactions, essentially happens at higher pressures, and we have HO 2 plus M, we have H plus OH plus M giving H 2 O plus M. And the rate constants of these 2 are given by this. And we just now showed on the board that the energy release in these chain termination reactions are very much greater than the endothermic heat release or the energy absorption in the chain initiation and the small values of energy release in the chain propagation and the chain termination reactions.

Therefore, it is possible for us using these known values of experimentally determined rate constants to, or the rate of a reaction, to be able to plot, to be able to determine the values of let us say H and OH. And let us say O, which are being formed in the reactions and find out the period or the time duration during which the chain initiation takes place, and the recombination reactions take place. Having said this, let us come back and take one last look at the chemical explosions. From the point of view of the following well, we said well hydrogen oxygen we will stick to this because it is quite illustrative.

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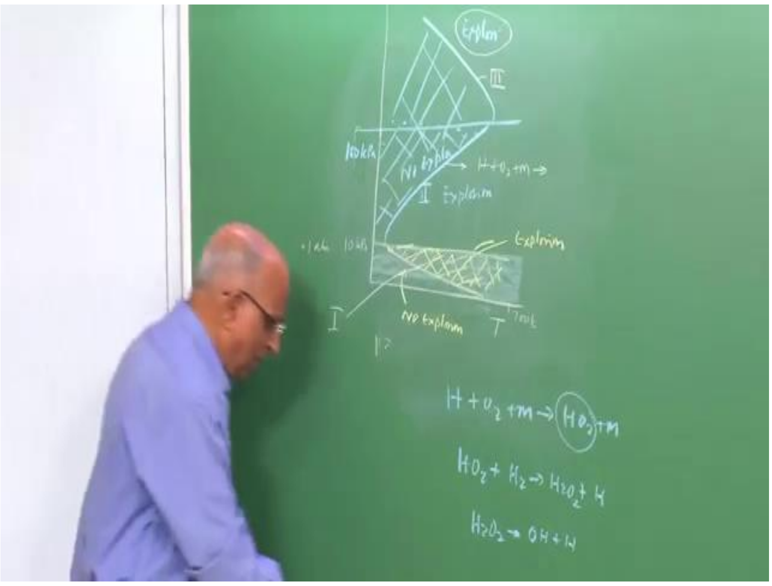

We say well I have let us say hydrogen and oxygen which is available. Can I say well, all along for all conditions of pressure and temperature that means, I want to take a look at the explosion diagram for pressure as a function of temperature.

In other words I have a mixture of hydrogen and oxygen in a container, have hydrogen and oxygen. Let us say, I vary the pressure and temperature I want to find out well does the reaction, does the explosion diagram look quite the same for all pressures and temperatures? Are there some regions of pressure and temperature in which no explosion is possible, are there some regions of pressure and temperature in which explosion is possible? And that is what I want to take a look.

Therefore, we just do whatever little we have discussed so far. Let us say, I am, I am interested in pressure let us, let us consider a pressure limit of let us say 10 kpa, which is let us say 0.1 of an atmosphere. And let us consider a temperature region let us, let us now restrict ourselves to a temperature region around. Let us say 500 degrees centigrade, or let us say 400 degrees centigrade. Because you know you will recall, we said that the auto ignition temperature of hydrogen oxygen mixture is around 440 degrees centigrade or so. Therefore let us, let us keep this in mind, let us say in Kelvin, I am interested in a temperature of around let us say 700 Kelvin. This is my region of interest which I am looking at.

Therefore, if I am basically interested in the low pressure region that is, sub-atmospheric pressures that is, I am interested in this particular region. Can I, can I say under what conditions will an explosion occur in this particular region? Well, I know that when the pressure is large that means, when pressure is large that is of the order of let us say somewhere over here around 8 or 10 kpa, pressure is large.

Therefore, the collisions between the molecule H 2 and O will be higher and therefore, we expect more change to be created when the pressure is higher, when the pressure is lower well, no changes are created. But if the temperature is higher well, the molecules have higher energy and therefore, I can say chains will be formed something like this. That means, when I talk of very low pressures and high temperatures, I can say well chains are created in this particular region.

That means, more chains are possible in this region as the pressure is increases at lower temperature more chains are being formed. And therefore, I tell myself this is the region in which more chains are being formed and therefore, this corresponds to a lot of chains and these chains can recombine and generate heat. Therefore, this shaded region that is the hatch region corresponds to an explosion. In this region, what is happening? Some chains are definitely formed, but they go back, they are absorbed by the wall because the chains are so few.

And therefore, this region corresponds to no explosion. This is in the region of sub-atmospheric pressures, let us now increase the pressure and still discuss this diagram further. Now, in the region let us say I go to something like 100 kilo or let us say, let us say I go to a 100 kilo pascal or little higher let us say 200 kilo pascal then, what is going to happen?

You know in this region well, chains are being formed, but we also found that the reaction H plus O 2 plus M forms something like H O 2 plus M, which does not really give that much of heat, but what happens? The chain H gets consumed and maybe at higher pressure and higher temperature, more and more chains are getting consumed and H O 2 is being formed and H O 2 you know is something which can be kept as it is for some amount of time.

That means, at intermediate pressures and temperatures it can form products. And therefore, this fellow continues to form H O 2 that is the chains get depleted here. We also find yes at higher pressures more and more of these things are getting formed, chains are getting consumed. Therefore, I can think in terms of the situations something like this wherein, maybe if the pressure exceeds this limit well, the chain gets consumed here.

Since, chain gets consumed over here, no explosion is possible in this region that means, I put the graph over here, I say in this region no explosion is possible. But in this particular region well, I have the chains which are being formed and recombination reacts reactions generate heat, but in this region pressure is high as temperature increases this reaction takes place, no explosion is possible. And ultimately therefore, I say well this is one limit wherein, no explosion and in this region I have explosion taking place.

And now if I increase the pressure still further, what happens? Well I have H O 2 being formed and this H O 2 can react with H 2 to form H 2 O 2 plus hydrogen that means, chain is getting formed again. And this H 2 O 2, I am sorry H O 2 plus H 2, H 2 O 2 plus H over here and the H 2 O 2 can again at high pressures hit against each other and form O H plus H. Therefore, at very high pressures I again start getting the chain carriers which can go, which can produce a lot of chains and these chains can combine to recombine to form heat release like H 2 plus O giving H 2 O or 2 H plus O giving me water.

And therefore, the curve goes back over here therefore, in this case I have explosion taking place over here, and in this region this continues over here no explosion. Therefore, what is it I see? Well, this corresponds to the second phase wherein, the chain termination reaction is not allowing the chains to take place and I have no explosion over here, but how will I get an explosion here. I have no explosion here, no explosion here beyond a certain value of pressure, I do get an explosion coming over here.

And therefore, this gives me an explosion diagram, this is the limit where we say is the first explosion limit wherein, the vessel absorbs the hydrogen and have no explosion. In this case, I have the chain termination reactions H plus O 2 plus M which absorbs all the chains and does not allow an explosion to take place. And well in the third one well, because of the high pressure effects more and more chains are being formed I have an explosion taking place. This is the explosion diagram, and this called the third one wherein, I form chains readily. I illustrate this in one of the slides which I will show now, and what is it we see in this particular slide?

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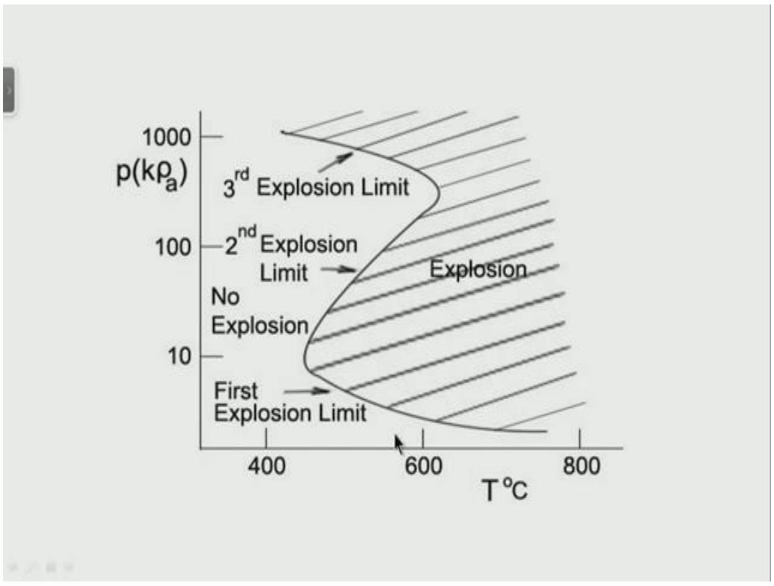

I just showed the three explosion limits well, this is the first explosion limit at low pressures, this is the second explosion limit wherein, the chain termination reaction robs of the chains over here, and I have at the higher pressures the third explosion limit. Therefore, we have a first explosion limit, only on the right side which is shaded, we have explosions, you do not have explosion in this particular region over here. And this is how we interpret explosions for the different explosives.

Well, this is all about it, let us, let us spend a couple of minutes on what I told earlier. Namely we wanted to find out whether I can control my explosion. Supposing I do not want an explosion, what is it I do? Let us, let us see what could be done. In other words, I want to do something to my explosive, let us again get back to the starting point.

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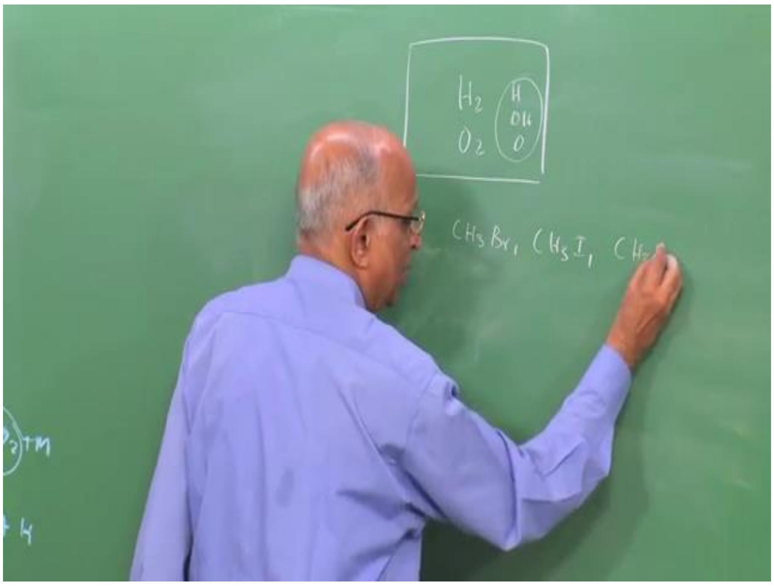

Namely I have a vessel let us say I have container containing hydrogen and oxygen. Now, to prevent an explosion, I must not allow my chains H, O H maybe O to sort of increase in large number, and these chains should not react and form the chain termination reactions or give an spurt in energy release. In other words, I want to control such that, I do not create these chains at all, and for this what is it we do? Well, we use some substances which are like methyl bromide, we say CH 3 methyl bromide, we say methyl iodide, or we say methyl chloride CH 3 Cl.

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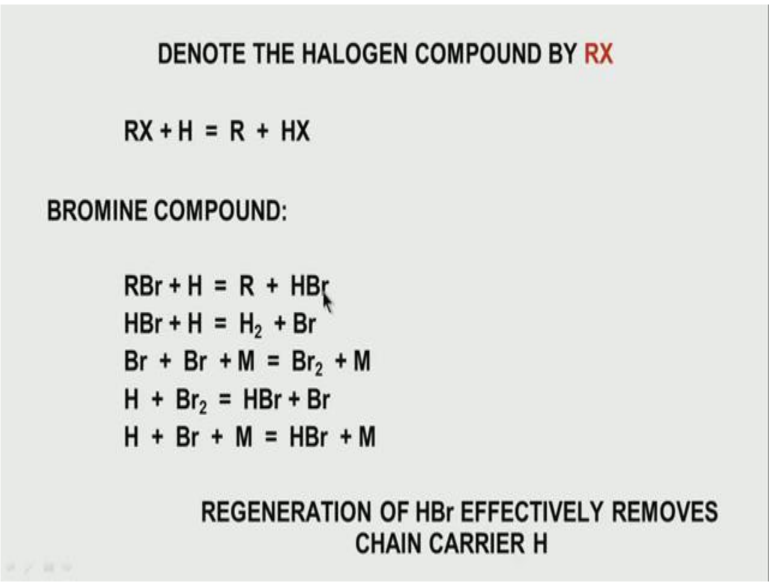

DENOTE THE HALOGEN COMPOUND BY RX

$RX + H = R + HX$

BROMINE COMPOUND:

$RBr + H = R + HBr$

$HBr + H = H_2 + Br$

$Br + Br + M = Br_2 + M$

$H + Br_2 = HBr + Br$

$H + Br + M = HBr + M$

REGENERATION OF HBr EFFECTIVELY REMOVES CHAIN CARRIER H

You know these are halogen based compounds. They can in general be denoted by RX where X is the halogen and R is the organic radical. The halogen compound RX reacts with the chain carrier H that means, it is robbing the chain carriers from the explosions forming HX, that is the hydrogen halide and the organic radical.

You know to be more clear about this let us just take the specific example of let us say a booming compound that means, we are talking in terms of R halide being bromine RBr. The RBr reacts with hydrogen, that is the hydrogen chain to form R plus hydrogen bromide. This hydrogen bromide so formed, reacts with more of the hydrogen chain that means, it absorbs or robs more of the hydrogen chain from the reaction, to form hydrogen molecule plus the bromine atom.

And therefore, now we have effectively taken pout H from the reaction that is the chain carrier reaction. The bromine ions act with bromine ions to form the bromine molecule, that happens in the presence of the third body that means, the other atoms and molecules in the reaction. And therefore, bromine forms the bromine molecule, and the bromine molecule further reacts with the hydrogen atom that is the hydrogen chains to form hydrogen bromide and bromine atom.

And now, what is happening is see again robbing hydrogen from the reaction or from the explosion that is the chain carriers are being further removed. And this bromine atom again robs further chains of H to form H plus Br in the presence of the third body to form hydrogen bromide. Therefore, you see a series of steps by which the hydrogen chain carrier is being removed, and also we find well hydrogen bromine also or hydrogen bromide gets further regenerated in the reaction, which effectively promotes further robbing of this chain carriers.

Therefore, the regeneration of HBr effectively removes the chain carrier H. And in this way you are removing the chain carriers, and when we remove the chain carriers, well, you do not have much of the chain carriers to prolong your induction time, and also accumulate chain carriers by which you have a spurt or a peaking in the reaction.

In the absence of chain carriers therefore, you do not get an explosion, namely a long induction time, followed by the spurt in the reaction. And this is how the halogen compounds like RX are effective in removing the chain carriers and inhibiting the chemical reaction, which could lead to an explosion. We must remember that phosphorous compounds similarly, react with chain carriers and eliminate them and therefore, also inhibit the explosion process.

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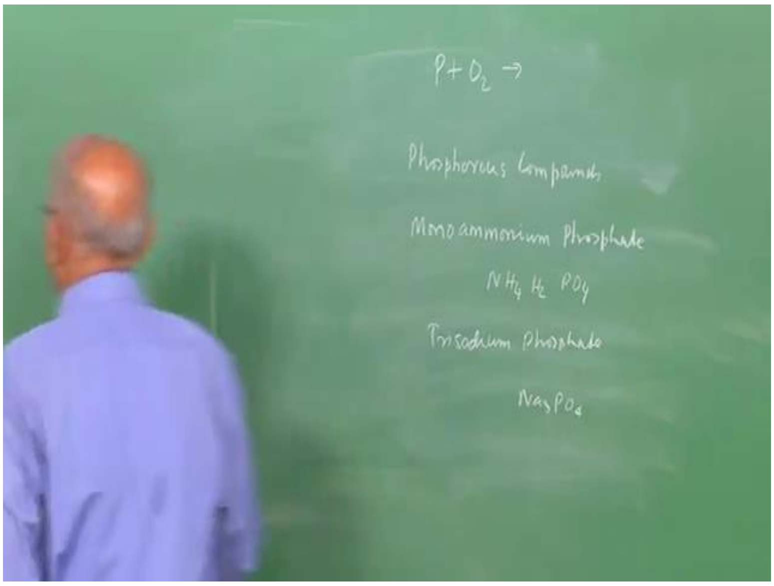

You use phosphorous compounds. And these phosphorous compounds could be mono ammonium phosphate, the formula being NH 4 H 2 PO 4 and the second being tri sodium phosphate, formula being Na 3 PO 4. Therefore, adding such inhibitors to our explosive substances will arrest the formation of chains and will not allow the explosion to occur. Well, this is all about the theory of explosions and it is time we go to the next chapter.

But before I do that let us, let us take one small model problem such that, we revise the total what little we have done. You remember we talked in terms of different types of explosions and I think, it is necessary for me to tell one last thing.

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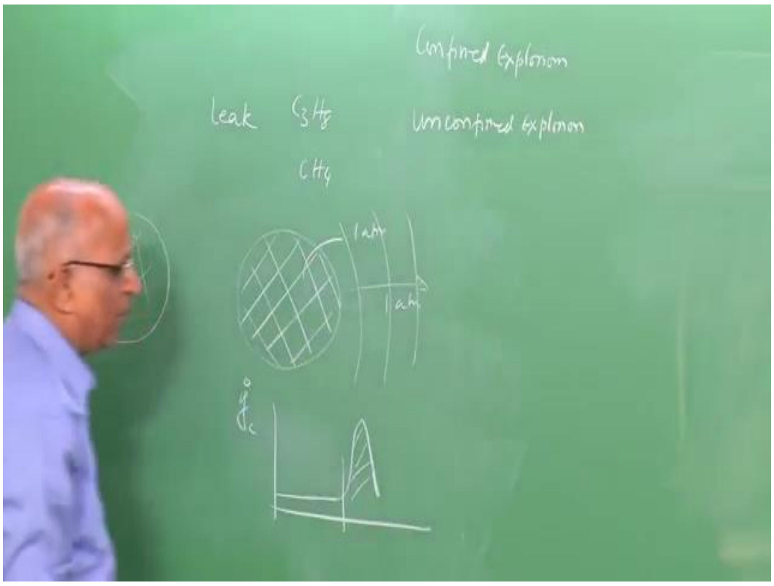

You know supposing let us say I have a leak, I have a leak of let us say propane C 3 H 8 or let us say I have a leak of methane, such as it happened in ural mountains in 1989 in which I formed a huge cloud of methane air mixture in because of some pipeline burst. And supposing let us say I have this methane air which is, which is accumulated as a huge cloud. You know mind you, this cloud is at atmospheric pressure, the ambient is also 1 atmosphere pressure.

Therefore, it is just an unconfined cloud as it were. It is not that I have a container or a bomb in which this particular gas mixture is available. I can understand when I can contain a mixture in a bomb well, pressure builds up and the bomb bursts, but this is in atmosphere itself. In atmosphere itself supposing, I have a cloud of methane or a cloud of propane with air, which is formed, can it result in an explosion?

The question is well, it is not confined, but I do realize that maybe propane methane or hydrogen cloud goes through the process of having, let us say, I plot it now the heat release from this particular cloud, what happens? The initially, I have an induction time, followed by induction time I have a spurt in the energy release because I have this spurt in energy release after this induction time. And this chemical reaction time during which actual heat release takes place is very small.

What happens is, because of this spurt blast waves are generated, and you can have an explosion even in an unconfined environment. It is not necessary that I put my explosive only in a bomb or in a container and have an explosion. It is possible to have unconfined explosions and this is what we will be considering subsequently. We will talk in terms of confined explosions, and we find even in unconfined conditions, that is open unconfined it is possible to have an explosion.

Let me quickly go through one last example, maybe a worked out problem in which I will now consider. Maybe the example of the Texas city disaster, we have done this problem already for the heat release, what did we say?

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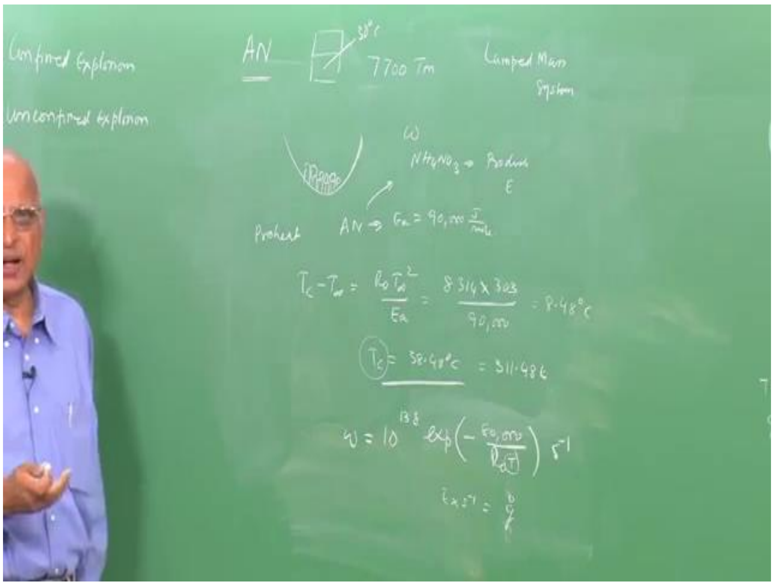

In the, of the Texas city disaster, we have ammonium nitrate and this ammonium nitrate was contained in bags, several bags of them, something like 7700 tonnes of ammonium nitrate. This happened in 1947, and what is there you have the hull of the ship in which all these bags of ammonium perchlorate were, ammonium nitrate I am sorry were all packed one against the other. You know this represented something like a well insulated system, and little bit of energy release, we said well under all conditions I can have some at, even at room temperature some element of chemical reaction takes place. There is a small amount of temperature increase taking place.

And therefore, the small amount of temperature lead to higher and higher temperatures and higher and higher energy released, and it resulted in a, in a very drastic explosion. Now, I want to find out what is the pre-heat required to cause this explosion. When we look at ammonium nitrate well, from literature I know that the activation energy is something like 90000 joules per mole.

And therefore, we will say, let on that day explosion occurred let the temperature be 30 degree centigrade. Therefore, now I know from what we studied is T c, that is the critical temperature minus the T ambient is equal to we have the value for R naught T ambient square divided by the activation energy. And therefore, I get the value of the critical temperature minus the ambient temperature as equal to 8 universal gas constant into T ambient, T ambient is 30 that is equal to 303 Kelvin divided by 90000. And this number works out to be equal to 8.48 Kelvin degree centigrade.

Therefore, the value of the critical temperature is equal to something like 30, that is equal to 38.48 degree centigrade. You find that the pre-heat temperatures are still small, the critical temperature is 38.48, which in Kelvin comes out to be equal to plus 273 is equal to the value is 311.48 Kelvin, I add 273 to it. Now, I want to find out the rate at which energy gets liberated, and we told yes I must evaluate at T c, and there are some experiments which are conducted on the rate of reaction for ammonium nitrate.

And it has been shown by Heiner in one of the combustion symposiums, that the rate of reaction of ammonium nitrate is given by 10 to the power 13.8 into exponential of minus 80000 divided by R naught T second inverse. That means, it is something in which even the concentration is not playing a role. It is just, this is the rate of a reaction. And therefore, how do we evaluate the heat release?

We find out the rate of the reaction under the critical condition that is T c that means, temperature is going to be 311.48. We evaluate so much second inverse, we already know if I have ammonium nitrate how much energy is liberated. We say well NH 4 NO 3, we have the products, we find out the heat of formation of the products minus heat of formation of the reactants. We know what is the energy, which is liberated per unit mass. Therefore, for 7700 tonnes, what is the energy which is liberated.

And this energy liberated into the rate at which it is being liberated so much per second, that is second inverse gives me the rate at which energy gets liberated in this particular reaction. And we find that the time constant of this T c is a small number compared to the, to the heat characteristic time and therefore, the explosion takes place. This is how we do any problem relating to an explosion.

Well, this is all about the theory for explosions, but mind you, we are made a drastic assumption. The assumption is we assume a lump mass system for the explosive. In the next series of classes, we will try to see what is the effect of the lump mass system, and whether we can really remove this assumption and proceed to interpret an explosion. And then, we go back and look at confined and unconfined explosions.

Well, thank you.

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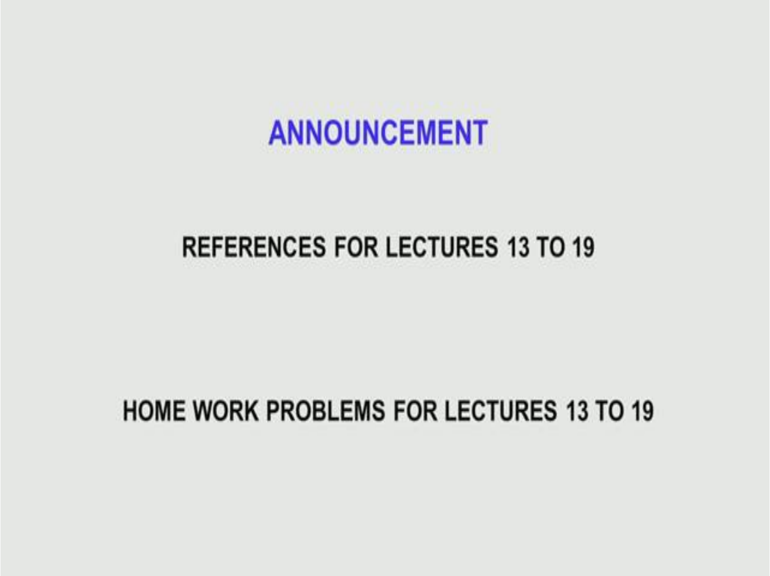

ANNOUNCEMENT

REFERENCES FOR LECTURES 13 TO 19

HOME WORK PROBLEMS FOR LECTURES 13 TO 19

An announcement please, in the lectures 13 to 19, the energy release, rate of energy release, and the thermal theory for explosions have been covered in detail. References for further reading connected with these lectures namely 13 to 19, and a set of homework problems are given in the downloads of this video course.