Rate of Energy Release: Concentration, Activation Energy, Energy Release Profile

Prof. K. Ramamurthi
Department of Materials Science & Engineering
Indian Institute of Technology, Madras

Lecture - 16
Introduction to Explosions and Explosion Safety

Good morning. In the class today we will look at the rate of energy release from explosions rather what we look at is may be de by dt that means, if the rate of energy release is e, we are looking at the rate.

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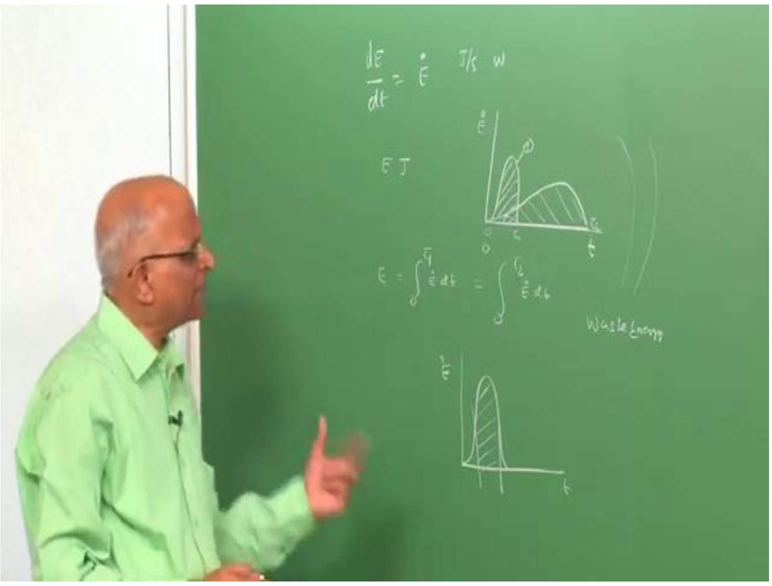

If you recall, in the last class we looked at the energy release. we just looked at the energy which is released in joules. Today we want to find out the rate at which it is getting released.

Let us qualify this, why do we want to do this? Supposing we have, let us say in this figure the x axis represents the time, the y axis represents the rate of energy release d E by d t say, in so much joules per second which is equivalent to a watt. What we say is, well the energy release of a given magnitude could either take place in a very short period, or it could take place over a prolong period.

Such that, this is the total energy which is released, that is the area under the curve, this is the energy which is released. And therefore, we say well the energy released, if the time of the first type of energy release 1 is over a period, let us say 0 to tau 1.

In the second case, it is 0 over a period to tau 2 over here. Well we say energy release is equal to 0 to tau 1 of, let us say E naught dt in the first case. This is the area under this curve, in the second case it is over a prolong duration that is, it is equal to 0 to tau 2 of E 0 into E dot into dt.

You know when the energy gets released over a longer period what happens, most much of the energy gets into heating the medium, and it is not really available to drive a blast wave. And you recall we had said that may be to drive a blast wave you need spontaneous energy release and late energy release which manifested is more as thermal energy and we call this energy which gets wasted as waste energy. Why waste energy? It is not available to drive the blast, may be from blast considerations well it is a waste.

Therefore, our aim is to find out E naught, and we are also interested that the energy is available as s spurt. Mind you let us take a look at this figure again, let us say if I have E naught in watts as a function of time, we said well the energy release could be like this. We are looking at an effective value, this is the effective duration of energy release and this is what we want, we want this time to be as short as possible.

Therefore, in today's class compared to what we did on the total energy, we take a look at this particular time, that is the characteristic time of the energy release, and the value of de by dt, this is what I will be doing today. Having said that, let us go back, let us let us take some examples so, that we can understand this and do it better. Supposing we have something like methane, you know methane was there in the in the greatest man made explosion ever when, methane diffused with air and formed an explosive, let us say when the two trains went by and created turbulence and mixing…

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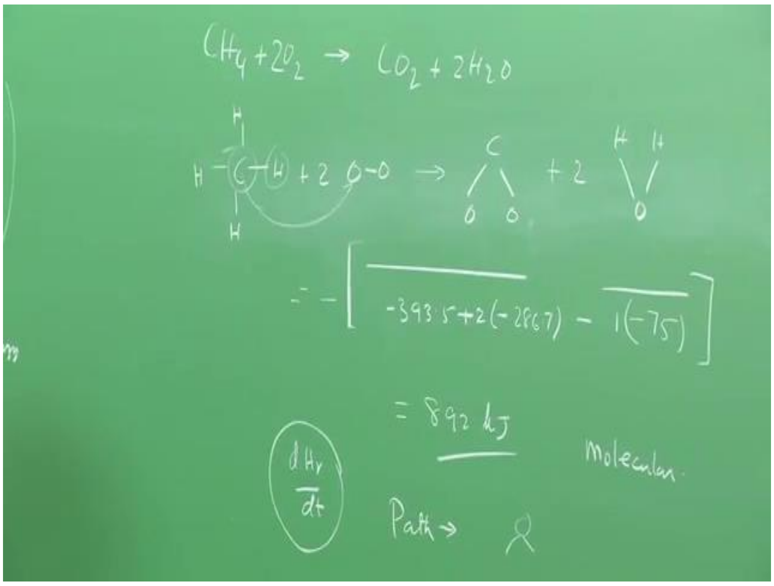

((Refer Time: 03:38)) methane, let us assume that it burns with oxygen because I am not interested in calculating energy. We know how to calculate the energy for stoichiometry compositions for fuel rich compositions, for furl lean compositions.

Let us just take the case of, may be it reacts with oxygen, and let us say I have completely burn products of combustion, in this case I have CO 2 and h 2 o. I want to balance this reaction, I find well 1 mole of oxygen produces a mole of carbon dioxide and water. Is it possible? Therefore, I say well I have 1 atom of carbon forms CO 2 here 1 mole, I have 4 of H 2, I said stoichiometry products, well I get 2 H 2 O, I have one O 2 two O here 4 that is 2O 2.

Therefore, in the reaction of methane with oxygen, I have CH 4 plus 2O 2, giving me 1 mole of CO 2 and 2 moles of water. If I, want to do this problem for energy release, well we know how to calculate the energy release. We say, well heat of reaction is equal to 1 into the, we found that if the products have a lower heat of formation compared to this well, energy is released. And therefore, I should have got started with a minus sign, I am looking for a decrease such that, the energy release is positive into 1 into heat of formation of CO 2 plus 2 into heat of formation of water.

Heat of formation of water at the standard condition, at the standard condition minus the heat of formation of the reactants, which is equal to 1, 1 into heat of formation of methane plus, I have 2 moles of oxygen therefore, 2 into heat of formation of oxygen.

Over here, this is the net heat which is given, which is available in the reaction and therefore, I know well it is it is an element, I do not need to consider it.

Let us put the heat of formation of these substances, if I say methane, the value of heat of formation of methane is minus 75. Therefore, minus 1 into 75 minus over here I have heat of formation of carbon dioxide is equal to 393.5 with a minus sign. That is 1 into minus 393.5 plus 2 into heat of formation of water is 286.7 minus 286.7, well this is the value of that. Energy released with the minus sign. And therefore I get plus 393.5 plus 2 into 286.7, minus and minus becomes plus with the minus sign.

Therefore, minus 75, and the heat of this reaction works out to be 892 kilo joules. Well this was a stoichiometric reaction, we got this heat. Now, in today's class I am not looking at the heat, which is generated, I want to find out the rate dhr by dt is what I want. Therefore, we look at this reaction again and tell what causes this reaction. Well I have something like if I, if I were to erase this, the way we calculate the heat of formation, and just put this behind below the reaction.

Well, I tell myself I have carbon, carbon methane is equal to all straight chain it is an alkaline, it is something like this. I have 2 moles of oxygen, some bonds are there. I am not really looking at double bond, triple bond, I just say two oxygen atoms are joint together in this, well I have 1 CO 2, C, O, O over here. I have 2 moles of water, well I have H over here, H over here both forming water over here.

Well, this is the reaction, and to be able to form this reaction, what is it we do? Well the structure of this particular methane, and structure of O is such that, the molecules have to individually collide with each other that means, all the molecules in one mole of methane in two moles of oxygen have to collide with each other. They have to knock out, C has to be knocked out from this, and this C has to combine with 2 of O to form CO 2. May be similarly, H has to be knocked out one H and one H have to combine with oxygen to form water. And therefore, you know if I look at the path by with reaction is going to happen then, in that case I have to consider individual molecular collisions.

But when I look at the heat of formation all what I said is, this is the final structure, this is the final structure, for the final structure this is the heat of formation. For this final structure of CO 2 this is the heat of formation, for the initial structure which is there this is the heat of formation, and I could get this.

Therefore, when I, when I talk in terms of rate of the chemical reaction, I cannot just say well the final structure is this therefore, I work with moles and multiply moles by the heat of formation in energy or joules per kilo mole, or joules per kilo joules per mole and calculate this, this is not possible. I need to know the path, I need to be able to find out how the transition takes place, to be able to find out with time how it changes.

Therefore, it becomes a little more complex therefore, we tell ourselves well, I have to consider the molecular collisions and why do you say molecular collisions? Well, I have methane here, I have 1 mole of methane 1 mole of methane consists ambient conditions we said it is at standard conditions, we are doing all the problems at standard conditions.

And what is going to happen, at standard conditions. I react this with this, and therefore, what is going to happen, 1 mole is contain going to contain, we said avogadro's number 6.023 into 10 to the power 23 molecules, this is going to contain 2 into 6.023 into 10 to the power 23 molecules. Each of the molecule must collide with each other and knock it out that means, the collisions must be energetic. It must also have a way of impacting such that, I am able to knock out the molecule that means, the geometry of collisions is important.

And I must consider all these aspects when I take a look at the rate of a reaction. You know it I cannot just say, well the final structure is this, and from the final structure and the initial structure I calculate the rate of energy release. Therefore, what is it? Let me go through this example again because we need to define something else to be able to define the rate of a reaction. Therefore, let me consider this example.

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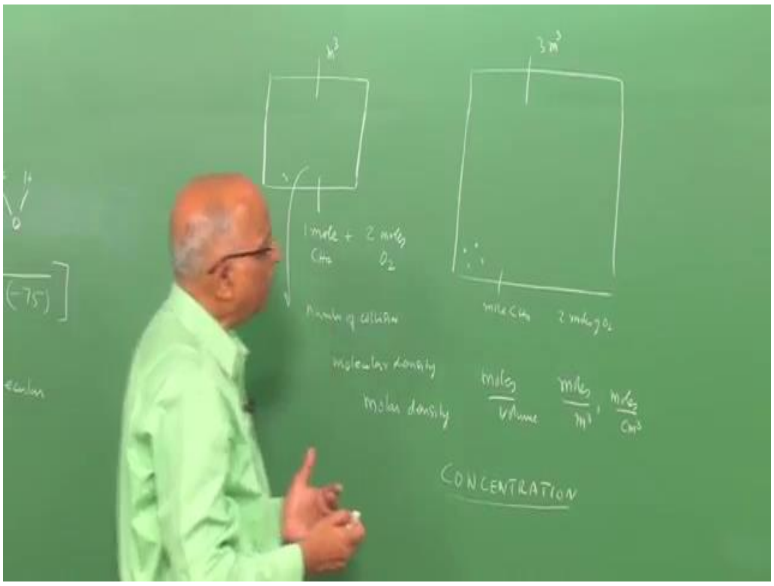

Let me consider a vessel, and in this vessel let us say I have a tank like this, in this vessel I have 1 mole of methane over here plus I have methane over here, plus I have 2 moles of oxygen over here, and now I want to react it. Now I tell, well this volume could be 1 meter cube. I also think, I do a thought experiment. I tell myself, well I could have a much larger volume, let us say instead of having 1 meter cube, I have 3 meter cube of volume. I put precisely the same amount here namely 1 mole of methane and 2 moles of oxygen.

Now, in this in the second case, what is going to happen? The inter atomic distance between the molecules is going to be larger because the same number of moles are there. I have 6.023 into 3 times the total number of moles here, I have the same number of moles here. Whereas, since the volume is small the molecules are near to each other, and mind you the pressure and temperature here is identical to the pressure and temperature here.

Since, the individual molecules are near to each other, they are more likely to undergo collisions. And therefore, in the case, in which I have a smaller volume may be the number of collisions is going to be higher, and we told collisions are required in order. Let us say collisions are required in order to strip the individual atoms and also combine with some other atoms.

And therefore, the number of collisions, when I have a smaller volume is higher therefore, maybe I have to look at something like a molecular density. That means, the number of molecules per unit volume, but since I talk of moles as 6.023 into 10 to the power 23, I can also talk in terms of molar density. Instead of talking in terms of individual molecules, I say well, for chemical reactions since I am interested in collisions, it is important that I talk in terms of number of moles per unit volume. And this could be represented as moles per meter cube, or if it is less I can represent it as moles per CC or centimeter cube. And that means, moles per unit volume, And this moles per unit volume is given name as concentration.

Therefore, while when we evaluate the energy release from a chemical reaction, we talk only in terms of moles, we talk in terms of moles of reactants, their heat of formation in the products, in the reactants. When we talk of rate of chemical reaction, we have to talk in terms of concentration, of the reactants concentration, of the products if you want to go from products to this. But if you are interested in some reactants going to products, well the concentration of reactants are necessary.

Therefore, we tell ourselves well compared to moles, we will talk in terms of concentration. Therefore, we are also telling well based on simple reasoning, we told for a chemical reaction to take place therefore, let us say a chemical reaction takes place.

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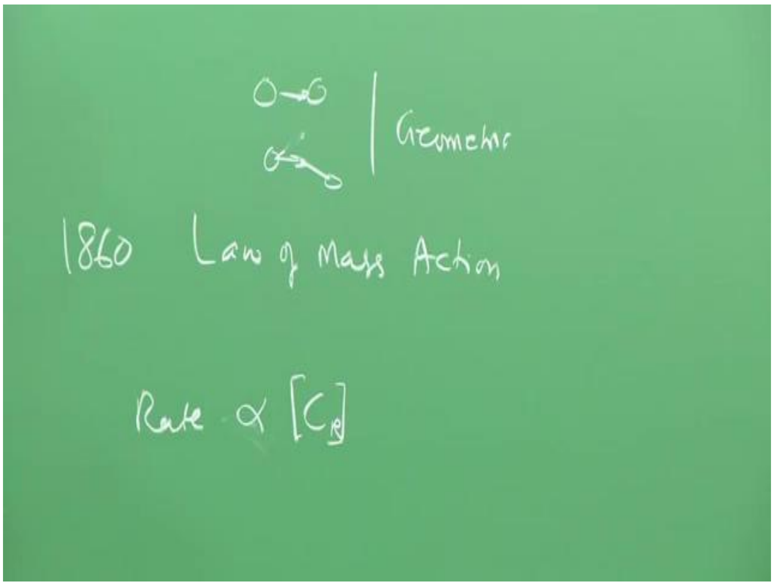

We again keep the same reaction in mind. We tell ourselves, well the chemical reaction will take place depending, if I have more number of collisions that means, if CH 4 hits against an oxygen more number of times, it is more likely to collide that is collisions, number of collisions are important.

It is also important to have the energy of collisions. If the energetics of collisions is much higher, well it can knock out the atom and may be recombine it together, energy of collisions is important. Well, you know, if I have molecules which are just hitting against each other, or may be hitting at an angle, may be one comes like this, the other comes at an angle, and they hit at an angle. May be the geometry of hitting is important because that is how what decides, how many of these molecules get out, this is known as the geometric factor.

Therefore, we tell well, based on simple reasoning we say collisions energy of collisions, the geometry of collisions are important. And therefore, you know, this was something which was systematically found out by experiments, and as early as 1860 we had a law, which was propounded by the chemist, which is known as law of mass action. The law of mass action told, tells, that the rate of chemical reaction is proportional to the active concentration of the reactants.

In other words, whenever a chemical reaction takes place, the rate of the chemical reaction goes directly as the active concentration of the reactants, rather if we tell well, my rate of a reaction is so much, it is proportional to the active concentration, I denote concentration by C. It is proportional to the concentration to the reactants. How do I translate it into something which is workable? Let us go back and say yes I am interested in a reaction, and let us put down one or two simple reactions and see whether, we can determine how to get the energy release.

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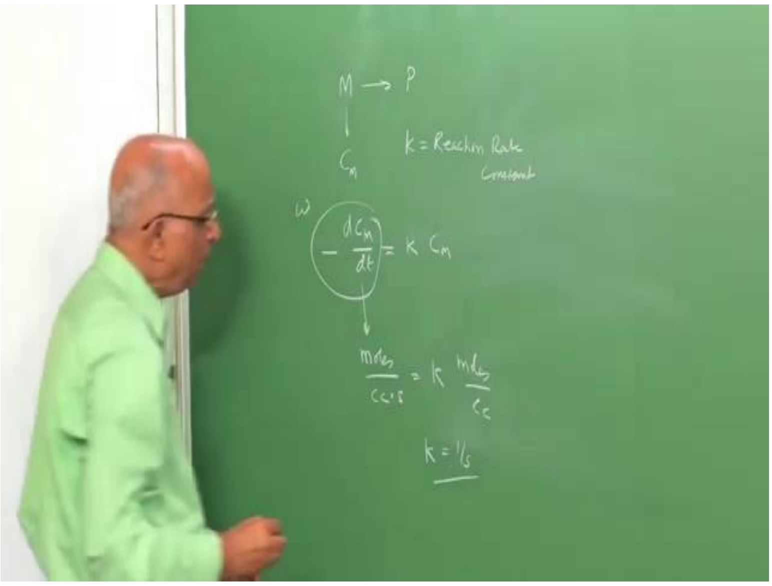

Well supposing I have a reaction in which let us say M, M is some substance gets converted into products P, I say concentration of M, I denote it by C m and then, I say the rate of a reaction. Well we said for reactions I must consider concentration and not moles therefore, I say I consider dC m by dt.

In this reaction, M gets consume, P gets formed therefore, the rate of a reaction is minus dC m by dt because it is gradually getting consumed. And as per the law of mass action which is based on experimental findings, it says that it is equal to a constant into the concentration of the mass. Well, this is what it says, but the law of mass action also says that, the rate of a reaction is proportional that means, I have a constant here. To the active value of the concentration here active because in some liquids and in some reactions well, we have to consider the effective value we will consider the concentration as it is.

Therefore, we say well dC m by dt is the rate of a reaction, I can call this as omega, which is the rate of a reaction, and what is the rate of a reaction? Let us put now the units down I have moles concentration, let us say CC is the volume into time moles per CC second is equal to the constant into the moles per CC. And therefore, for this reaction the unit of the k comes out to be 1 over second. And k is known as the reaction rate constant.

You know if k is 1 over second, let us see you know see, but whenever we are been talking of reactions. We say between a fuel and a oxidizer I form products and therefore, if I were to write an equation for fuel and products, what is it I get? Do I get exactly the same value for k or do I get different units for k?

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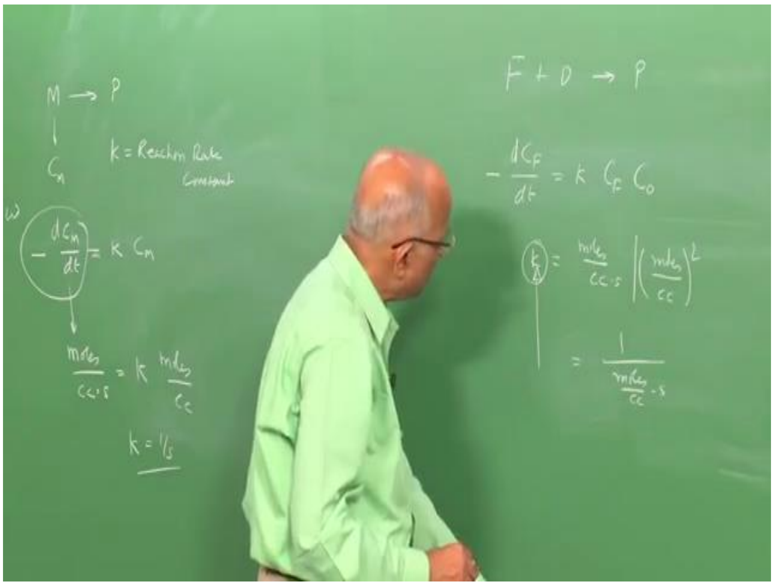

I need to be a little cautious here and therefore, I say well, previously I have been considering fuel plus oxygen or oxidizer, gives me products. And now I am interested in the rate at which fuel is getting depleted well, the rate of a reaction is concentration of fuel divided by dt, it is minus. Well in this case it is equal to k into concentration of fuel, well the reactants are concentration of fuel and oxygen, I consider concentration of the oxygen.

Therefore, the unit of k in this case is going to be k has units of well, in this case I have moles per CC, second divided by moles per CC square because k bring it to the denominator here. And the unit of k in this cases becomes 1 over moles per CC into second over here. Therefore, depending on the type of reaction well, the unit of the reaction rate constant changes. If I have 3, if I have 3 of them well, it is going to be 1 over moles per CC square into second.

And therefore, we call these things as order of reaction, we say first order reaction and second order reaction, if three are involved, fuel plus oxygen plus something else I say third order reaction. But we will not get into the details of these reactions, but we note well the reaction rate constant has different units depending on the type of reactants and the number of reactants, what we have. Having said that well, can we guess something more you know, what is this k? We told well, the reaction rate constant tells me how fast or how slow a reaction progresses, how it is related to the concentration.

We also know if I have more energetic material or if I have more number of collisions well, this could change. And therefore, you know people have been looking on how to model k or the reaction rate constant. And therefore, let us try to build up a case of how what should be the parametric formation for k? Let us say for the present…

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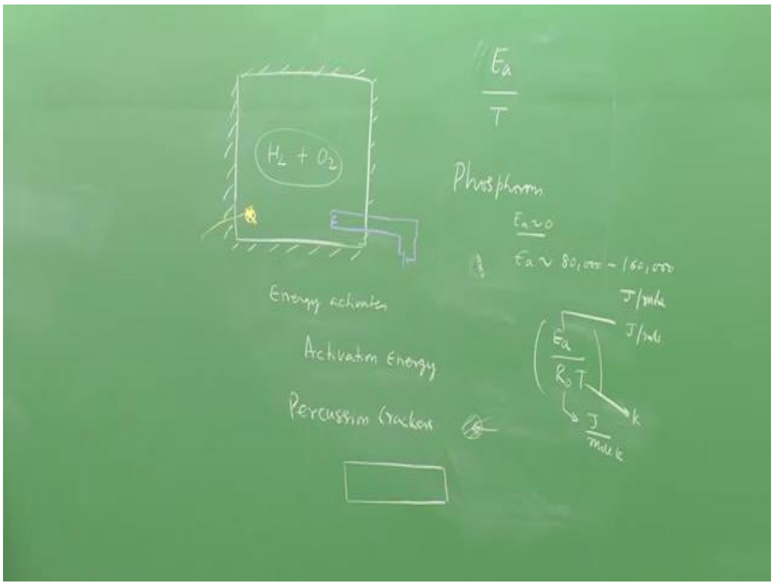

Well, I have a given volume in this volume which is, let us say a tank or something, I have certain amount of oxygen, let us say I have 1 mole of oxygen, I have some moles of some moles of hydrogen, some moles of oxygen, I have this mixture of gases in a particular tank. All of you know if I have this tank, which is sort of insulated, I do not heat it or I i do not do anything with it. I can allow this hydrogen and oxygen. I could be, I could store it for years together nothing is going to happen, mind you hydrogen is a fuel, oxygen is the oxidizer well, these two put together form the explosive.

And therefore, this explosive gas I keep here, I can store it for years together reaction is not going to take place. In order that a reaction will take place in this particular substance, all what I have to do. I need either I deposit an electrical spark like in an IC engine well, I have petrol mixture in which I, in my cylinder I put an electrical spark over here.

And if I put an electrical spark that means, I release some amount of energy over here, I can activate the chemical reaction and well it will go with a bang it will explode. Or rather instead of putting a spark, I could also put some heat over here. Maybe I put some electrical resistance wire, I connect it to a battery over here and then, if I heat this wire well I started that means I deposit some energy.

In other words, we are telling is an explosive by itself remains fairly cool, it does not react by itself, I need something to activate it. That means, I have to provide some energy, which activates the reaction or which starts the chemical reaction. And the energy required to start progressing with the reaction is what we call as activation energy.

Let us take another example, you know when we were children what we used to do? You know in the market in the earlier days, we used to get some fire crackers known as percussion crackers. You know these percussion crackers used to be small hand held things, and what we used to do when we want to burst it, we used to hit it against the wall and it used to go with a bang.

In other words, for the percussion cracker it has some particular explosion composition. If I subject it to an impact well, it just blows up and this is what that means, I supply some blow or say I supply some energy, and that is the activation energy. You know, but the percussion cracker could be stored in the house for long only if it is hit against something, and I transfer some energy to it well, it blows off.

Similarly, I can have let us say dynamite or may be TNT example which is said in the form of rod, I could store it in a store house for years together, nothing is going to happen, only thing may be some element of reactions take place, but it is not going to start a chemical reaction and this to explode. Therefore we say to be able to start the reaction even in a powerful explosives, or in some of these crackers, or any mixtures, we need to supply some activation energy.

Therefore we say well, to start a chemical reaction I need activation energy, which I denote by E a. We also know if the initial temperature is higher, well it is little easier. Therefore, you know the ratio of activation energy divided by temperature might be something because you know, if the activation energy is more well, I am talking about one scenario.

If the temperature is more, well it is much easier to start a reaction. Well in some cases, like say phosphorus. You know, phosphorus, you know it is mind and kept outside, and we will see you know by the side of the railing we see some phosphorus, it is available as powder and you know, the moment it come in air it begins to glow and react. That means, P 2 O 5 is formed that means, it reacts with ambient immediately.

In this case well, the activation energy is almost 0 very small. But most of the explosive what we consider, in our, in the actual sense like we say hydrogen, oxygen we say different types of substances, most of the explosives which we deal with, the activation energies are quite high, typically of the order of 80000 to something like 160000 joules per mole. I will come back to the unit again, we tell ourselves well, as temperature increases the reaction can go faster, we will have to take a look at it.

And therefore, we find that well I can have a unit like activation energy divided by the universal gas constant R naught into temperature. If the activation energy, if the unit of R naught is joules per mole Kelvin, the temperature as units of Kelvin. If the activation energy is also represented as joules per mole well, this becomes a non-dimensional term, and we use the non-dimensional term to be able to quantify the reaction rate constant k.

That means, we tell ourselves that k has different units depending on the order of reaction, whatever be the units well, I can relate it to something like E a by R naught T and the equation which does this is known as Arrhenius rate equation. Let us put that down, we tell well, I talk in terms of Arrhenius rate equation…

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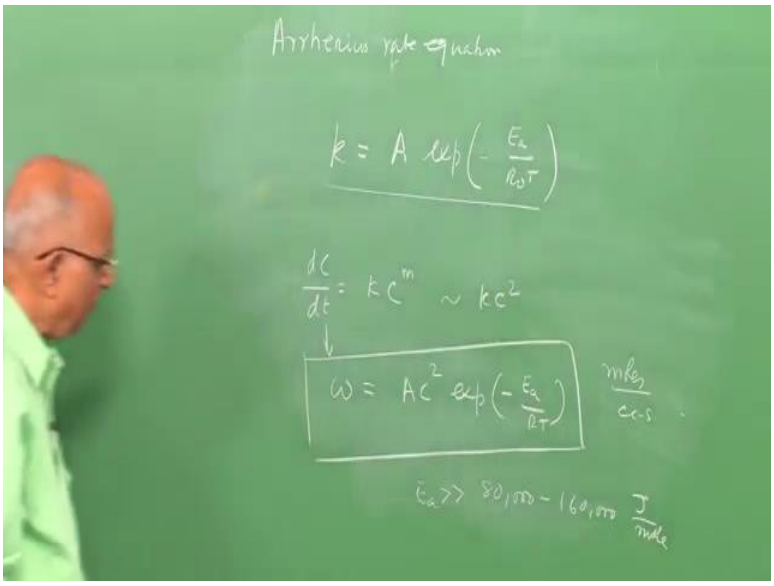

Arrhenius rate equation

$$k = A \exp\left(-\frac{E_a}{R_0 T}\right)$$

$$\frac{dc}{dt} = kC^m \sim kc^2$$

$$\boxed{\omega = AC^2 \exp\left(-\frac{E_a}{RT}\right)} \quad \frac{\text{moles}}{\text{cc-s}}$$

$$E_a >> 80{,}000 - 160{,}000 \ \frac{J}{\text{mole}}$$

Arrhenius, this k is equal to a constant into exponential of minus E a by R naught into T. As temperature increases the rate constant increases, and we have this factor A, which depends on the order of a reaction, it also depends on the geometry by which the angle at which the collisions takes place.

Therefore, it is also known as a steric factor, it also tells you on the, it depends on the pressure to a large extent and therefore, we say well k can be represented by this. And if we say well k is represented by this form, the rate at which a reaction takes place let us say in general dc by dt, I we already know. By the law of mass action, I tell it is equal to k may be any reactor c to the power m.

Well, I am just considering some reactant which is being formed, I am not taking minus dc by dt, I just said the reaction rate is given by c to the power m or where m is the number of constants which are reacting together. Maybe it is an m th order reaction a plus b plus so on up to m. In general most of the reactions are second order it will be k\c to the power square. I have c plus c giving you products, and therefore, I can write the value of dc by dt, which I can say as so much moles per CC second I denoted by omega is equal to, I write a that is k is equal to ac to the power square into exponential of minus E a by RT.

Well, this becomes the expression for the rate of a reaction so much moles per CC into second. Well, now we have arrived through arguments using the law of mass action and the arrhenius rate equation, saying that the rate of the reaction in moles per CC second is given by a into concentration square into exponential. If it is a simple reaction like a single substance like a first order reaction in which m goes to P, it could be ac into exponential.

If it is third order, fourth order, it could be to the power cube, bu, in genera most of the reactions that we encounter are second order like ac square Having said that, you know I want to explicitly determine, what is the role of temperature in this? Let us do one exercise, let us calculate.

The value of the reaction rate at two different temperatures and see what is the role of temperature, but mind you, we are still telling for most of the explosives which we encounter, the value of E a is a large number, and this number we said is between let us say typically between 80000 to, let us say 80000 to something like 160000. The value is so much joules per mole is the value of activation energy. We will, we will, we will get some feel for it, but you know I have not told, why some activation energy is required?

You know we looked at the example, we said well I need to activate something, let us try to put it graphically down.

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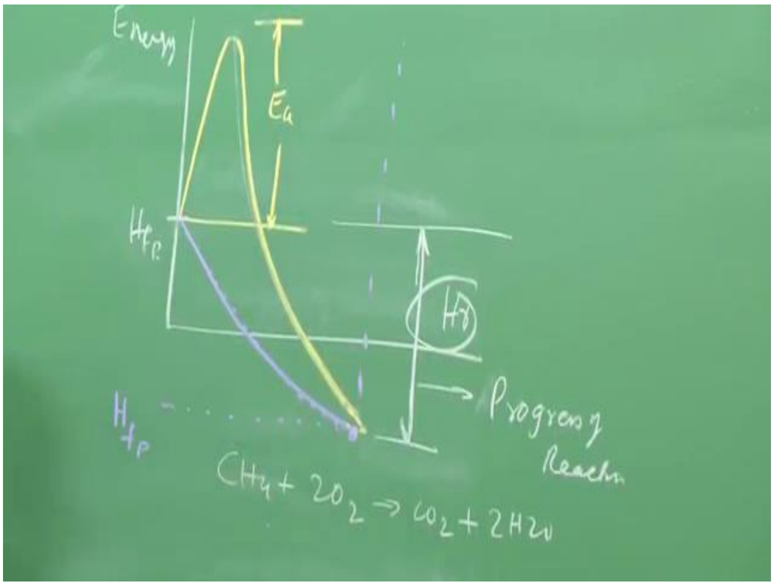

Let us say we work back, we go back to the example of methane, what we had? Let us say we have methane CH 4 plus oxygen 2O 2 giving me CO 2 plus 2H 2 O.

Well, can I, can I put down how the activation energy is there? Well, initially I have these substances over here, the value of the heat of formation of CH 4 and 2O 2 is somewhere over here, heat of formation of the reactants. Well, some energy gets liberated we worked out the energy which gets liberated, after the reaction let us say this is the time. That is the, let us say time that means, positive time that means this coordinate is progress of reaction.

Well, this is the energy of the reaction, energy we say, initial energy is the value of the reactants what we have total heat of formation of the reactants. Once the energy is, once the chemical reaction is over well, the energy could be over here, we say energy of the products heat of formation of the products is over here. And what happens well from reaction it comes to this that, means this is the way the reaction progresses, this is what we think.

But we told ourselves well, I can store this indefinitely, I do not, unless I give some energy does not get started. Therefore, if this reaction has to take place well, I have to supply some activation energy some value of E a, which starts the reaction and then, it comes over here and therefore, this is the value of activation energy.

That means, I need to pump in some energy to start the reaction, once the reactions takes, once the reaction gets started it comes to the products, it is comes backs over here, I get the thing. Therefore, the heat liberated in this particular reaction if I were to put it on this plot, I am going to get the heat liberated is equal to the heat of formation of the products minus heat of reaction with a negative sign. Well this is the heat of the reaction over here, this is the value of the heat of reaction. But if I have the products and I want to form the reactants well, I have to have a activation energy of this value which is equal to E a plus Hr.

Such that, it can come to products over here, which means the reverse reaction is very difficult and I always get the forward reactions since the activation energy is smaller. In some cases, well the magnitude of the reverse reaction can have the values of activation energy which are comparable. But most of the reactions have forward activation energies to be much smaller than the reverse values of the activation energies.

Well, this is the way we look at the progress of a reaction, this is the expression for the rate of a reaction. Let us quickly find out what is the effect of temperature on the rate of a reaction? Let us quickly do that and then, we go back and try to find out. You know our mission let us not forget, our mission is to be able to calculate what is the rate of energy release in a reaction? We have not still not come to that, we are still talking of rate of a reaction.

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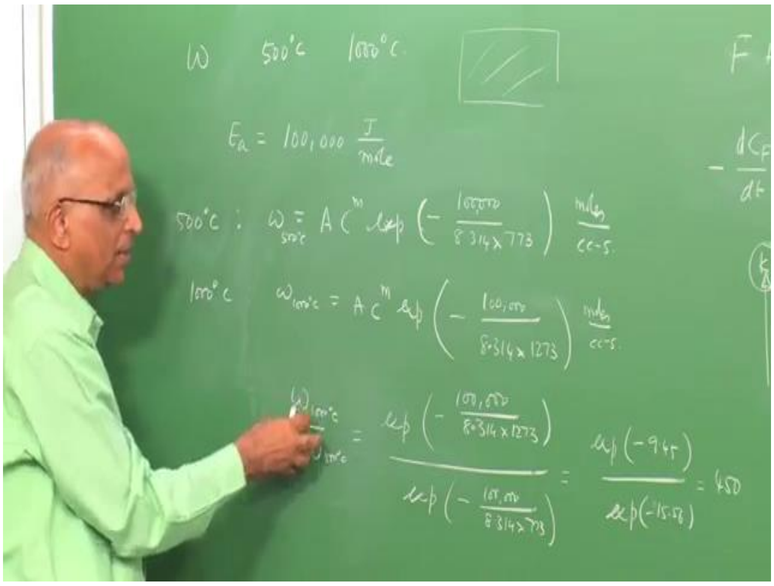

Let u say I am interested in omega at temperature of let us say, 500 degree centigrade, and how it changes when the temperature is let us say, 1000 degree centigrade. Excuse me, I have the activation energy of this reaction well, we say activation energy is of the order of 100000, which is of the order, which we said is so much joules per mole.

Therefore, at 500 degree centigrade the rate of a reaction omega is equal to as per what we wrote down is equal to A into C to the power let us say, m th order m over here into exponential of minus Ea that is activation energy 100000 divided by R naught. The value of universal gas constant is 8.314 joules per mole Kelvin into 500 plus 273 in Kelvin is equal to 773 Kelvin, this is the value so much we have moles per CC second.

And if I have the temperature at 1000 degree centigrade well I similarly, have may be omega, this is at 500, omega at 1000 degree centigrade, 500 degree centigrade is equal to AC m into exponential, I just do this same thing again minus the activation energy is 100000 divided by 8.314 into 1000 plus 273 Kelvin, 1273 Kelvin so much moles per CC second.

If I were to find the ratios of this may be, reaction rate constant at 1000 degree centigrade divided by the reaction rate constant at 500 degree centigrade, what is the value I get? I get exponential of this divided by exponential of this because I presume that the concentrations of the reactants are still the same to begin with.

And therefore, I say that the rate of this reaction if I were to simplify it, it comes to be equal to exponential of minus 1000 that is, 100000 divided by 8.314 joules per mole Kelvin into 1273 divided by exponential of minus activation energy 100000 into 8.314 into 773. And this gives me a number equal to exponential of minus 9.45 divided by exponential of minus 15.56, which gives some value of something like 450. That means we have doubled the temperature, the temperature has increased twice, but the reaction rate has increased something like almost 2 to 3 orders of magnitude into 450 times.

Therefore, the influence of temperature on a reaction rate is very fast and this is why we are, we are always worried. You know if you go back to explosion involving ammonium nitrate in the hull of a ship in the Texas city well, you have ammonium nitrate. Initially, it was stored well, the temperature slightly increased because of some incipient reactions. And as temperature increase, well the reaction rate goes up, and when reaction rate goes up. Well, the temperature further increases, and if the temperature further increases, well the rate again goes up and it sort of explosive, you know very rapidly it goes up.

And therefore, all the reactions which we consider will have such a trend namely for changes in temperature, small changes in temperature I have, or small increase in temperature, the reaction rate goes up enormously. Well, with this background of may be the temperature effect on reaction using the Arrhenius law, using the concept of activation energy, some energy is required to start a reaction. Let us go back and try to find out what will be the type, can I get a value for energy release in a reaction and if so, how should it behave? Well, we come to this part now, we tell ourselves well, I have calculated already omega.

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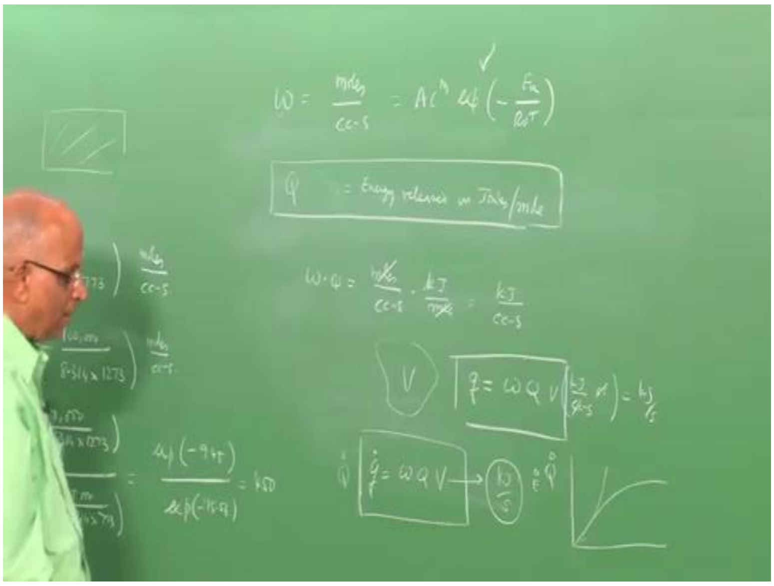

I know how to determine it is equal to so much moles per CC second, I know, I know this. But you know we must also remember I have already calculated Hr, which we can say is equal to Q, which is equal to the energy released in joules in a reaction.

And in a reaction how did we calculate? We have some moles of the reactant giving you product Hr was for the total number of moles. I tell myself well. instead of writing Hr, I write Q as the energy released per mole of the reactants. Therefore, I say joules per mole is the energy which is released. I know how to calculate this, I have done it, I have done, I know I have done some several model problems, I know how to calculate this.

Therefore, now if I take this particular value and say well omega is moles per CC second, I multiply by Q, what I get omega into Q gives me moles per CC second into the energy release. Normally, we denote the energy released in kilo joules per mole and mole gets cancelled. And omega, the product omega Q tells me, how much energy is released per unit volume per second?

Or rather if I can multiply this by the volume that means, I have a volume of mixture which is V and I know well, the rate of this that which reacts, I know the value of omega, and we said omega is equal to AC to the power m exponential of minus activation energy divided by R naught T over here, I know this.

Well, I can calculate the energy released in this volume, I know per unit volume. And therefore, I say well the energy release per unit volume is omega Q and therefore, the total energy released, energy release rate is equal to omega Q into volume, which I call as kj cc second multiplied by volume in cc, well this cancels. I have kilo joules per second and this is how we calculate the rate of energy release.

We tell ourselves well q is equal to therefore, equal to omega into the energy release in the reaction which we calculated per mole based on heat of formation into omega. And therefore, to determine the rate of energy release, since we are talking rate of energy release. Let us put a dot over here, we are talking of dQ by dt or if you want you can still use the Q provided, you do not confuse, we can still say Q dot or Q dot over here is equal to omega QV, which is the rate at which energy is released in a particular reaction.

Now, I want to be able to relate this heat release with the parameters over here therefore, let us, let us quickly do that, but now I am in business, I know, I now know well, I know how to calculate, the rate of energy release in kilo joules per second and this is what we set out to do. Let us go further, let us try to see whether I can modulate in some way, I can find out explicitly whether the shape of the curve, we said Q dot or you remember we started with E dot, whether it should be like this, whether it will be like this.

How should the shape change? Let us try to find out how the shape of the heat release will look like, may be as a function of time we would like to find it out and therefore, let us let, us let us proceed further. Therefore, all we have to do is substitute whatever we have been doing one into the other and therefore, we say well the heat release in a, in a heat release rate now.

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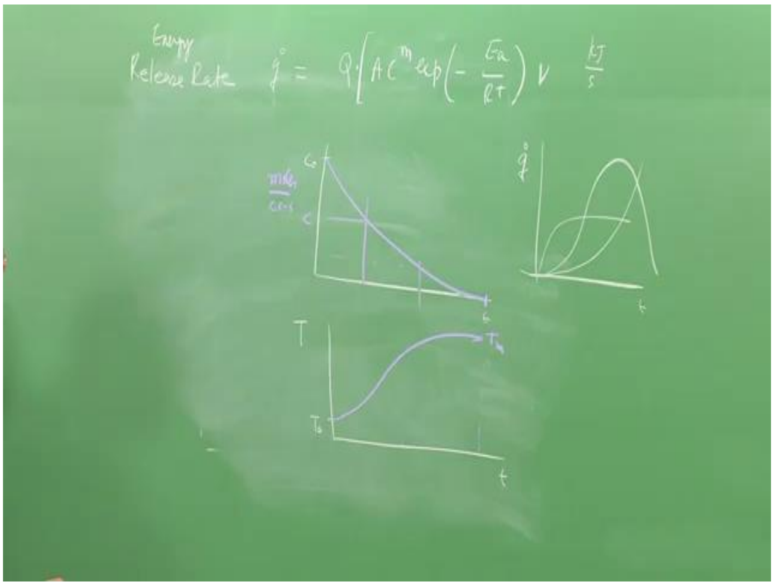

Energy release rate, which we say is Q dot is equal to Q into…We say that the value what we say is omega, and what is omega is equal to AC to the power m exponential of minus Ea by RT into volume so much joules or kilo joules per second is the rate.

Now, we know if I look at this particular expression, I can also tell myself yes the rate of heat release depends on the concentration, and how the concentration will change? Supposing I have a chemical reaction may be the reactant initially, let us say fuel has an initial concentration Co and what happens the fuel gets consumed over the time of the reaction.

And ultimately when the reaction gets completed, the concentration of fuel that is so much moles per CC to begin with, it has a value high value, it is, it has not reacted and may be progresses and at large time it becomes 0, this is when the chemical reaction gets over. This is the type of variation of let us say C at any time therefore, we have C at any time, this is the value where we see at a later time comes to 0.

And therefore, we find well you know C naught, C naught that is to begin with the concentration is C naught, it becomes 0, this is the way the concentration of the fuel will keep changing. How should we think the temperature could change? We will we need to get some idea on this. Well, if this is the say the concentration, the temperature of the products in the reaction will also change with respect to time. Initially the temperature is

T naught, the ambient temperature, the chemical reactions starts, if the chemical reaction start well, the temperature begins to build up.

May be when the chemical reaction gets over, the temperature reaches the maximum value, let us say Tm to begin with, it is T 0 and then, the chemical reaction will go like this and reach a maximum. Perhaps this is the way it should proceed, according to what we think because initially something gets started and it reaches the maximum value over here. Therefore, is it possible for this particular reaction, can I say what must be the shape of the curve?

That means I am interested in finding out how should the shape of Q dot, that is the rate of energy release which I say as Q dot. How should it change with respect to time, is it going to be something like this? Is it going to be something like this? Is it going to be something like this? You know this is what I am interested in finding out.

Therefore, let us try to solve this equation to be able to give the shape. Yes we recognize the concentration of the reactants keep decreasing, the temperature of the products keep increasing, this is what the temperature of the products is. Therefore, let us try to see whether I can solve that equation, let us quickly do that. You know, let us make the problem a little simpler.

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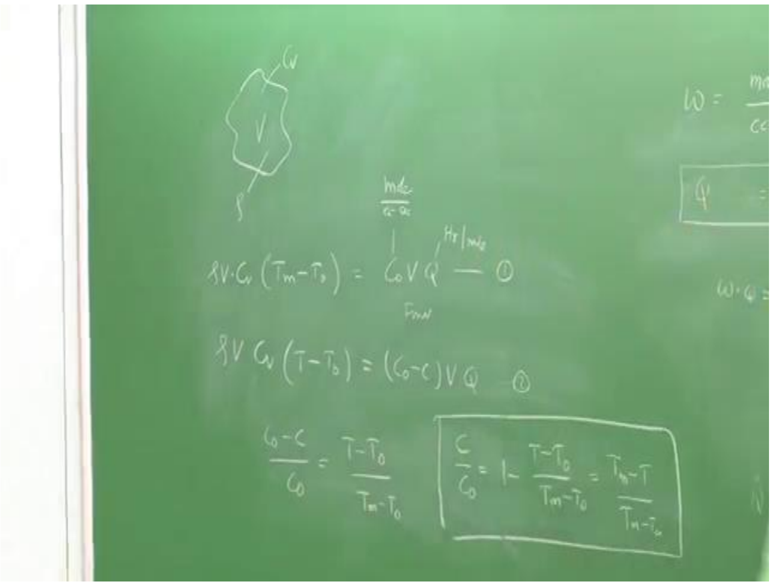

We say, well I have a certain volume of the substance over here, that is the substance which is reacting, let it be of density rho therefore, rho V is the mass over here. Let the specific heat since the constant volume which reacts and explodes therefore, the specific heat is Cv. Therefore, we tell the mass is equal to rho V into the specific heat and what happens, what is the maximum temperature reached? We say it could be Tm, the initial temperature is T 0 and this is the total energy what has, what is available to you, and what is the total energy?

If the concentration initially is C 0 per unit volume, I have volume here, this is the total number of moles of the total number of moles react and per mole of reactant. If I from the heat liberated is Q joules well, I can say rho V Cv into Tm minus T0 is equal to C 0 V into Q, as long as may be as concentration changes. I have heat which is getting this is the total heat of the reaction, which is equal to Hr per mole over here. If in the same reaction may be this is the final when all the energy is released because finally, I get the value of Tm, let us take a look at this graph again.

Finally, I have a temperature. Finally, all the concentration is over at the value of T, C 0 becomes 0 therefore, C 0 minus 0 is C 0 at which I have the maximum temperature. If I am interested at some intermediate value at which, let us the concentration is C over here at some time T well, the change in concentration is from C 0 to C. Therefore, the heat liberated is going to be C 0 minus C into the volume which is the change in moles into Q, that is the heat liberated, and at this particular time let that temperature be T.

Therefore, I can write the second equation as well, I have rho V into Cv into I get now, my temperature is T minus T naught is equal to, I have C 0 minus C is the change in concentration into volume change, the number of moles which have reacted, and Q is the amount of heat generated per mole which reacts. And therefore, this becomes my equation two for inter an intermediate stage. And I keep telling this because to be able to calculate the need, calculate the rate we need the path.

Therefore, I am looking at some intermediate value I take this is my initial value and if I take the ratio of these two that means, I divide equation 2 by equation 1. What is it I get? I get C 0 minus C divided by C 0 is equal to I come and take a look at this I say, I get T minus T 0 divided by Tm minus T 0.

Or rather if I were to simplify this, I get the value of C by C 0 is equal to I have C by C 0, I take on the right hand side, this is what I am writing is equal to 1 minus. The value of T minus T 0 divided by Tm minus T 0, and this is equal to the value Tm minus T 0 minus T plus T 0, T 0 and T 0 gets cancelled, and it gives me the value of Tm minus T divided by Tm minus T 0, this is the value of C by C 0.

Therefore, in the particular reaction in which I had concentration at any particular time, I can go and substitute C is equal to the initial concentration into Tm minus T divided by Tm minus T 0, and let us do this on the, for the equation which we have already written over here. In other words

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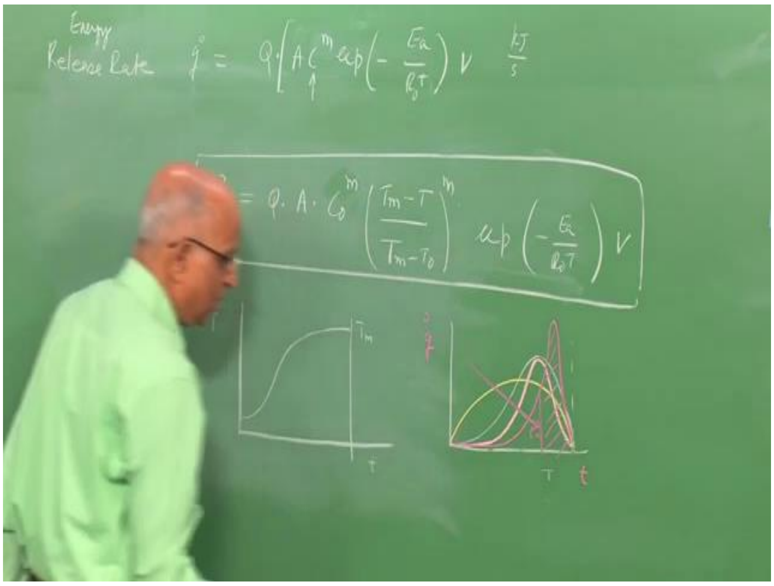

I am substituting the value of C by the value which we just obtained, Q is equal to Q into A into I get now C 0 that is the initial concentration to the value m. I still assume that I have an m th order reaction that means, number of things are reacting over here into Tm minus T divided by Tm minus T 0 to the power m, into I get exponential of minus Ea by… Mind you it should have been R0 over here universal gas constant T into V over here, and this becomes my rate of energy released.

Now, let us just take a look at how to represent this equation well, we find that when the reaction is over and the temperature is Tm well, I do not get any perceptible heat release over here because Tm minus T is 0, the heat release is 0, and how should this relation look like? Well, let us first plot the value of T versus time over here that means, we said well the reaction will get started and go like this and get the, when the reaction is over I get the value of Tm

Let us therefore, plot this as a function of T before I can put it over here. If I plot it as s function of T, what is it I get? When the value I have Tm, it comes to 0, initially when T is small, the reaction rate is 0 and therefore, the reaction goes like this and comes back and comes over here. If I have an activation energy which is negligibly small, like we said phosphorus immediately reacts, in which case Ea is very small. And if Ea is very small well, this drops off and the rate of a reaction is going to be something like this it will come over here and come over here.

If the activation energy now becomes a larger number that means, I am talking of 50000, 60000 well, the curve shifts, this becomes dominant, the rate of energy release goes like this and comes like this. If my activation energy is still higher, what is going to happen? Well Ea is still higher may be this pulls down initially quite a bit, but when temperature increases ,it goes up it comes like this over here.

Therefore, we find that as the activation energy increases that means, I am talking of temperature, temperature is proportional to time, temperature versus the rate of heat release Q. It seems to have a signature that has activation energy increases, I start slowly and all of a sudden I begin to have a spurt in the reaction that means, my energy release period is taking place over here, and this is the duration of energy release.

The initial period, I do not have much energy release, but if the activation energy is small, initially itself I start getting some energy release and the type of energy release. Therefore, what we are saying now is depends on factors like this, we tell ourselves for most of the explosives in which the activation energy is large.

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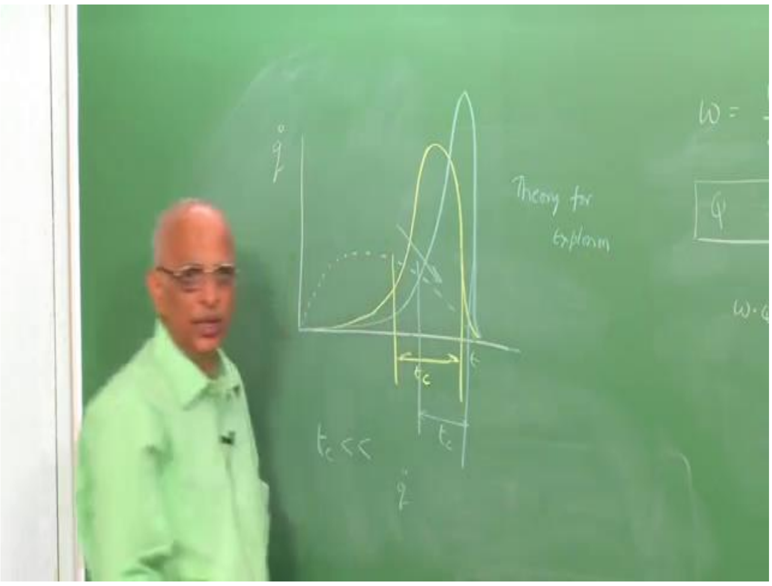

The rate of energy release with respect to time Q dot, as function of time the reaction starts off rather slowly takes some time to build up, and you have a peak and it comes down over here. If I have further increase in activation energy well, it comes over here peaks over here, and comes down over here.

Therefore, but if the activation energy is small, what is going to happen? Well, the reaction goes like this. Now, if I now put, what is the energy effective duration of energy release over here? The effective duration of energy release is somewhere over here to here, and this is the characteristic time of the chemical reaction.

If I look when the activation energy is still higher, we say this is for increasing values of activation energy well, the duration is now even smaller that means, this is the value of the characteristic time of chemical reaction. And therefore, we find that, as the activation energy increases, the spurt in the rate of reaction goes up and what we get is, we say well, the time of the chemical reaction gets reduced and the rate of chemical reaction goes up.

Therefore, we now have a feel for the rate at which a chemical reaction proceeds with respect to time that means, the effective energy duration is over here rather than from here to here. Because in the initial phase it is quite slow and with this in mind, we will now take a look, we have now done their energy release we know how much it is, we have a feeling for the rate of energy release, we will put both the things together and develop theory. For let us say explosion or a thermal theory for explosion. And this is what I will do in the next class.

Well, thank you then.