Chemical Reaction Engineering 1 (Homogeneous Reactors)
Professor R. Krishnaiah
Department of Chemical Engineering
Indian Institute of Technology Madras
Lecture No 18
Basics of Kinetics

Yeah, so the other, the design expressions what we have discussed, design expressions for ideal reactors

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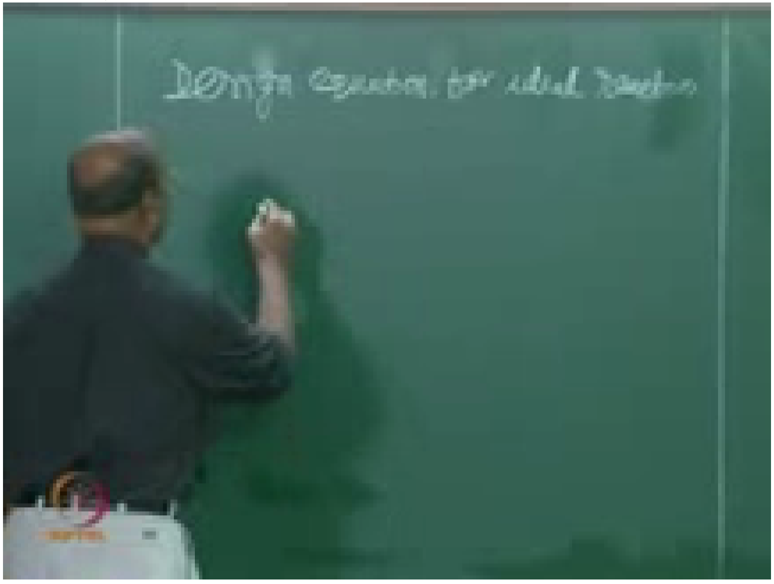

Ok, so for batch you have t by C A naught equal to zero to X A d X A by minus r A.

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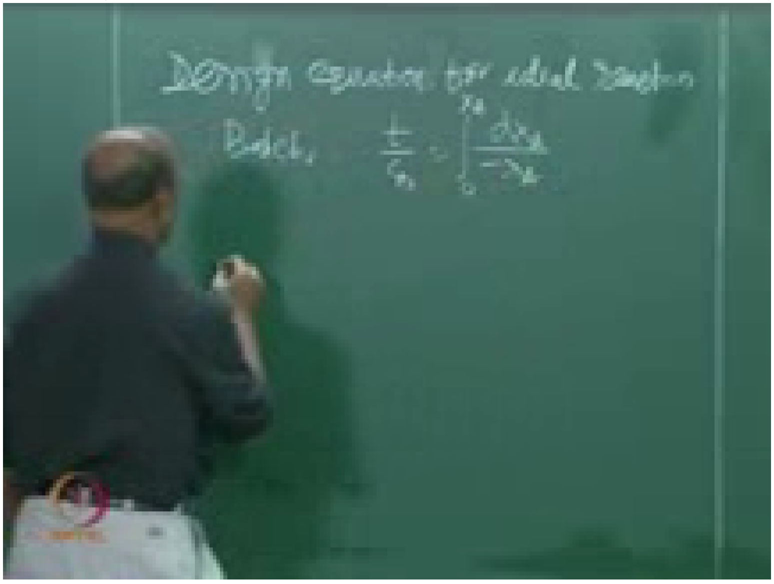

For P F, V by F A naught equal to zero to X A d X A by minus r A.

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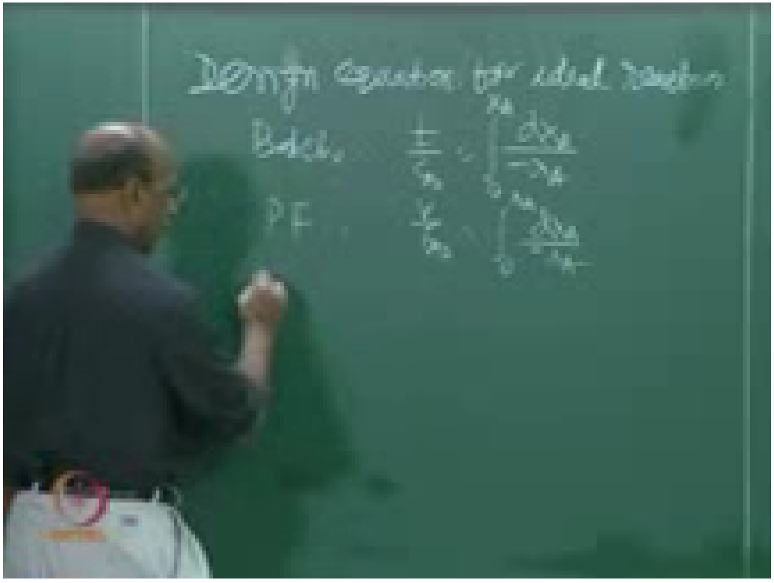

Design equations for ideal reactors

Batch. $\frac{t}{C_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A}$

PF. $\frac{V}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$

M F equal to V by F A naught equal to X A by, or X A f by, this is also X A f by minus r A, to be very precise I should write minus r A f. Because I have written here X A f. Because that is rate corresponding to only at the outlet.

Yeah, so these are the 3 equations which we have derived. We spent lot of time in understanding what is batch ideal, plug flow ideal, mixed flow ideal and all that. Finally you have very simple equations. The simple equations have come because we have very beautiful assumptions, what is perfect mixing, what is

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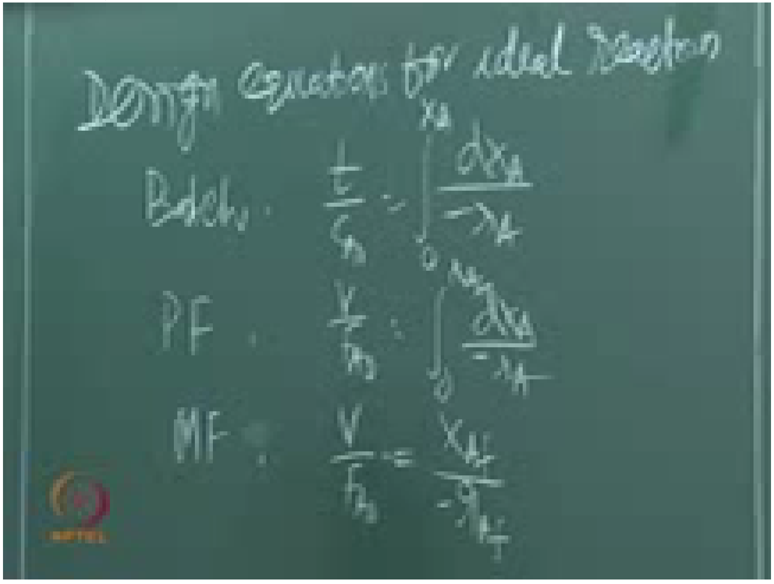

Design equations for ideal reactors

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PF. $\frac{V}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$

MF. $\frac{V}{F_{A0}} = \frac{X_{Af}}{-r_{Af}}$

ideal plug flow, what is ideal batch. Because of those equations, assumptions only you could get very simple equations, right? Good.

So now if you go back to your that information required for reactor design, this is input, output, kinetics, and I have contacting, then here we have batch, continuous, P F, M F Ok, that way, this is physical, chemical, right? So this is the design,

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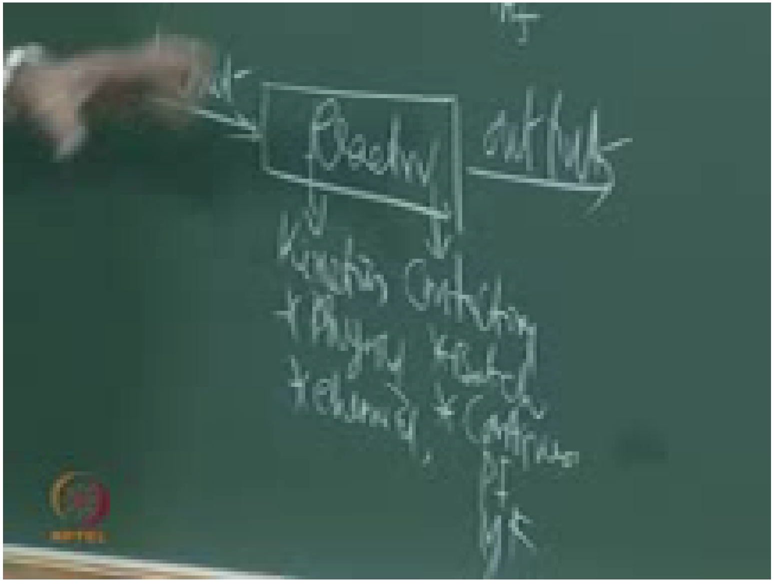

information required for the design. This all kinetics will give me minus r A. This will give me what?

(Professor – student conversation starts)
Student: Size of reactor

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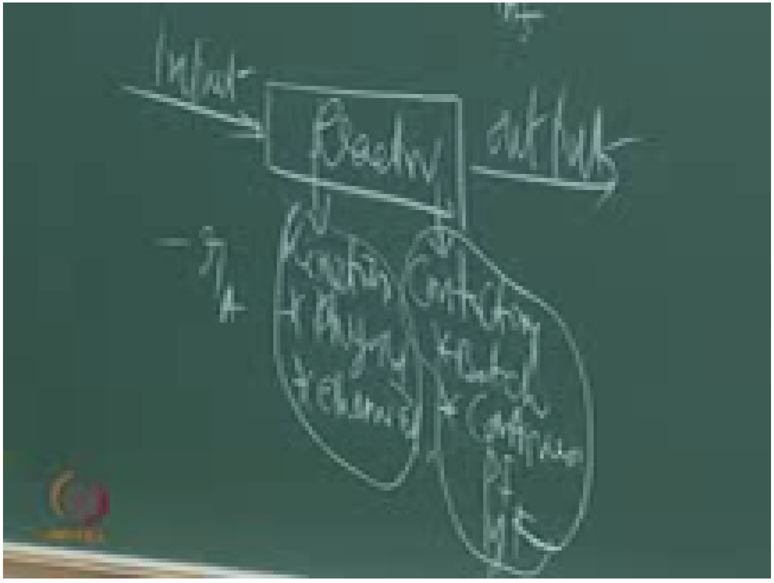

Professor: Size of reactor, volume only but exactly what volume are you talking?

Student: Reaction mixer

Professor: Reaction mixer is also not the one. That entire thing will give you what kind of reactor you have to use first. Contacting.

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Ok.

(Professor – student conversation ends)

So you have to choose that whether you have the batch or continuous and out of that you have to choose now, you see so many times repeating also, you are not able to get still the points no?

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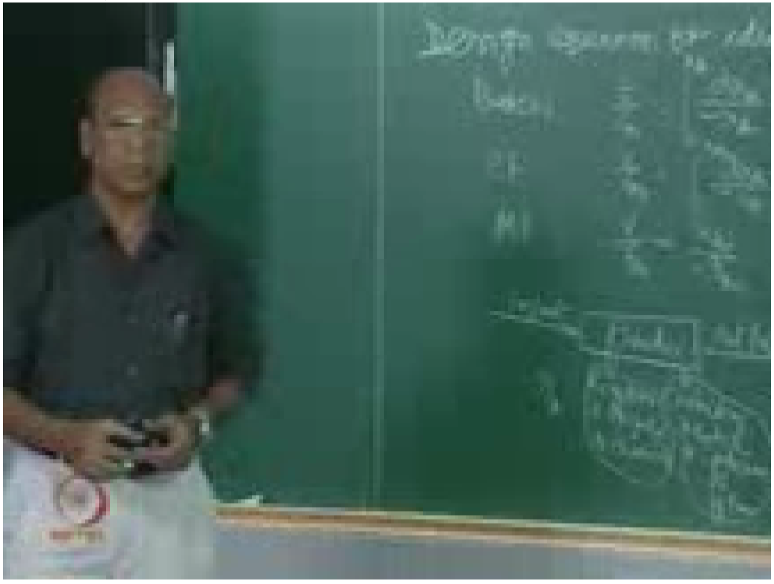

Yeah all this will give me the type of reactor which I have to choose. This suddenly will not give you the rate. Or someone was telling, Abdul was telling conversion.

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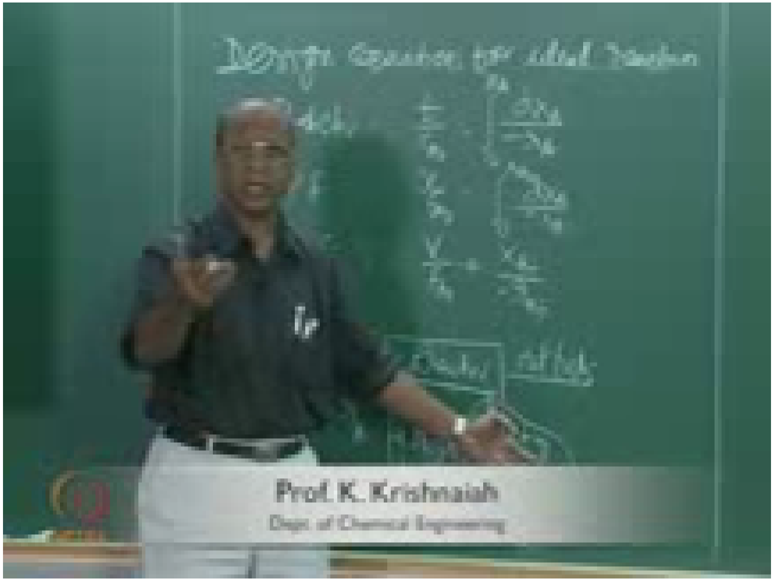

How can you get conversion the moment you take contacting? Ok. So you need again, for get conversion, you need what kind of reactor you are going to use. What is the rate expression and what is the input? Ok. So now these are the...then output will be volume, if conversion is known and conversion if volume is known. That is all. Ok. So now by deriving these equations what are the quantities you have now with you?

(Professor – student conversation starts)
Student: Kind of reactor
Professor: Very good. What kind of reactors

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we have discussed? So how do you choose we have discussed so that means I have information

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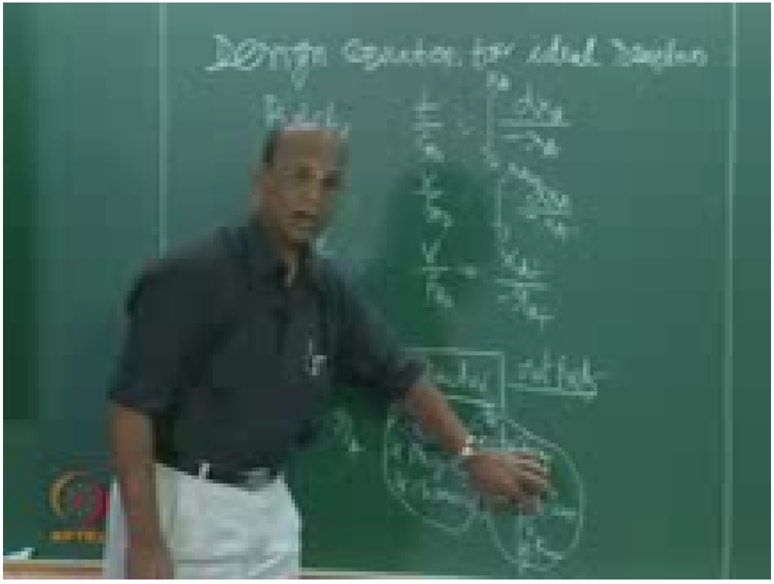

on this, Ok, yeah. And then? That is all? That is all? What is performance equation?

(Professor – student conversation ends)

Output equal to,

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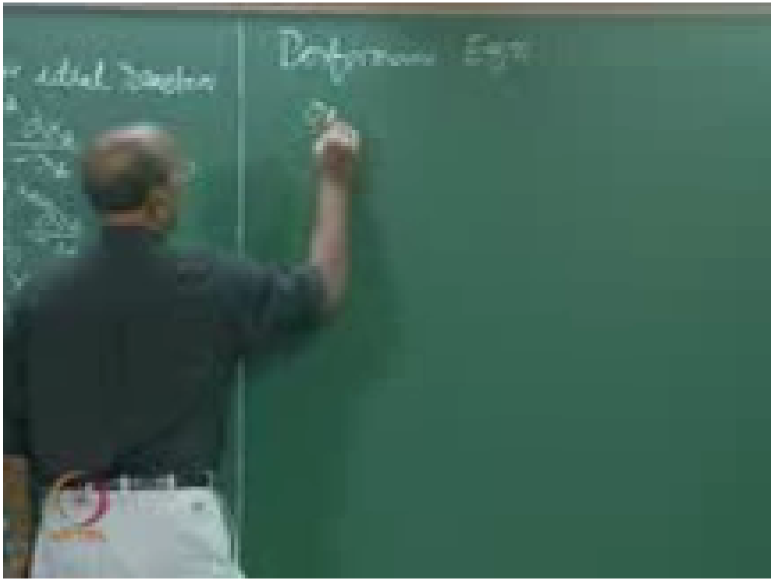

is a function of input, kinetics, contacting. Yeah, Ok, yeah. So what is information

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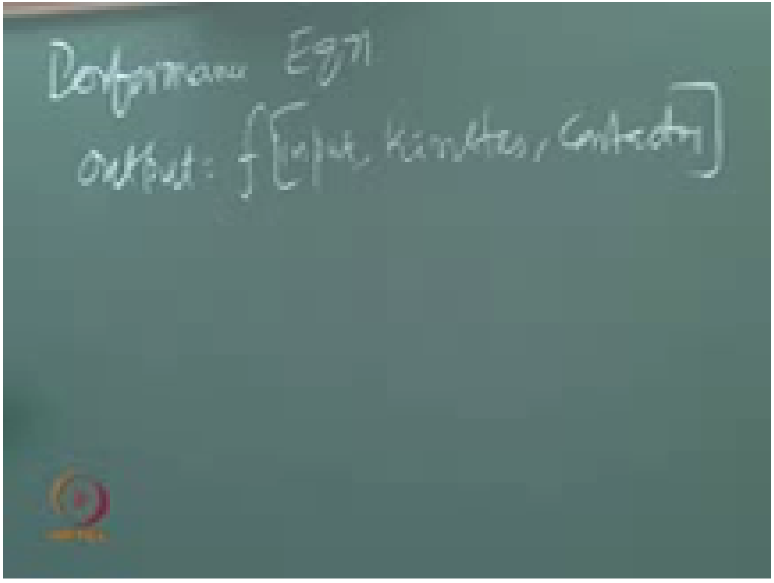

till now we have covered for that, using, yeah, for this equation if you want to calculate finally either volume or conversion? What is the information? You said contacting you know.

That means you know how to choose a

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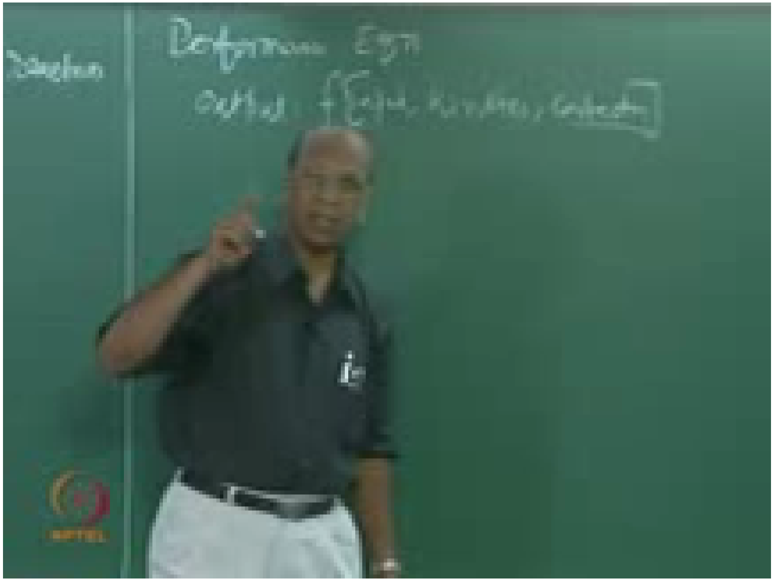

reactor. Ok. So then you know again kinetics?

(Professor – student conversation starts)

Student: Yes

Professor: We do not know. We have not discussed anything about how did you get this minus r A, Ok this minus r A,

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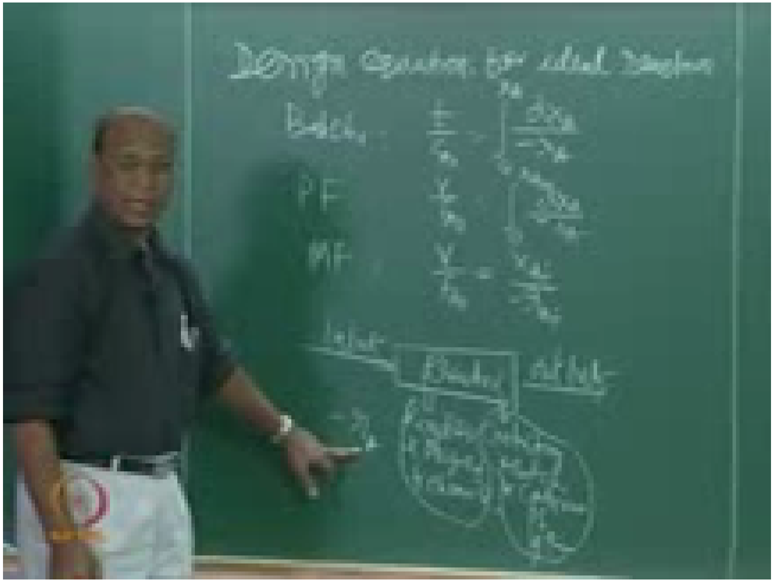

right. Then what about output, sorry what about input? Input did we

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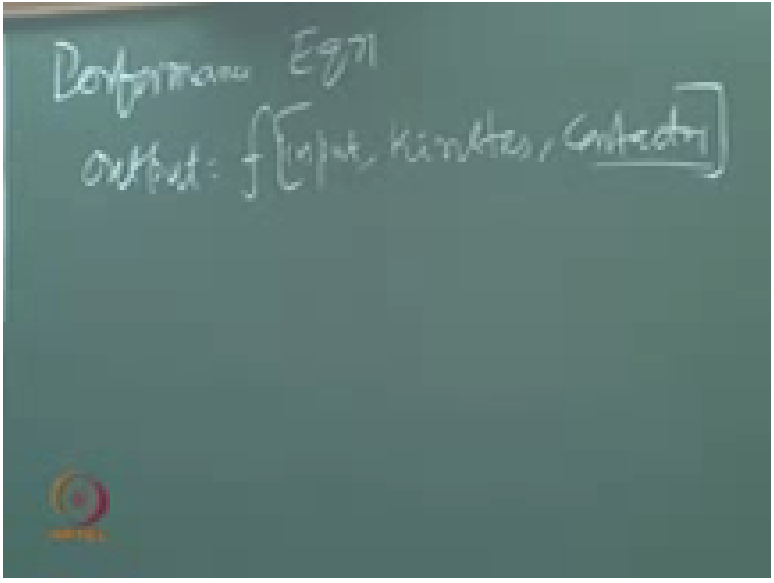

Performance Eqn

output: f[input, kinetics, contactor]

discuss?

Student: It is based on output.

Professor: Not discussed?

Student: Based on the kinetics we can

Student: Based on the output we can decide

Professor: Ok, yeah. So input we have never discussed.

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Input we never discussed? F A naught we have never discussed

Student: Sir we can decide the output, but we cannot decide the input.

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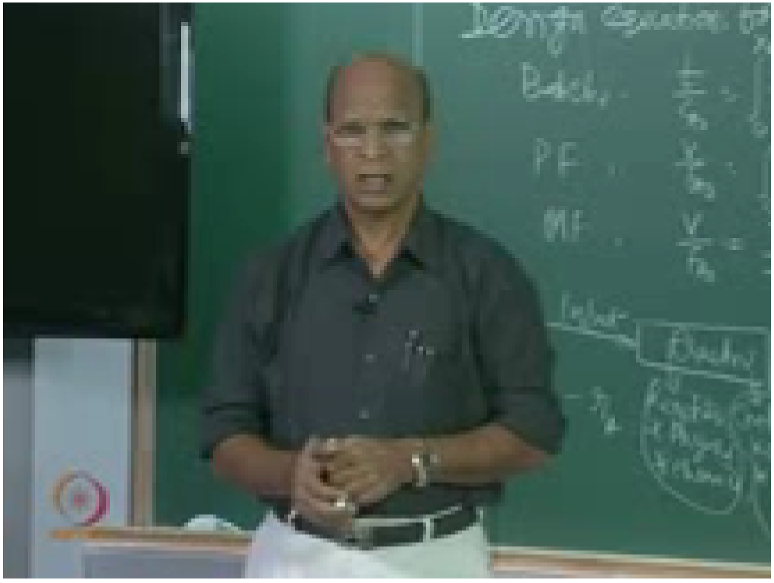

Only by the rate we can decide the input.

Professor: Oh my God!

Student: Based on...

Professor: 0:05:43.8. How do you get F A naught, we have not discussed?

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Student: From the output, we have discussed.

Professor: That is the first thing we know,

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before starting any plant. What Abdul, what has happened?

Student: We will first begin

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with the output, Sir

Professor: Yeah, you have to produce some output. For that you know what is the

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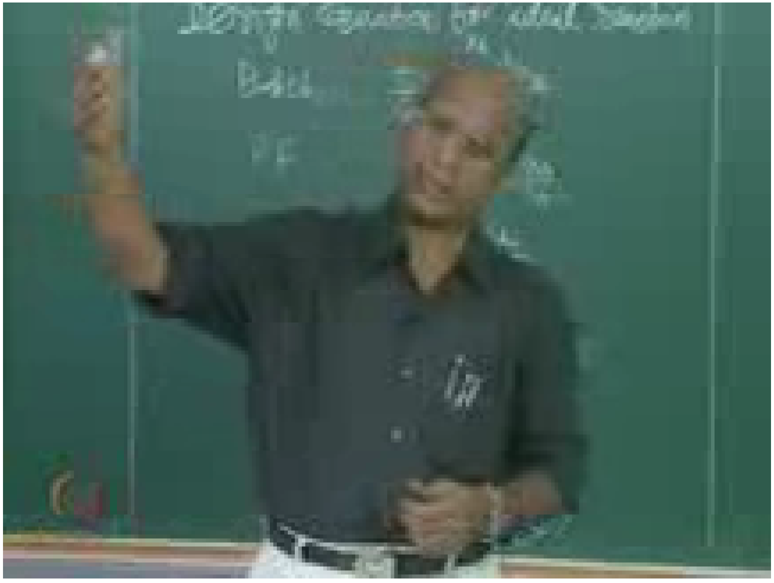

kind of reaction stoichiometry? And how much reactants you have to get. I was telling you so many thousands of times that F A naught we know, F A naught we know, F A naught we know. F A naught is input. In language F A naught is what?

Student: Input

Professor: So then why do you say that...?

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Student: (laugh)

Professor: Then why do you say that input is not known? We have not discussed. So many times

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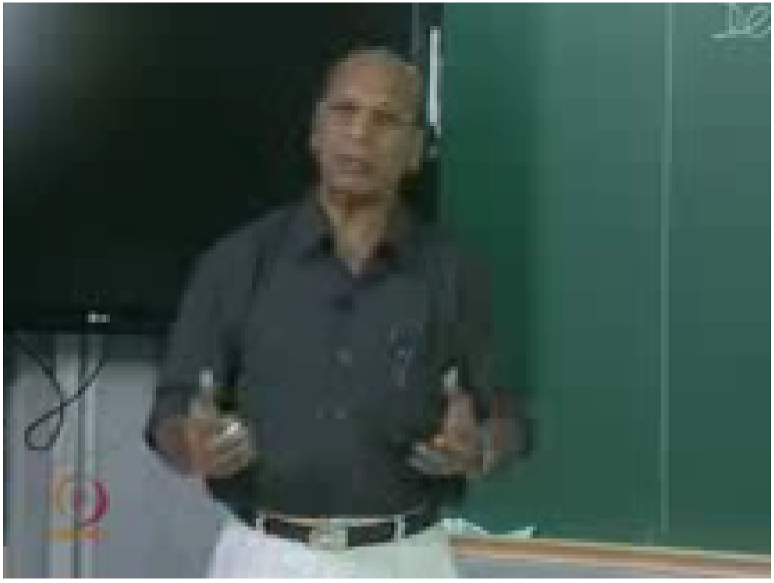

we have discussed about input.

(Professor – student conversation ends)

And then I was telling you, you know, if you do not have time, appoint a M B A guy and get all the, ask him to do the market survey and get what is the total capacity for this plant we have to design. So F A naught is the first thing you know.

I think what I told is you identify a product, and find out which stoichiometric equation is giving you, and from there calculate the, what is the you know, amount you have to produce, amount to produce is product and how much reactant you have to use, so that is what is F A naught. We know in the beginning itself.

So right now, what you do not know is only minus r A. You know F A naught, right and you know, you do not know minus r A. But this equation or this equation or this equation which equation you have to use will come from contacting. Right? Whether you take batch reactor or you take continuous reactor, or in continuous reactor again you take P F or you take M F. All these things we have discussed. So that is very clear for you now.

Ok, just to take the sample, Gopinath when do you choose mixed flow reactor?

(Professor – student conversation starts)

Student: 0:07:49.3

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Student: Exothermic reactions.

Professor: Yeah,

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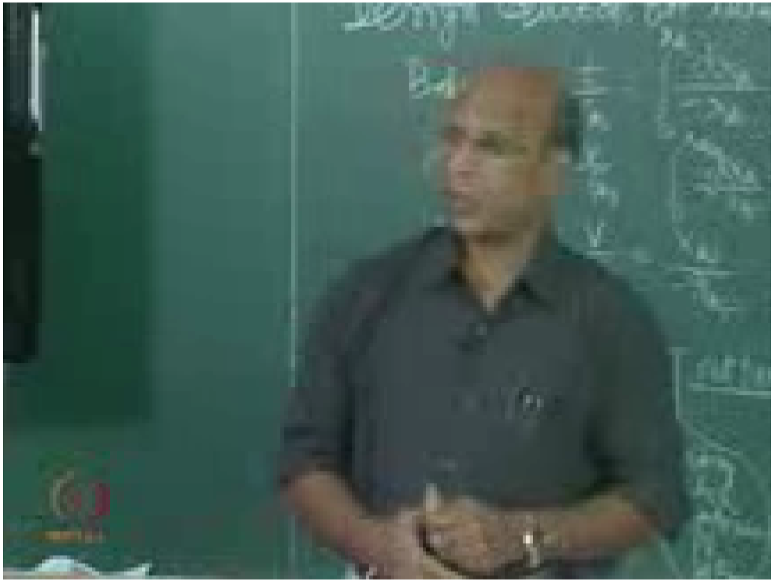

when do you choose mixed flow reactor? Janhavi?

Student: Exothermic reactions.

Student: Exothermic reactions.

Professor: Yeah. First of all, liquid phase reactions, I mean, high resident times will come. Mixed phase, most of the time, liquid phase reactions. Ok. Then even if it is gas phase, sometimes if the temperature control is very crucial, then temperature, you know when you have exothermic reactions, so under those conditions only you, you choose mixed flow reactors. Ok when do you choose batch reactor?

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Student: Small scale production

Professor: When I asked Debian, except Debian every one talked.

Student: (laugh)

Professor: Ok tell me

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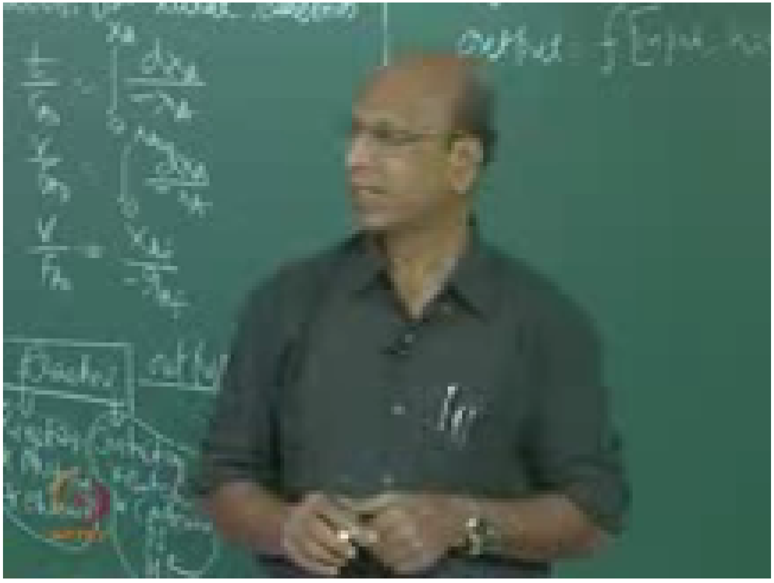

Student: When your demand is very less, that time

Professor: Ok, so small productions like may be 10 tons, 50 tons, 30 tons you go for batch, but I think you know somewhere 80, 100 we do not know which one is right but definitely 1000 tons per day is continuous, Ok.

(Professor – student conversation ends)

So that is why you have all the information. I think do not disappoint me. Because so much time I have spent on contacting so that that will be permanently printed in your brain. But it might be printed but you are not able to recall. You know, the information recalling also important, no? What is that, Random Access Memory, R A M? So that access is not there. You are printing somewhere.

I think you know computer also stores somewhere. But to get that file out, your interest must be there. You should not forget so easily. Ok so anyway. So all this we have spent lot of time in deciding which reactor you have to use. Either this reactor, this reactor, this reactor. That comes from this. This is your type of reactor. And this is what? F A naught.

And now we have to find out what is minus r A, right? Ok so now let us talk about rate of reaction. I just started the little bit rate of reaction, rate of reaction; mainly it is our key reactant minus r A we call. And I may have a rate A going to R, general rate or it may be having any complicated

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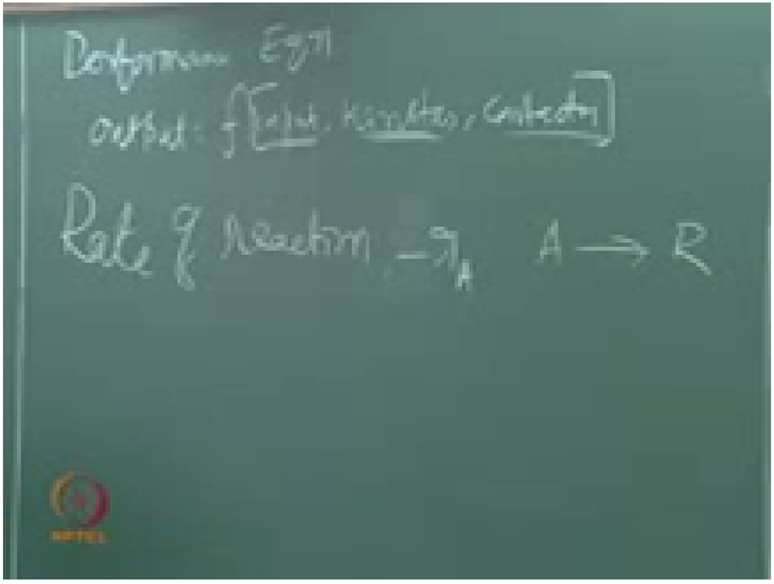

rate, right? So how do I determine my rate and we are talking first about the homogenous systems and then we can talk about heterogeneous?

Homogenous, homogenous means either

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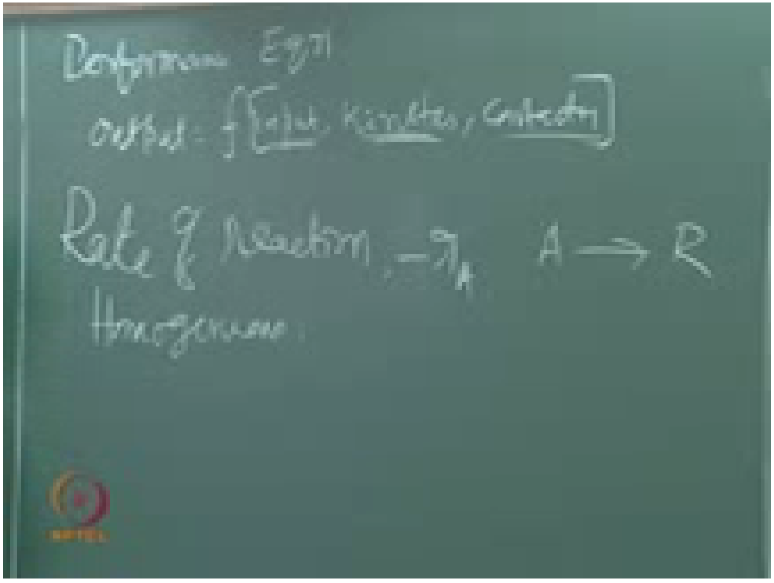

I have gas phase reaction or liquid phase reaction. Everything is available that phase. If there are two reactants, two liquids thoroughly mixed, two gases you do not have to do anything, they will anyway thoroughly mix, Ok so we were talking about only gas phase or liquid phase for homogenous reactions.

Now if I have homogenous reaction between A and B giving me R l how do I know what is order of reaction?

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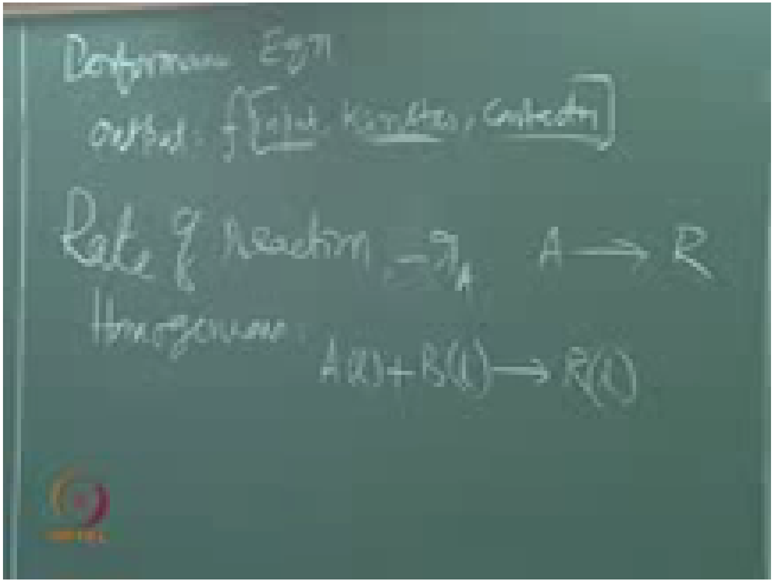

Ok. or I may have A gas going to R gas plus S gas.

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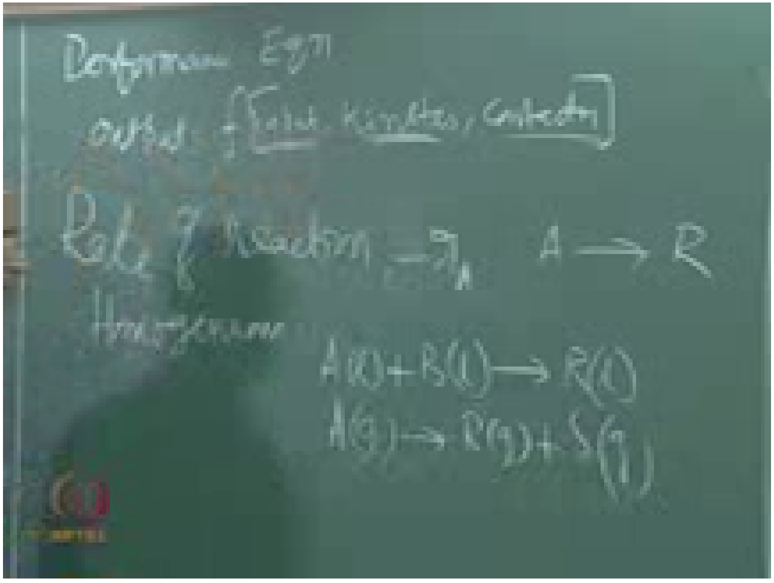

I cannot have l and g, because that will become heterogeneous system, Ok. And before this we have also defined now what kind of

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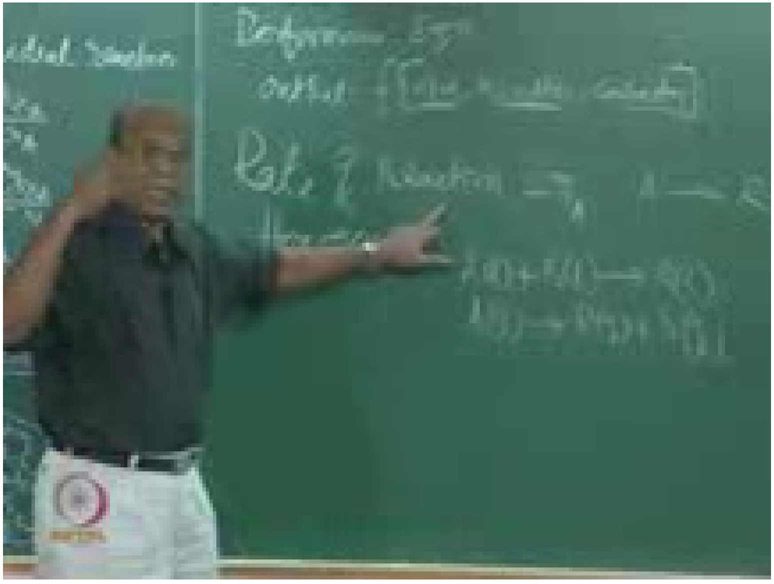

rates you can express.

Like homogenous means mostly it is liquid, yeah volume of the liquid or, Ok volume of the liquid or otherwise you have many possibilities for heterogeneous system. That we will come a little bit later. But this one, so if someone tells that Ok now I have A plus B going to now onwards please write in the bracket what is the state of the reactant when it is reacting, not at room temperature, when it is actually reacting, Ok.

You may have both A and B liquids at room temperature. So under actual reaction conditions both may be vapors. So that is again homogenous but gas phase reaction. Now you have to see whether the reaction time is very small or large. So depending on that, because you have the reactants liquid phase does not mean that you choose only C S T R.

We are talking about, those conditions we are talking about whether gas phase or liquid phase at the time of reaction only. Because these small things also you know, sometimes you may not get the idea. I have now, this is first order.

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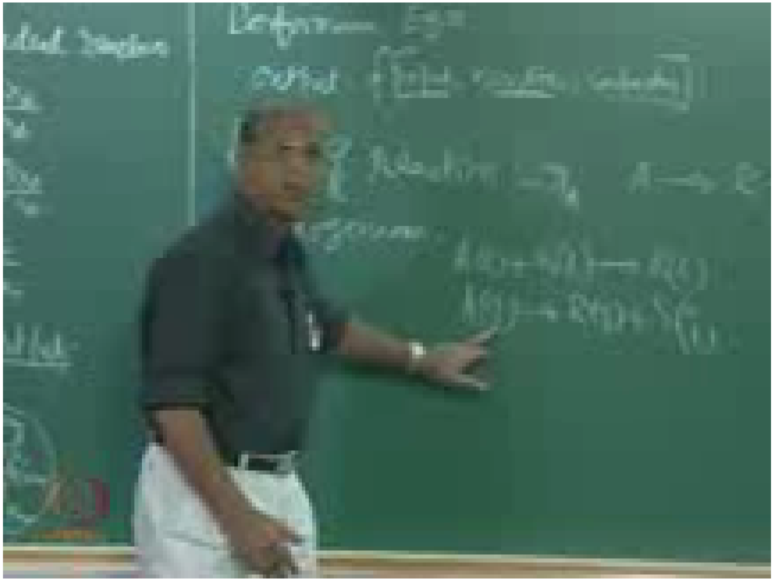

But how do you know it is elementary? When I just asked you, how do you know it is elementary?

(Professor – student conversation starts)

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Student: It depends on 0:12:31.2

Professor: Pooja, you are telling something?

Student: If it takes place in one single step

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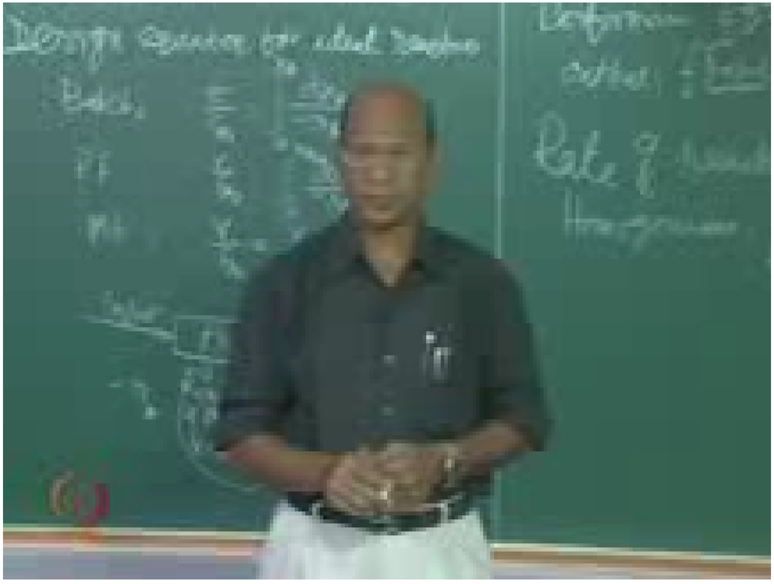

it is called elementary.

Professor: How do you know, you cannot see...see the actual reaction whether it is taking place in single step or two steps you do not know.

Student: 0:12:46.7 experiment

Professor: Yeah that is very important. So you can never say anything about the rate equation or order of rate or what kind of rate equation you get unless you conduct experiment.

(Professor – student conversation ends)

So that is why chemical reaction engineering always associated with the experiments. So do not tell very proudly that no, no, no I am high funda guy. So I only talk about mathematics. And I cannot conduct any, any experiment. You have to conduct experiments. Ok. So otherwise you will never get a rate expression.

But if it is someone did and if you are copying, copying is very easy, you can do many things, Ok. That is not the one. So always reaction engineering associated with experiments because the first thing I do not know is whether this reaction is elementary or non-elementary I do not know. Then what kind of rate form I will get I do not know, right? And I will ask you another question.

I have 2 A l plus 2 B l giving me R l,

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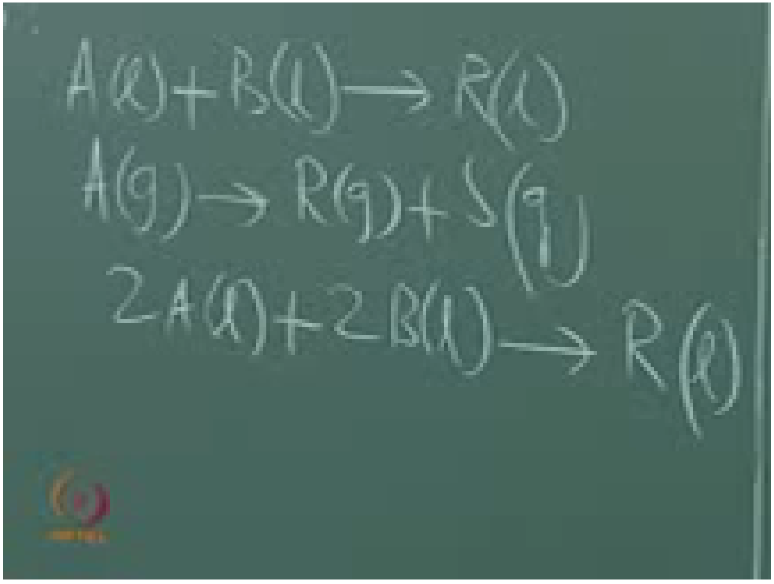

$$A(l)+B(l) \rightarrow R(l)$$

$$A(g) \rightarrow R(g)+S(g)$$

$$2A(l)+2B(l) \rightarrow R(l)$$

what is the order of reaction? Can I take this one as elementary reaction?

(Professor – student conversation starts)

Student: No

Professor: Why?

Student: Order greater than 3 is

Professor: Why order greater than 3 is, I mean why are you very angry with orders greater than 3? Or why you do not like orders greater than 3?

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Student: Lot of intermediate steps

Professor: How do you know there are lot of intermediate steps?

Student: It can be, I am just saying.

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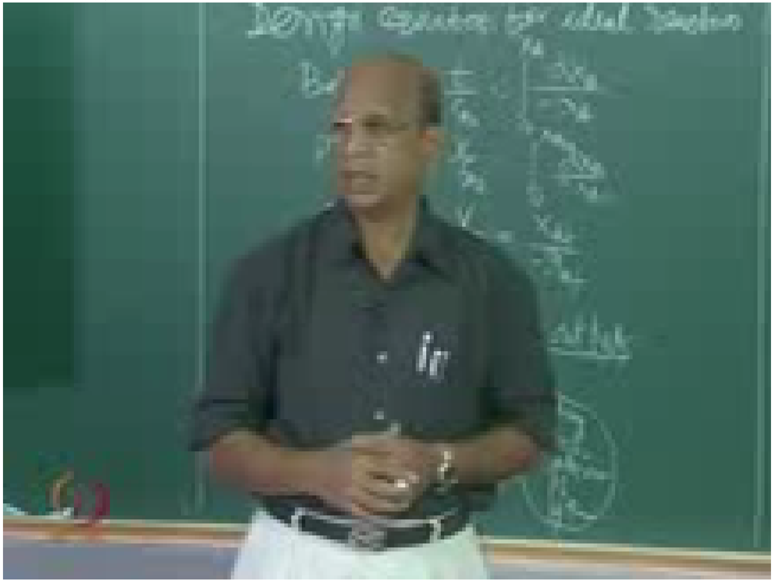

Professor: First of all, why are you telling that orders cannot be more than 3?

Student: Probability of 4 molecules colliding together is very rare.

Student: Very rare.

Student: Yes

Professor: That you have to remember.

(Professor – student conversation ends)

In nature, if I have only A going, A decomposing, easiest, right. So when I have, that means 2 molecules come together, two As and again they collide and then they decompose, Ok, some kind of activation energy all is required.

So in the, if you have A and B 2 different molecules coming, they come together, again collide Ok so depending on the energetic collisions they will have more and more product coming. But important thing is molecule collision. So when you go to third order that means 3 molecules coming together, so the probability will fall very drastically.

Two coming together is good. One is, of course just decomposition reactions are many, right? Two. Then three, probability is less. Four, probability is zero, almost, may be point zero zero zero 1. So that is why you do not have 4 molecules together or 3 molecules also together and then coming and happily getting reacted, reacting is very, very difficult.

So that is why in nature people have not seen that orders beyond 3. And third order reactions also I told you, what is the order I gave you?

(Professor – student conversation starts)
Student: Nitrogen N O plus
Student: 2 N O plus O 2

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Professor: Yes 2 N O plus O 2, that is one thing in the third order.

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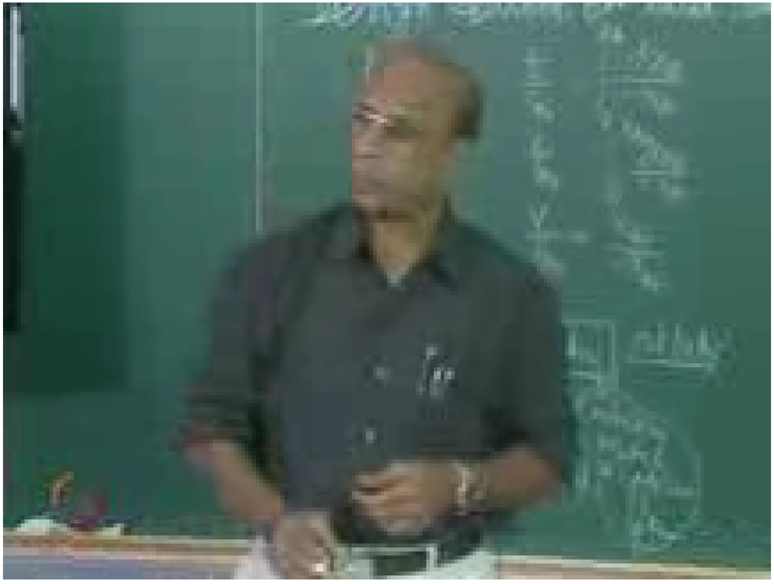

(Professor – student conversation ends)

That means 2 N O molecules are coming, one O 2 is coming, together they are able to collide and they are able to give you know the product so that is why people observed that experimentally, later proved that yes this is a third order reaction where two moles of this and one mole of this coming together and reacting.

So that is why, absolutely, I told you in fact, that is what I have been telling you many times, contacting is the easiest one to remember in chemical reaction engineering. It is the actual reactions which are very, very difficult to remember. Or very, very difficult to get the information on rate of reaction.

This is simply homogenous. And the moment I go for heterogeneous, you will have real hell. It is not easy for heterogeneous reactions to get, right? So simplest equations if we take, even combustion, coal combustion there are hundreds of equations. Ok, heterogeneous system, right? So that is why the easiest one in fact is of course, input is easiest one. You need not do at all. Ask the MBA guy to get information.

Second easiest one is contacting because you have only 3 ideal systems. You know now at least, you know under what conditions you choose what reactor and then the next one is to get the output is the kinetics

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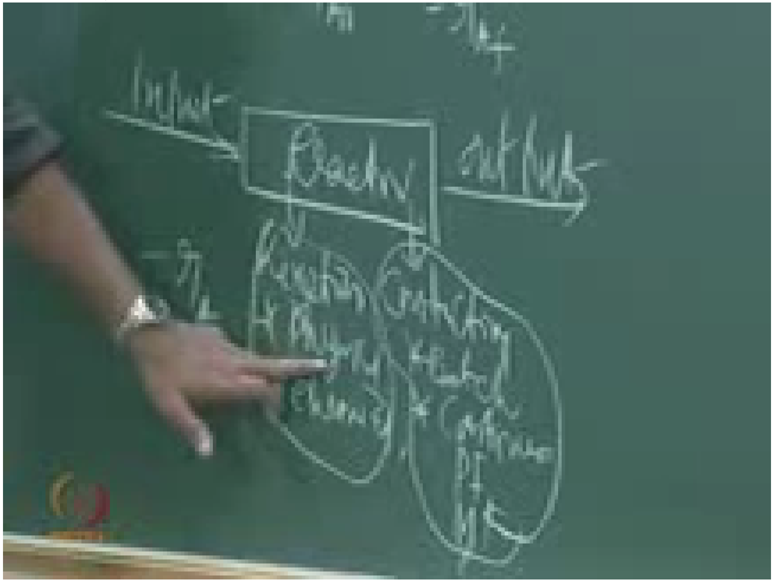

and the kinetics is the most difficult part.

For example, very innocent looking equation

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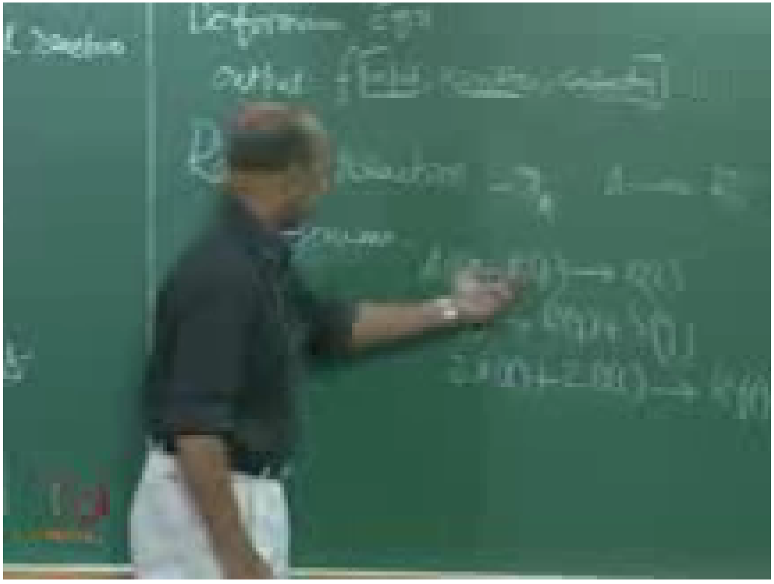

like this, A plus B going to R, you do not know what is happening there. It can be very, very complicated equation. It is not simply second order, right? Or it cannot be simple pseudo-first order. By looking at that you can never tell that.

So that means you have to go to experiments. And experiments you have to prove that whether it is elementary, with respect to A

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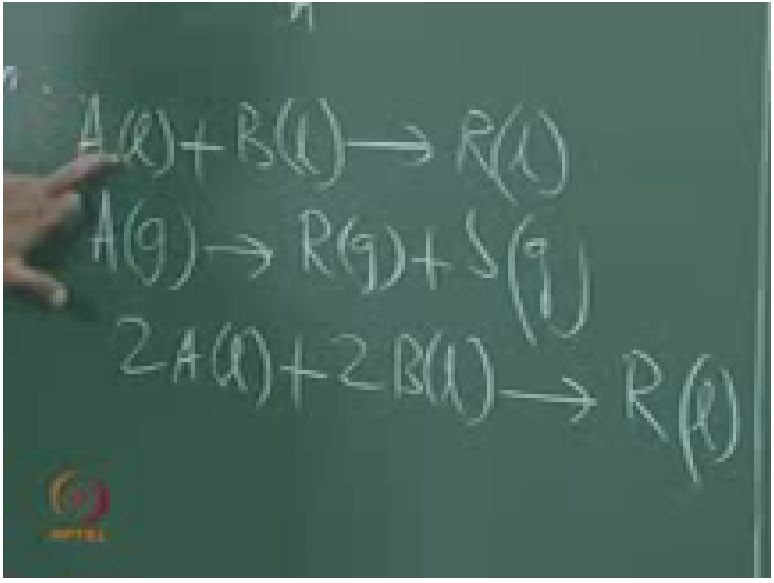

$A(l) + B(l) \rightarrow R(l)$

$A(g) \rightarrow R(g) + S(g)$

$2A(l) + 2B(l) \rightarrow R(l)$

if it is first order with respect to B, if it is first order then you may think that Ok, one molecule of A, B colliding or yeah, reacting with another molecule of B, then I am getting product, all that imagination comes after doing the experiment and then proving what is the order.

Then your model will come. Or otherwise in the beginning itself imagine that A is colliding with B, develop equations, finally have some rate equations, go to laboratory, do the experiment and then check whether what you have written those equations exactly tallying with your experimental data. That is another way. I am not saying whether is right or that is right.

So depending on your convenience you may start this way, you may start this way. Either from experiment or from theory. So that is why. But what we know at this point of time is only one thing, rate is a function of

(Professor – student conversation starts)
Student: Concentration
Professor: That is all. Rate of reaction is a function of concentration and temperature. That is all I know.
(Professor – student conversation ends)

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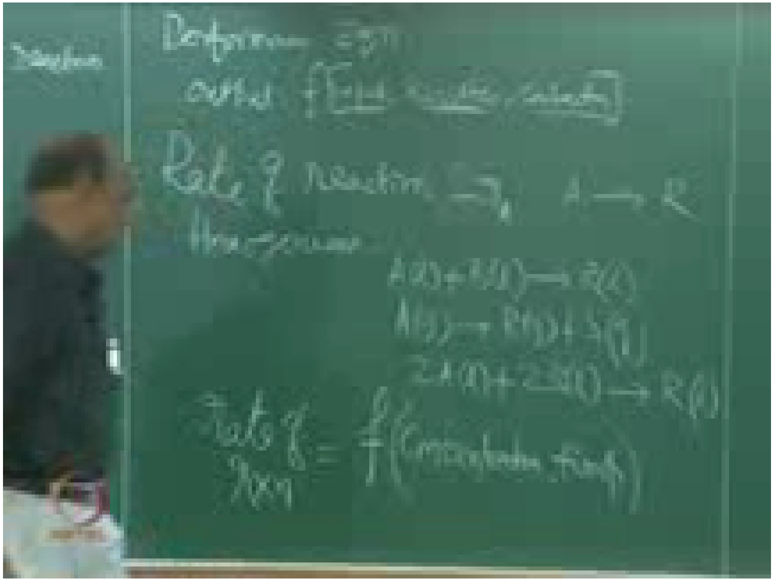

Now that functionality I have to find out. So that is why for convenience sake I can also write this one as, as a function of, Ok C A and T which also can be written as some kind of function f 1 T and f 2 C A. I have divided that function into two groups

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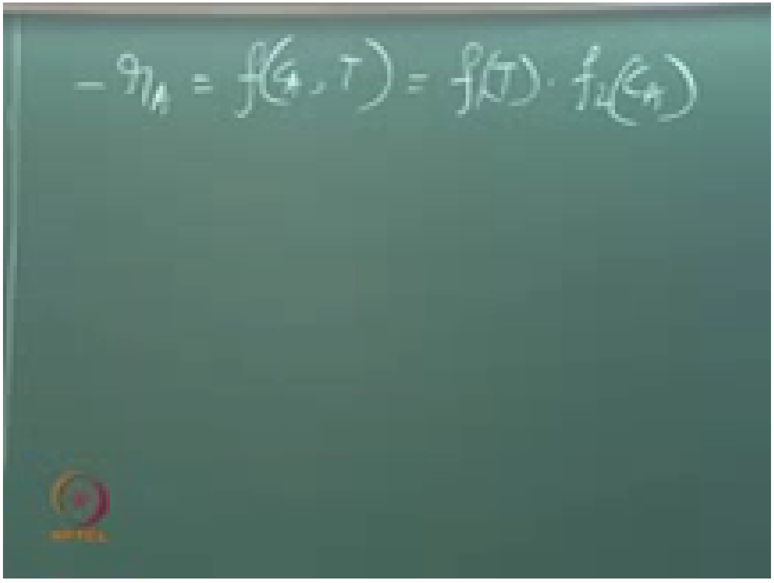

where, the term which is depending on temperature and the term which is depending on concentration.

So by keeping the temperature constant that means at 100 degrees Centigrade, exactly isothermal condition then I will vary various concentrations and all that and try to find out what is the concentration dependency on the, rate dependency on concentration. That is one thing.

So once I know that this is the Ok, for easy thing which is first order, then I know that term, that functionality. Now I will vary the temperatures. 100, 120, 140, 160 then I will get now the temperature dependency or rate dependency on temperature. Concentration is already known. So that is the two terms what we have to now learn.

And fortunately for us f 1 T is only k naught e power minus E by R T. who has given this equation? Arrhenius. That is only equation you have? There are many. Finally it is distilled to that level,

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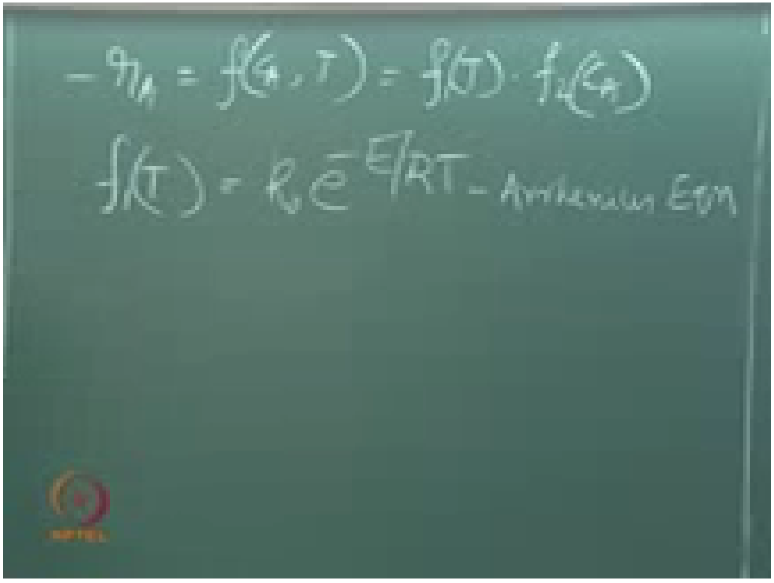

$$-r_A = f(C_A, T) = f_1(T) \cdot f_2(C_A)$$

$$f_1(T) = k_0 e^{-E/RT} \text{ - Arrhenius Eqn}$$

right? So how do you get this format?

Like for example that functionality, you know that functionality T can also be called as k, rate constant, so that functionality is an exponential function. How do you know that? Experimentally people have also found but from thermodynamics, from collision theory, from transition state theory people have different equations for rate constants. Ok.

So this, if I say this one as rate constant k, k now, the functionality of k can be obtained from thermodynamics and also from kinetic theory of gases, kinetic theory, in this kinetic theory again we have collision theory and yeah, another one transition state theory, yeah but finally all these things will

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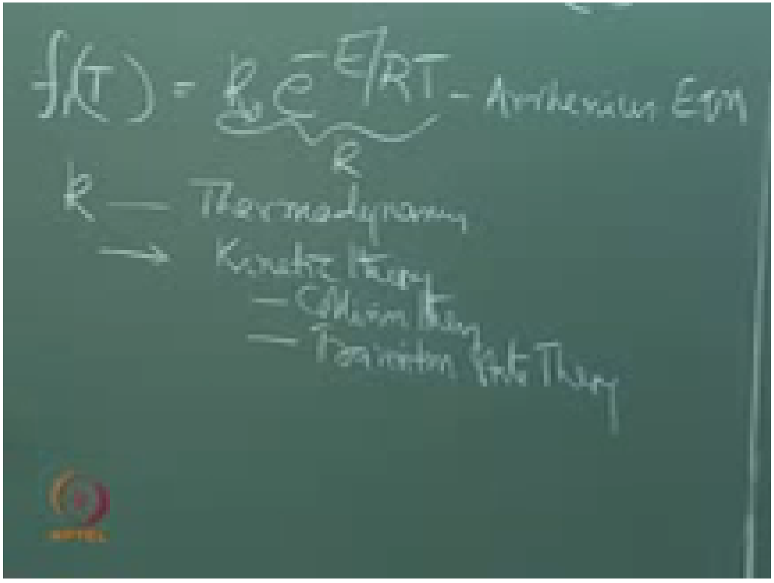

give me that format.

And actually that format is a simplification of all these things except of course for thermodynamics almost straight you get. So now let us quickly see how do we get that format because that is easy to start. Ok. The functionality that concentration is much more difficult.

But here at least with temperature we have only 1 term, and that is easy to get and from thermodynamics let me tell you how do you get that format, this format means exponential term, Ok. You know, we are now trying to find out that k functionality using thermodynamic information and you know

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thermodynamic information, temperature dependency of rate constant from thermodynamics. Ok, good.

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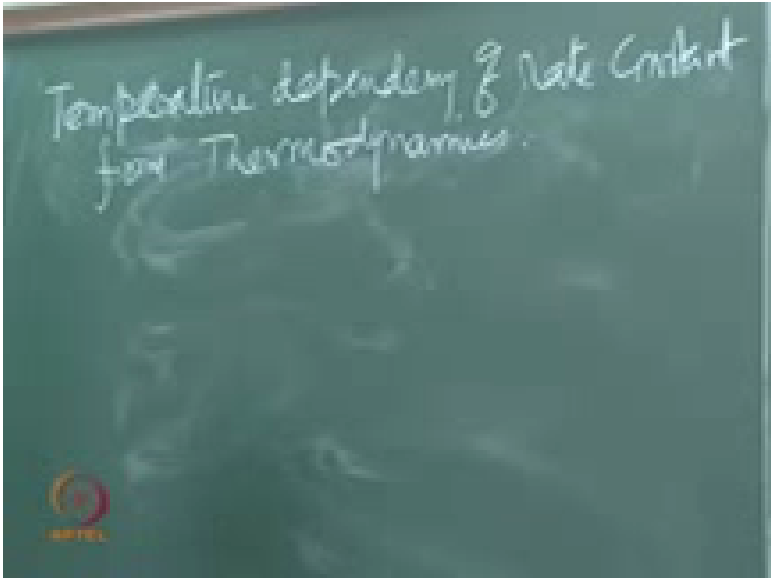

Temperature dependency of Rate Constant from Thermodynamics.

If you have, because you know simple equations we will take just to get the point A going to R,

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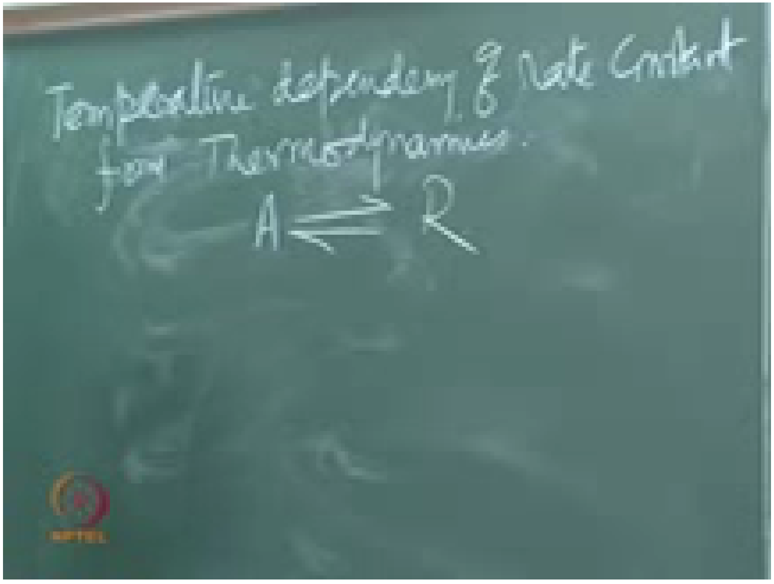

Temperature dependency of Rate Constant from Thermodynamics.

$A \rightleftharpoons R$

may be A gas going to, I mean R also gas, then I have k 1, k 2, it is equilibrium reaction. rigt. So you heard of Van't Hoff equation, Van't Hoff yeah, so the Van't Hoff equation will give me, yeah that equation in terms of differentiation capital K, yeah this one here equal to delta H R by R T square.

Ok, that is the first equation I have written for kinetics. Right I mean, these things are Ok, this equation, 1, 2, this is 3, yeah, so this equation,

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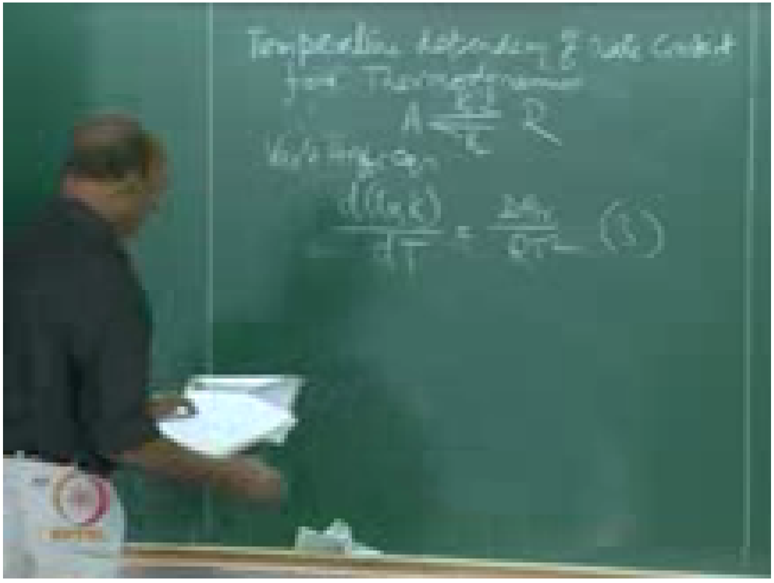

we can also write, you know. This K is nothing but k 1 and, this is equilibrium constant, capital K and I write small k like this, Ok and capital K like this, there is no round there, Ok. So this is capital K, Ok where capital K as k 1 by k 2.

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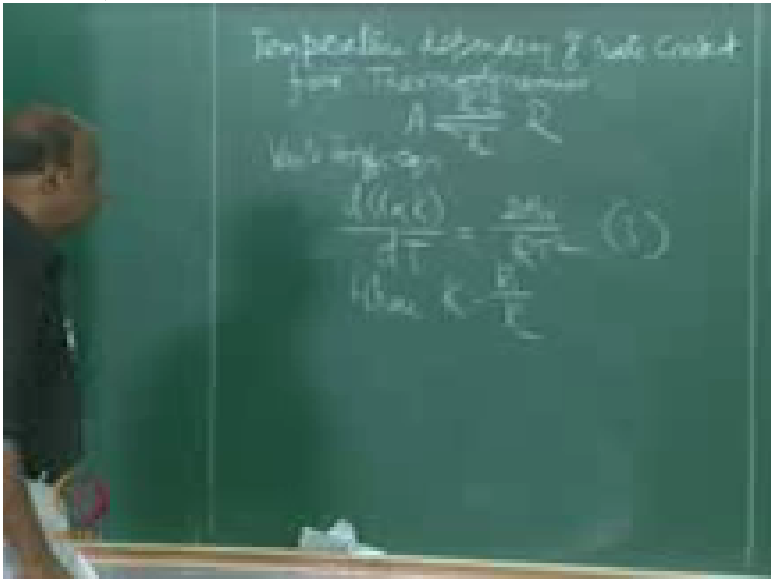

Ok, so now I can also write the same thing here. This will be if I write substitute, this is equation 4. If I put equation 4 in 3, then what I get is, l n small k 1 by d T minus d l n small k 2 by d T also equal to e 1 minus e 2 divided by R T squared where,

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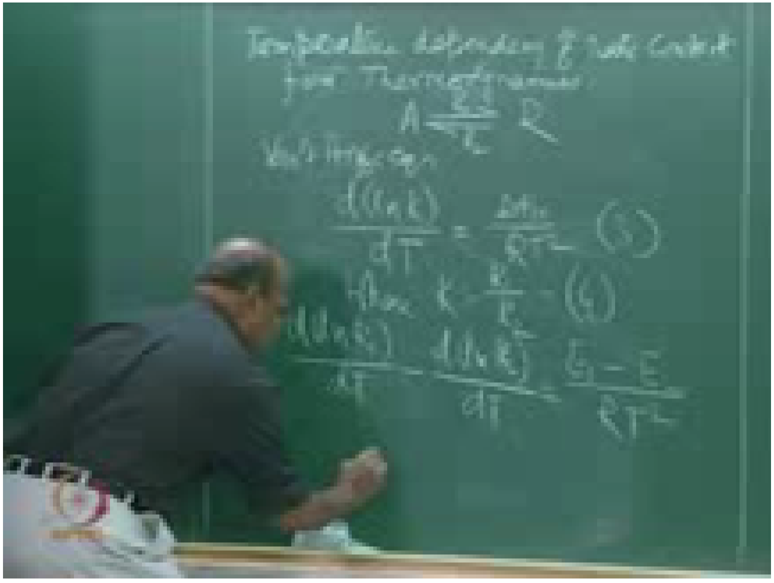

Temperature dependency of rate constant from Thermodynamics

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R$$

Van't Hoff equation

$$\frac{d(\ln K)}{dT} = \frac{\Delta H_r}{RT^2} \quad (3)$$

then $K = \frac{k_1}{k_2}$ — (4)

$$\frac{d(\ln k_1)}{dT} - \frac{d(\ln k_2)}{dT} = \frac{E_1 - E_2}{RT^2}$$

you have this information, where e 1 minus e 2 equal to what? Delta H R, right? Yeah. Good. So now I can take that similarities here, for example this term is equivalent to

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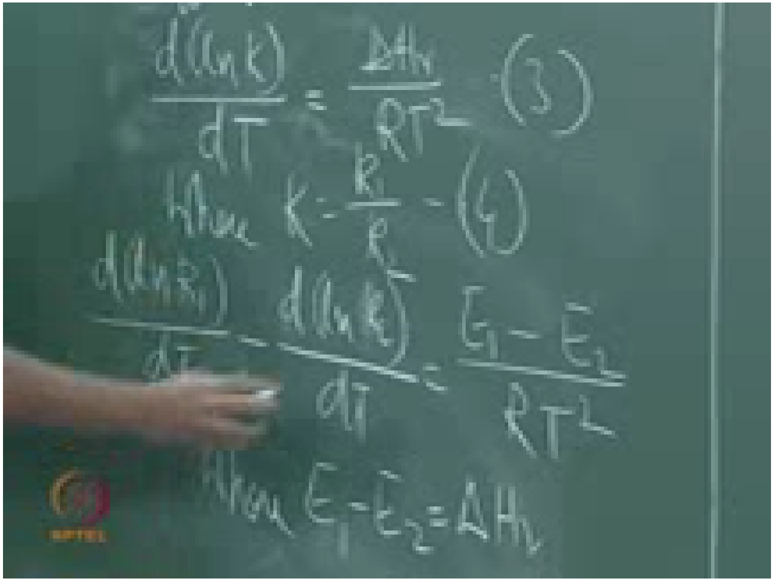

$$\frac{d(\ln K)}{dT} = \frac{\Delta H_r}{RT^2} \quad (3)$$

then $K = \frac{k_1}{k_2}$ — (4)

$$\frac{d(\ln k_1)}{dT} - \frac{d(\ln k_2)}{dT} = \frac{E_1 - E_2}{RT^2}$$

then $E_1 - E_2 = \Delta H_r$

this term. This term is equivalent to that term, Ok. So if I,

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Ok, yeah so this is equivalent to d ln k 1 d T equal to e 1 by R T squared.

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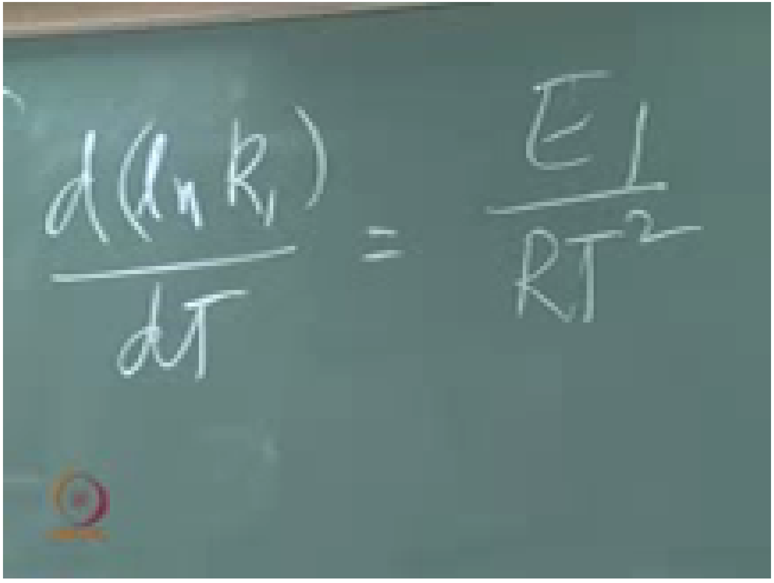

$$\frac{d(\ln k_1)}{dT} = \frac{E_1}{RT^2}$$

(Professor – student conversation starts)

Student: Minus E 1 by R T squared

Professor: Yes?

Student: Minus E 1 by R T

(Refer Slide Time: 26:14)

Professor: Because you know the answer, you are telling. But I think also want mathematics. All of you done it? Yeah.

(Professor – student conversation ends)

So this may be a surprise test.

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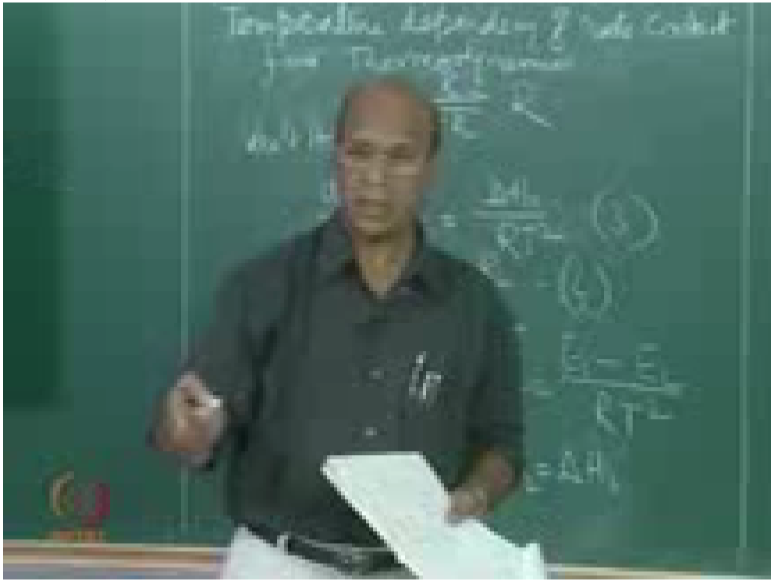

So if you simply write without writing anything in-between the answer, I will put zero. Because I cannot go to your mind and then see what you have done. I want something on the paper, Yeah, so this is equal to minus E by, or E 1 by R T.

So this is one of the forms,

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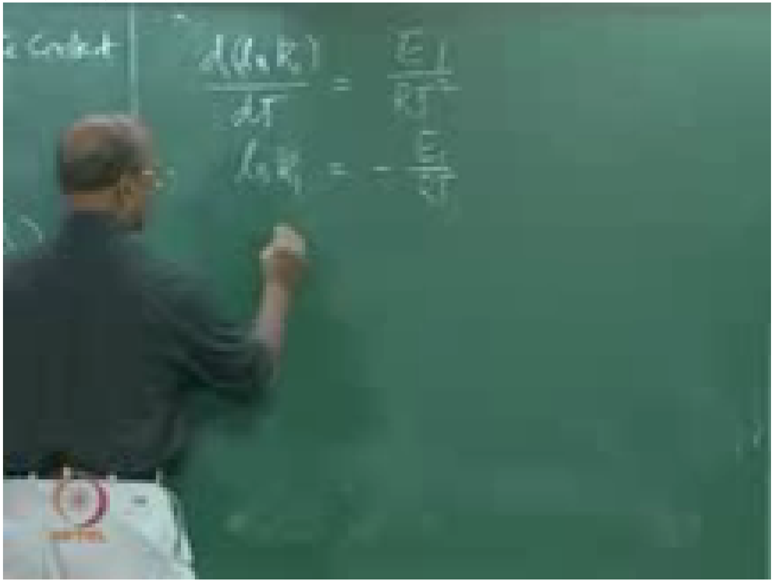

$$\frac{d(\ln k_1)}{dT} = \frac{E_1}{RT^2}$$

$$\ln k_1 = -\frac{E_1}{RT}$$

you know, yeah ln k 1 is minus E by R T, instead of just writing E 1 and k 1 like that.

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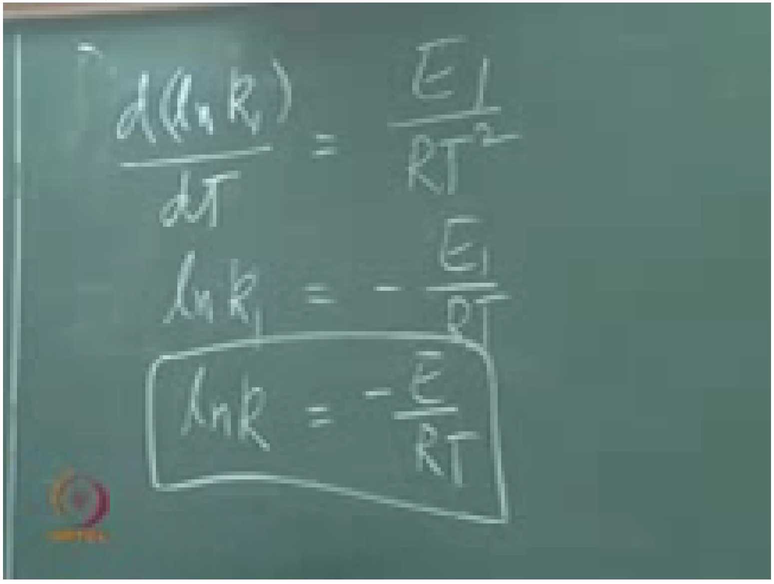

$$\frac{d(\ln k_1)}{dT} = \frac{E_1}{RT^2}$$

$$\ln k_1 = -\frac{E_1}{RT}$$

$$\boxed{\ln k = -\frac{E}{RT}}$$

Yeah, so integration constant, then I will write, equal to K naught into exponential, yeah that is what.

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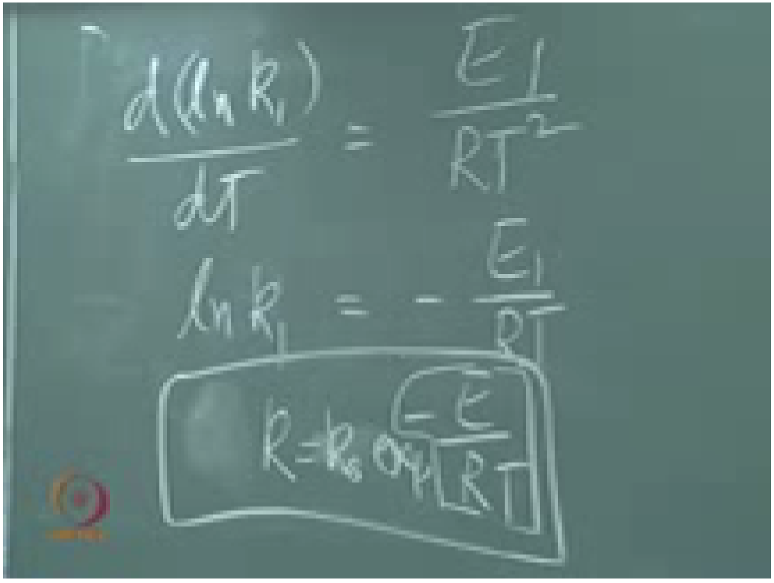

$$\frac{d(\ln k_1)}{dT} = \frac{E_1}{RT^2}$$

$$\ln k_1 = -\frac{E_1}{RT}$$

$$\boxed{k = k_0 \exp\left[\frac{-E}{RT}\right]}$$

Integration constant, yeah we should not forget. Yeah so numbers if I give, this is 4, this is 5, 6 Ok, 7, 8.

So this is one conclusion from thermodynamics that

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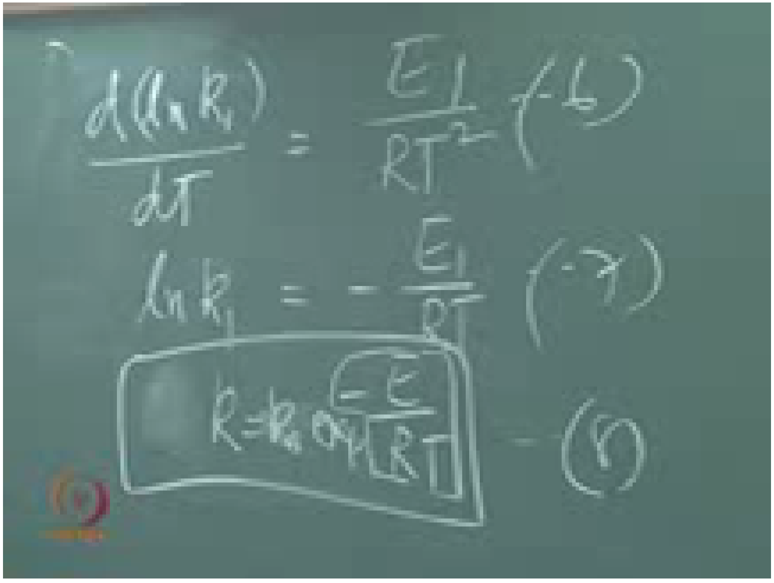

$$\frac{d(\ln k_1)}{dT} = \frac{E_1}{RT^2} \quad (6)$$

$$\ln k_1 = -\frac{E_1}{RT} \quad (7)$$

$$\boxed{k = k_0 \exp\left[\frac{-E}{RT}\right]} \quad (8)$$

the rate dependency, no not rate dependency, k, rate of reaction, rate constant dependency with temperature may be something like this. But again it is not true unless you check with the experiments, Ok.

So now you can come and discuss with, you know the kinetic theory, kinetic theory particularly collision theory. Yeah in collision theory, what is the assumption? Yeah so all the particles will come together, they will be colliding

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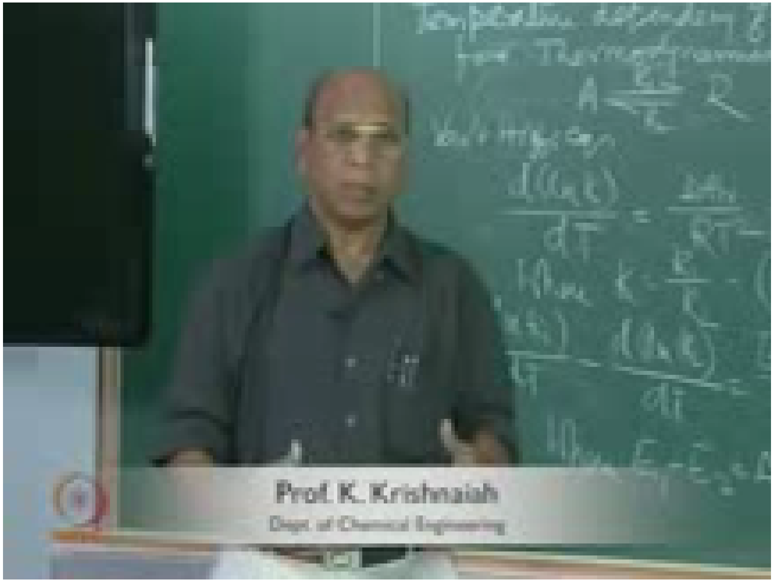

but all the collisions are not energetic collisions. They may not be resulting. Only a fraction of the collisions will give you the product.

That fraction is, mathematically it can be proved, as this term, exponential minus E by R T, by the way what are units of this, minus E by R T? Unit-less. So that exponential term will give me

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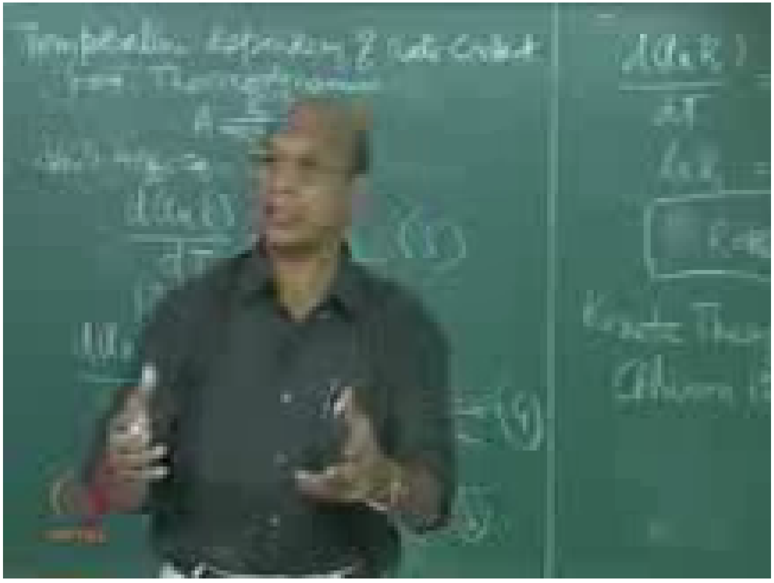

the fraction of collisions which are resulting into the product. So that is why that fraction, this fraction will increase if I increase the temperature.

When you are increasing the temperature the energetic collisions will increase. So that is why at high temperatures you will get high rate of reaction. But from kinetic theory of gases, we have an equation.

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The equation is k is proportional to T to the power of half e power minus E by R T.

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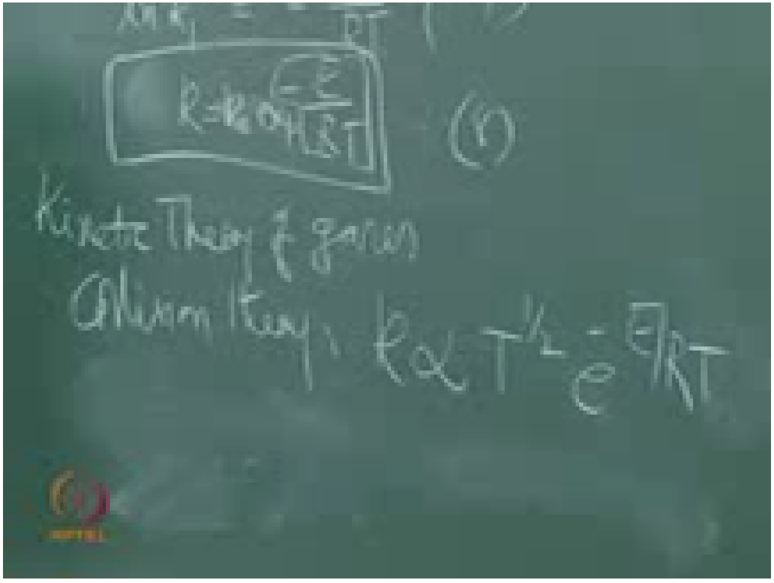

Or if I remove the proportionality constant, this may be some k naught dash T to the power of half, e power minus E by R T.

That is

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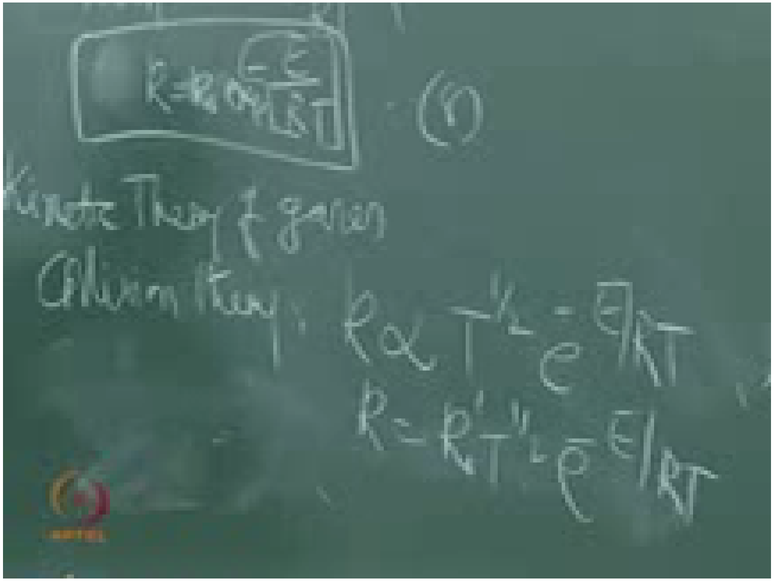

the equation, so equation 9, equation 10. Ok, so definitely this is different than

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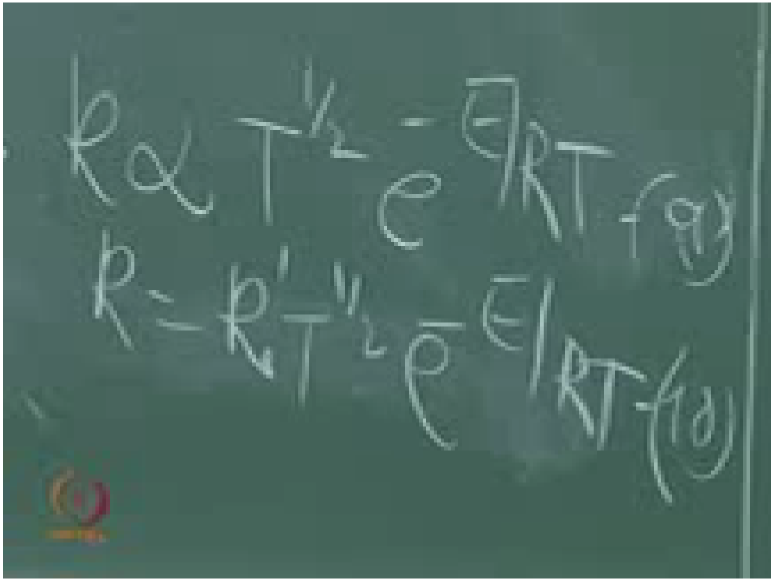

$$k \propto T^{1/2} e^{-E/RT} \quad (9)$$

$$k = k' T^{1/2} e^{-E/RT} \quad (10)$$

the thermodynamic relation, right, Ok good. So now the next one. Next one, because here I am not going into details. I am just telling you, we have kinetic theory, there is lot of information, this is very, very, very old one, I think 100 years back also they did that, Ok. So finally there are equations and all that.

But our final information what require is, because we need an equation for k value which is depending on temperature. So this is information what you have to remember. Or if you want to remember I think actual derivations also you can remember, right? Physical chemistry people would have done it already, good, so then.

Yeah the next one is transition state theory. What is the assumption in transition state theory?

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Anyone who has come across this transition state theory. Transition state theory Ok, yeah that tells us if I have again you know a reaction A plus B going to R

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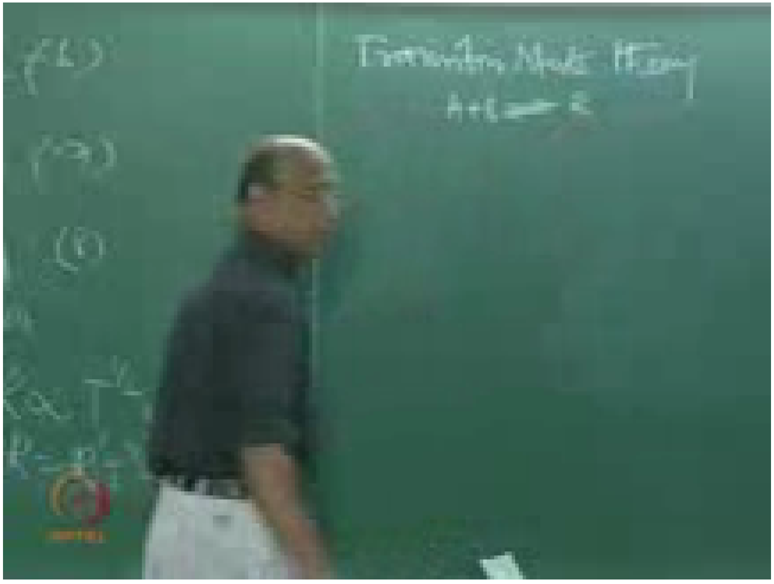

here our imagination is that first A and B again will collide, that collisions must be there because they are moving; they have to collide, Ok. No gas will be at rest unless you go to

(Professor – student conversation starts)

Student: Zero Kelvin

Professor: Zero Kelvin, Ok.

(Professor – student conversation ends)

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Because

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A and B is always moving you will have the collisions. Now those collisions will not give you directly R, right? Yeah then what

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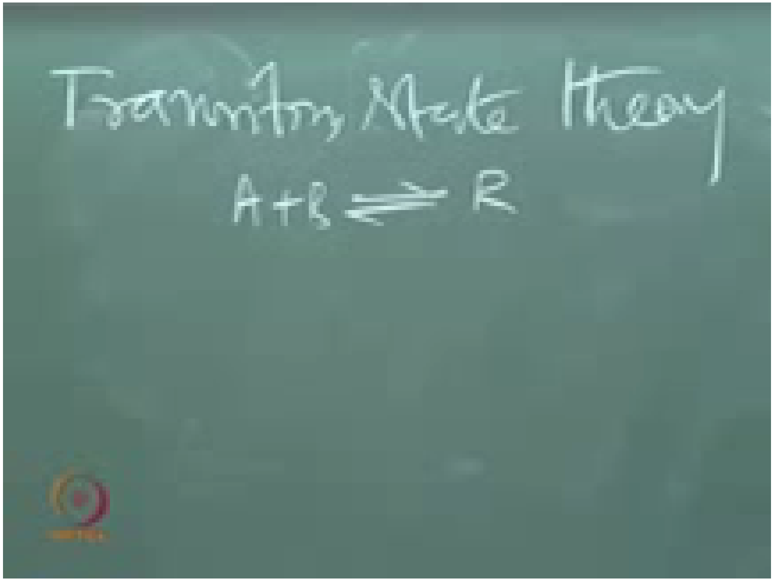

it will give? Our assumption is that, that is leading to some kind of intermediate. Then intermediate will have sufficient energy. And then that will decompose to product. This is another imagination. You see you can have for the same experimental data, thousands of models.

When you conduct for example, A plus B going to R, experimental data, right? And you measure what is the K values or what are the conversions or rates, rates you can measure there. So now you go to collision theory and now imagine that A plus B getting collided and then you will have rate of reaction, some conversion, or rate of reaction can be expressed now, in terms of collision theory, you will have a rate equation, right?

So similarly now you have another model in your mind. All models are in our mind. Why? Why they are in our mind?

(Professor – student conversation starts)
Student: They are only assumptions, they are not real.
Professor: Yeah. Because exactly what is happening there, it is there or not I do not know. That is why now I am imagining probably this is what is happening.
(Professor – student conversation ends)

Like exactly, I am looking at you, I am thinking that I am doing a very good job but I think, by looking at you but I think you may not understood anything till now what I have talked. 17

class over. Ok, so my concept, you know in my mind what I am thinking is that you may be understanding. But actually you feel that you may not have understood anything.

How do I find out? Test. That is experiment. Correct no? Similarly here also, you have any number of models and now final test is doing experiment. So once you have experiment, 0:33:08.7 does, he cannot get the same conditions, he won't get, he should not get different r A because that means you do not know how to do the experiment.

If you differently get at different places, but conditions are same, exactly same concentration, same temperatures, if you maintain all that, anywhere in the world you do, you should get the, that is constant. Experimental data is the truth, but your model is not the truth. Why?

This imagination of A plus B giving us intermediate product, then it is decomposing to the final product. All that is a model. Your experimental data, if it verifies there, then you can say that Ok, my transition theory is right. But in this case, if someone tries with, Ok 0:33:54.2 tries with collision and Sushmita tries with transition state theory, Ok.

What do you do if both are correct in theory? In experiments they may be right, no. So this is what is the current problem also because these models approximately tally all these. They tally a little bit. It is not that one theory is perfect for this; another theory is perfect for this. So that is the reason why even now we do not understand what is actual molecular collisions and then giving us the product.

That is why we are lucky as chemical engineers because we do not have to worry. Why? At the end only I will see whether I get conversion or not. How they are reacting, who cares, Ok, yeah, chemists they have to break their mind saying that Ok, no this molecule is not reacting, that molecule is not reacting, because they are poor fellows, they have to find out.

Because our objective is to produce the chemicals somehow Ok, yeah that is the reason but still, we should know the theory. That is why we are telling that this transition state theory, and one imagination as I told you here is A plus B giving me, that is again a reversible step, A B star that is the intermediate, then this intermediate is, it is not reversible, intermediate is, this is again an assumption, so now I have here k 1, k 2, k 3 yeah Ok all these constants, right.

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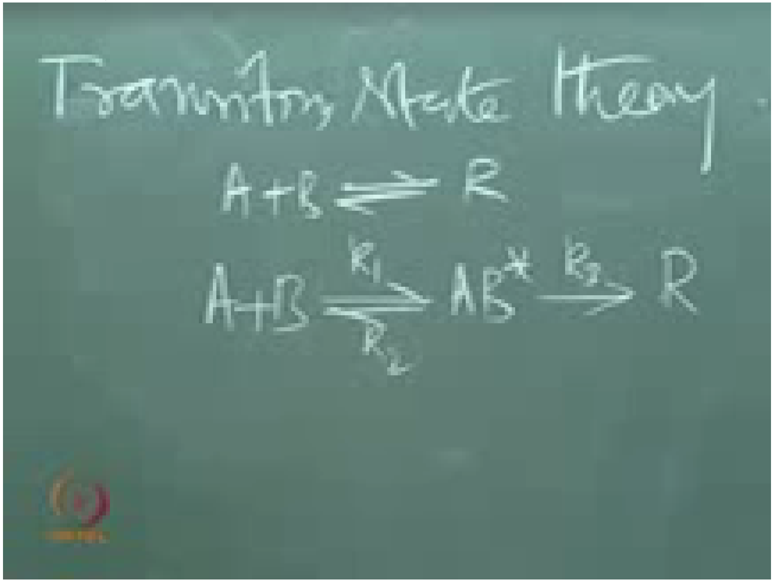

So intermediates is not permanently there because after some time that will disappear. But temporarily it will form and then go away. So then another imagination for this is that I have energy and here we have reaction path, reaction coordinates what you say and then reaction coordinates what we will say then we will have a little bit of dip here, may be energy, yeah Ok, this may be one situation

And another situation you have again energy reaction for, so it may be starting at low, very small, for some reactions you do not see that also much, yeah, like this. So this one, this one is E 1, this one is E 2 energy Ok and here also I have this one E 1, this one E 2, did you see this diagram earlier? And here we have the activated complex.

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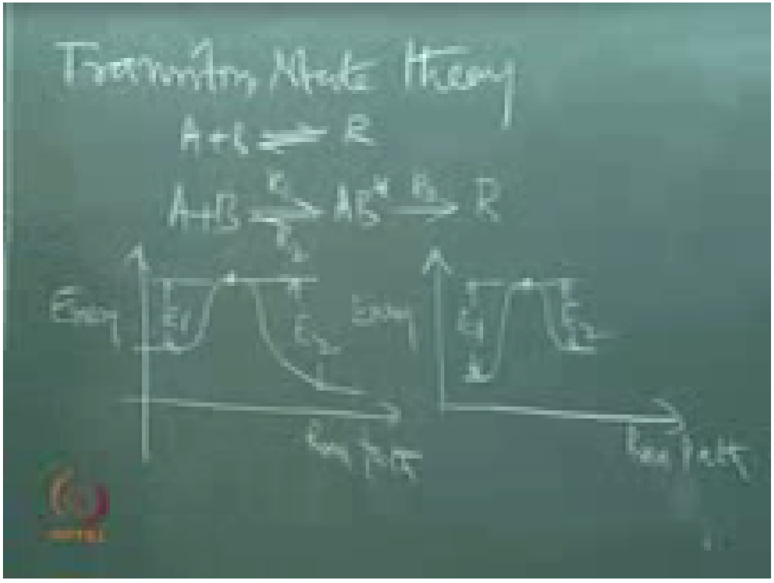

So it needs some energy to reach this peak and from there it is decomposing, Ok. Energy decreasing, that activated complex energy is decreasing so then you will have in this case one type of reaction, this case another type of reaction Ok. It is E 1 minus E 2. Can you tell which is exothermic reaction, which is endothermic reaction? First one is...

(Professor – student conversation starts)
Student: Exothermic
Professor: Exothermic, why? e 1 minus e 2 is
Student: Energy level is less.
Student: Negative
Professor: Yeah, exactly so this is minus delta H R so which is exo, and this one is minu/minus, Ok delta H R, no, yeah plus delta H R which is endo.
(Professor – student conversation ends)

This diagram is also

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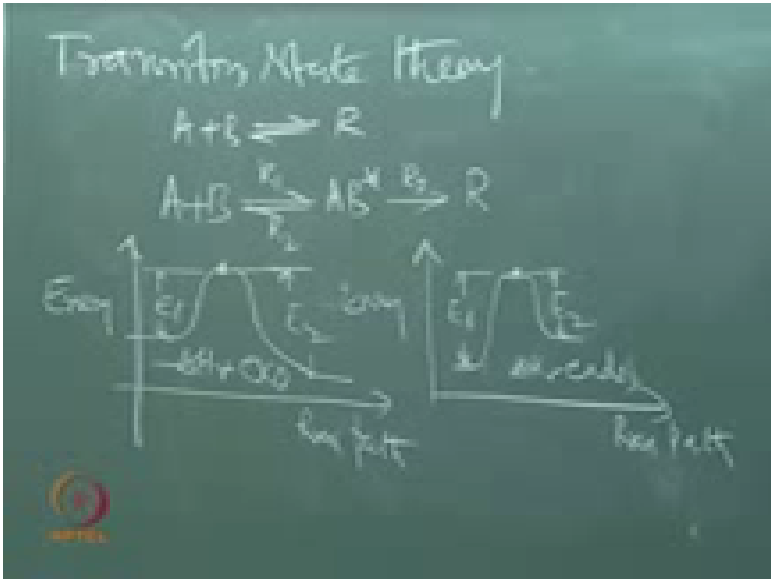

important, because sometimes in the interviews and all that, I may also ask in surprise test because surprise test is only for 5 minutes. You have to clearly write, draw the reaction coordinates, and if you do not draw anything and then only draw those two lines, I do not give any marks. I am just telling you. Good. So this is the one.

So this is another way of imagining the reaction rate but we are not going to that kind of so much details, right but our functionality here is k is proportional to, T to the power of, sorry not T to the power of, T into minus E by R T. This is another equation. So this is equation 11, and this also k is k naught dash, for example T E power minus E by R T, this is, yeah.

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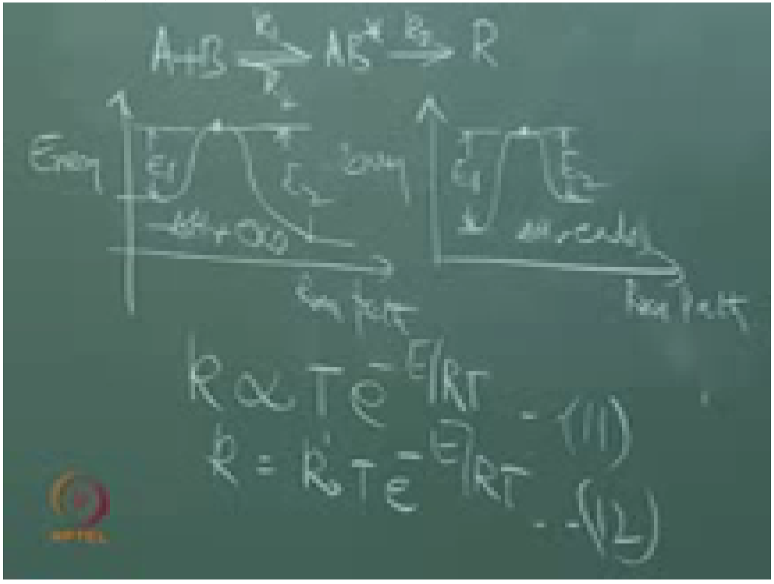

So now you see you have the real problem. That is why I told you kinetics are really difficult for us. Ok. So now you have 3 equations, one from thermodynamics which gives me nice equation like this.

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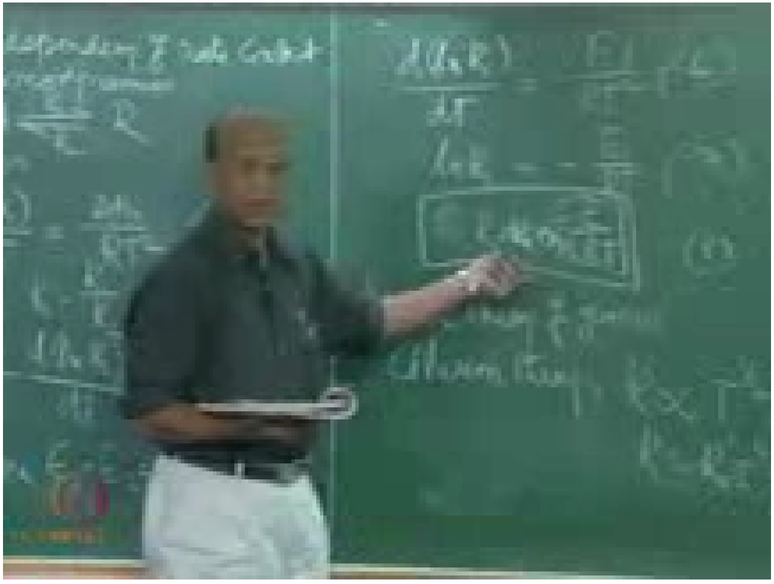

One from collision theory which gives T to the power half, some constant,

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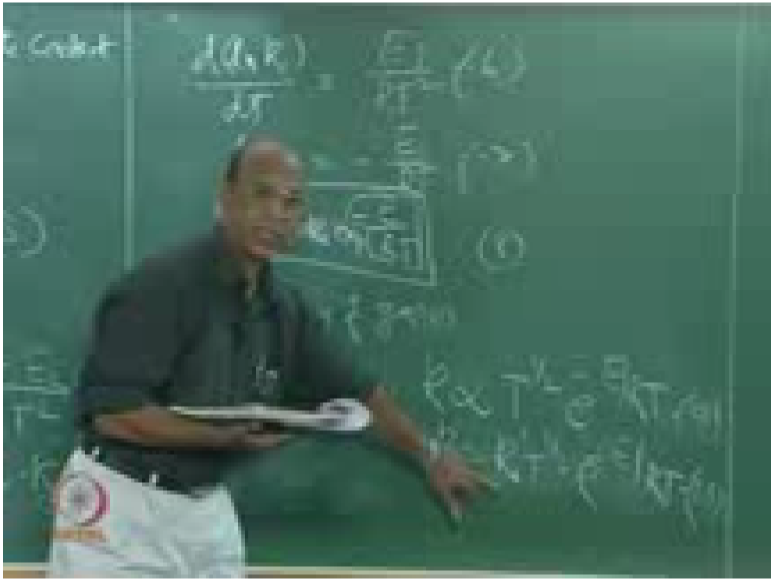

right and here another

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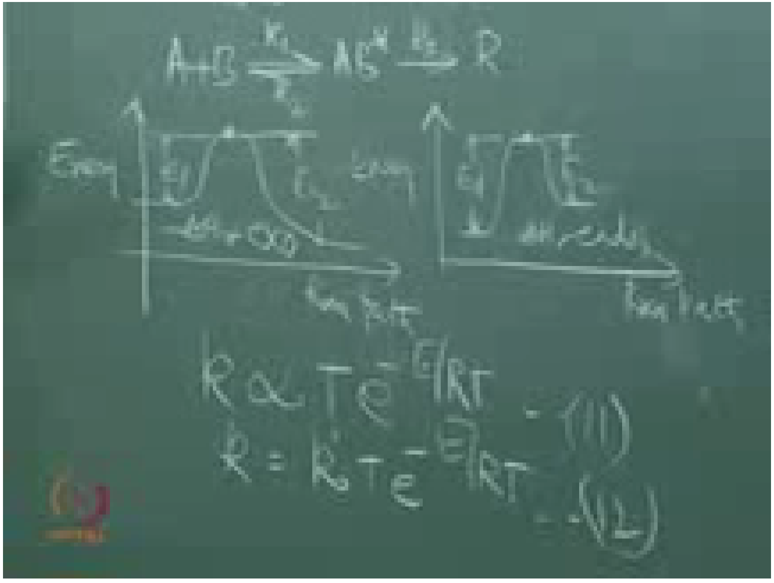

equation from transition state theory with you know K is proportional to T. This is here; K is proportional to T to the power of half. This one here, K is proportional to T to the power of zero. Ok, which one is right, we do not know, Ok.

So people say that, Arrhenius was very smart and then he told that, it does not matter. So the variation of this term, because exponential term is much, much higher compared to the variation of this term, K zero into T to the power half the T, so you take this entire thing as a constant which is independent of temperature.

So that means the variation in that constant will not be, it is not much. So that is why, finally Arrhenius equation in this format it is accepted. And that is what we use 99 point 9 9 times in all C R E books. Ok, in all C R E books. Good.

So now at least you have one term very confidently known as that f 1 T, function of you know, function of you know, temperature, f 1 that term, now we are taking only Arrhenius equation term. That means K equal to K naught into e power minus E by R T. People call that K zero as collision factor, yeah, so all kinds of things we can,

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yeah. Ok.

So finally that term f 1 of T will be k naught e power minus E by R T, right. I mean actually we can also prove that, you know Levenspiel does that, I do not know in which volume he has done it. Yeah he does something like this.

k equal to k naught, e to the power of M, yeah, T to the power of M into e power minus E by R T,

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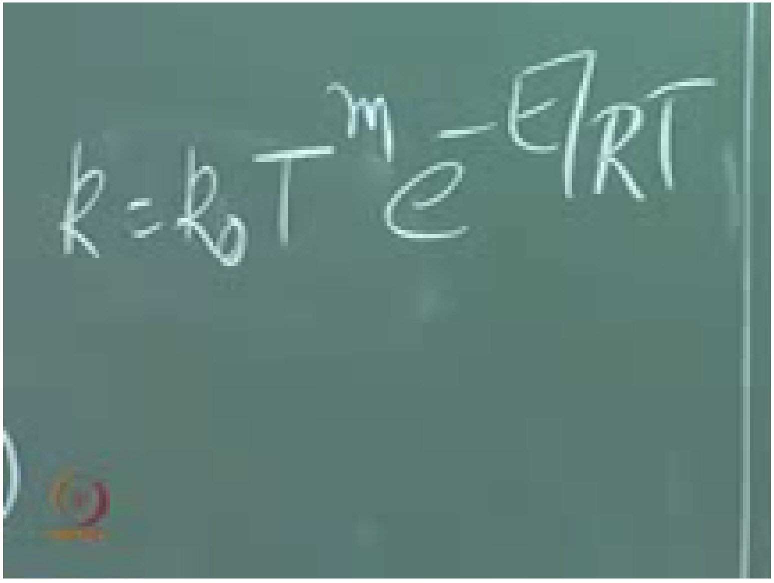

$$k = k_0 T^m e^{-E/RT}$$

yeah and differentiate with respect to, no take log for, lns of this, for ln K equal to ln K naught plus M ln T plus, correct, minus E by R T. Now differentiate this with respect to, with respect to temperature.

Ok. d sorry, thank you, thank you, who is telling that? d l n, oh Pooja, Ok, d ln k very nice,

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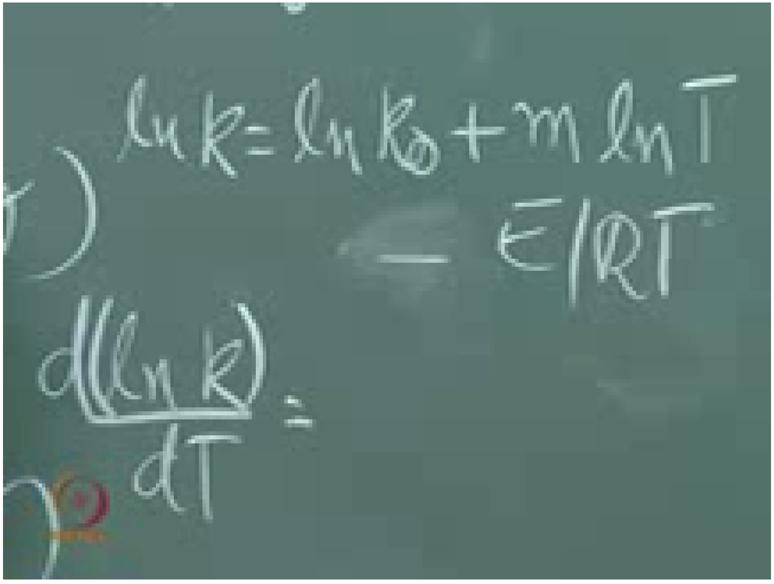

$$\ln k = \ln k_0 + m \ln T - E/RT$$

$$\frac{d(\ln k)}{dT} =$$

so d ln k so then the equation what you get is, yeah I will leave it to you, Ok. I will just leave it to you. Then finally this can be written as m R T plus e by R T square, because I may ask this also in the surprise test. That is why that mathematical details I have to see in your 0:42:54.1, Ok so I lost equation, this is 12, this is 13, this is 14, side business I have started here. Ok. This is 15, this is 16, Ok. So now

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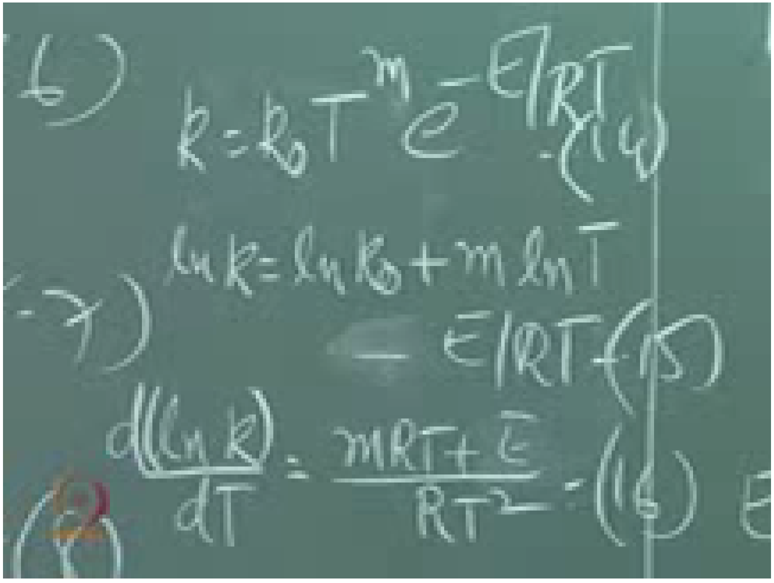

$$k = k_0 T^m e^{-E/RT} \quad (14)$$

$$\ln k = \ln k_0 + m \ln T - E/RT \quad (15)$$

$$\frac{d(\ln k)}{dT} = \frac{mRT + E}{RT^2} \quad (16)$$

for many reactions what they found was m R T is almost negligible, approximately, I do not say zero, Ok, it is negligible when compared to, I think I will write here, Ok, negligible compared to, compared to E.

This is very crucial. m R T,

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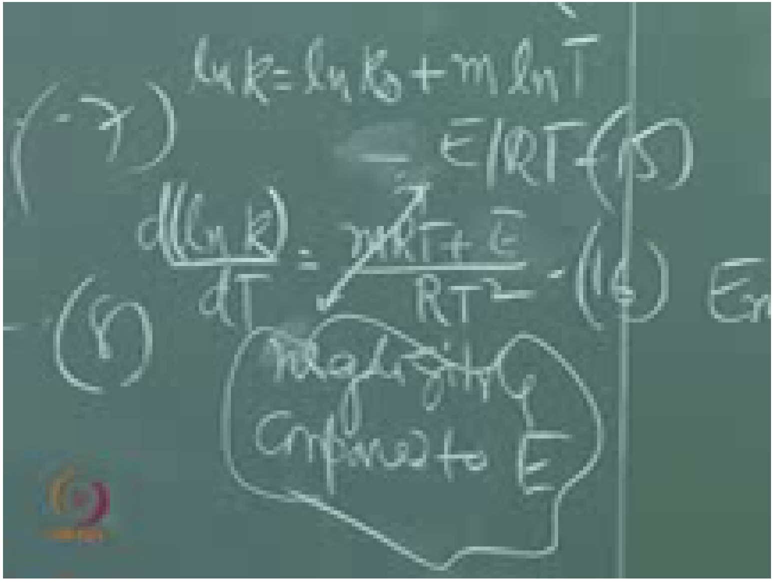

$$\ln k = \ln k_0 + m \ln T - E/RT \quad (15)$$

$$\frac{d(\ln k)}{dT} = \frac{mRT + E}{RT^2} \quad (16)$$

negligible compared to E

m multiplied by R, m is that exponent, Ok, we think that m is only, either it can be zero, zero means Arrhenius equation, half means collision, 1 means, yeah it seems there are some models which m is 4.

In some models, kinetic models, kinetic theory of gases, some more models will also give you not only half and 1, I think sometimes I have this information, which model I do not know, but I have that, you know sometimes it can go to even 3 also, 3 and 4 also, Ok but anyway we are happy to ignore this so that we have this kind of rate expression which is nothing but k rate constant equal to k naught e power minus E by R T. So this is the final term correct.

(Professor – student conversation starts)
Student: 0:44:42.6
Professor: Yes, whole R T square, Arrhenius. Whole R T square that is why you have to derive that and then you find out, Ok. You derive that. Do not ask me now. Ok.
(Professor – student conversation ends)

Because if I ask, I will tell the answer and you will read the answer. Because I also want people you know, when they do not write also, I am happy. Because correction is less. Ok anyway, good. Anyway it is very simple. You can just differentiate and then take the L C M and all that you will get it. Ok. I am not really trying to say that you should not write anything. I am happy if all of you get S, really, not by copying and all that. Ok, good, Ok.

So this is the one what we have, in that first, you know, two parts, we have the K part, f 1 t and we have the other part is f 2 C A. Now what kind of thing, what kind of format do you get for this f 1, f 2 C A.

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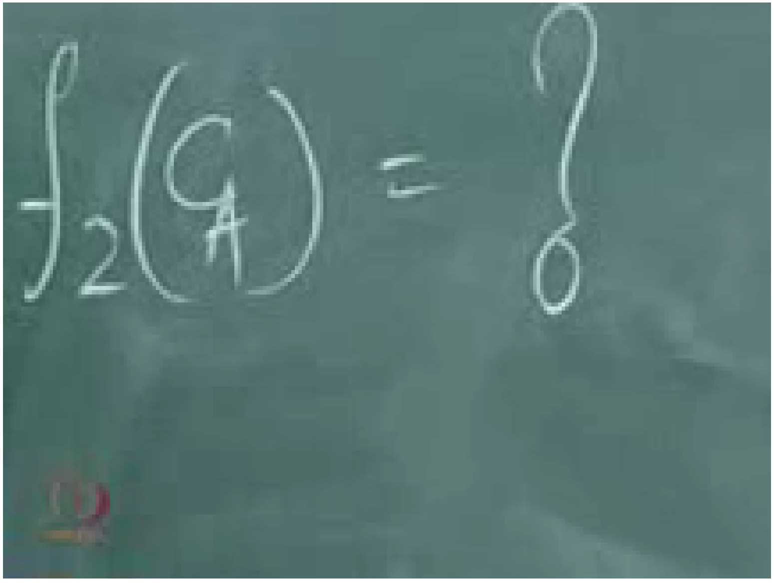

Ok, if you are very lucky then this will be simple, Ok 1. 1 means if I have rate equation, minus r A equal to simply k, C A equal to 1, C A to the power of zero. So it is zero order equation. Ok. So zero. That is why it is 1, we have to, yes

(Professor – student conversation starts)

Student: 0:46:12.7

Professor: There is no fourth order. In nature...

(Refer Slide Time: 46:17)

Student: 0:46:16.8... 2 means 2 molecules are colliding. 1...

Professor: If they are elementary reactions. That is very, very important.

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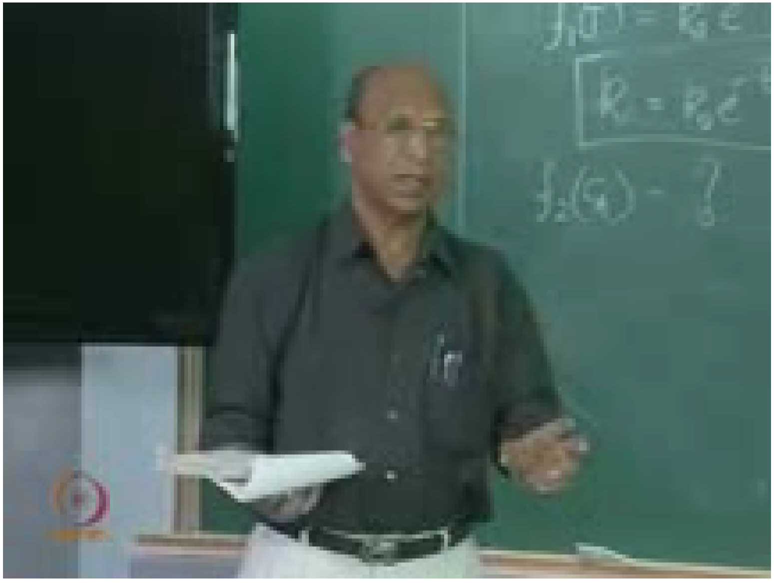

Elementary reactions means they are behaving the way they are supposed to behave, right? (Professor – student conversation ends)

But if they are not elementary, then non-elementary means that kind of mechanism should come. Which one? A plus B going to again some intermediate, now it is straight forward, that intermediate is going to only directly R. So that fellow will go to something else, Ok.

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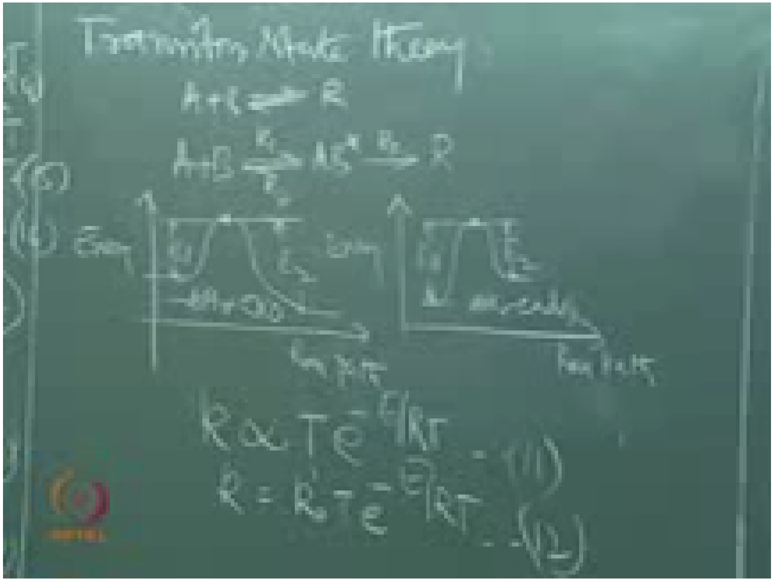

So like that you will have 4, 5 steps.

The best example is H B r decomposition reaction no? Yeah, H 2 plus B r 2 giving you yeah 2 H B r, it is not decomposition, it is the actual reaction. There how many steps, and also there are some 4, 5 types of mechanisms which are possible but experimental data is only 1. So you have to quit one of those things but that anyway I will tell you a little bit later.

So this is one, or this can be, C A, Ok, I am telling about only that part because we told that minus r A is f 1 T into f 2 C A. So now this one I know. This is equal to k, where k equal to this. Oh this equation number 14, 14 na, oh 17 yeah,

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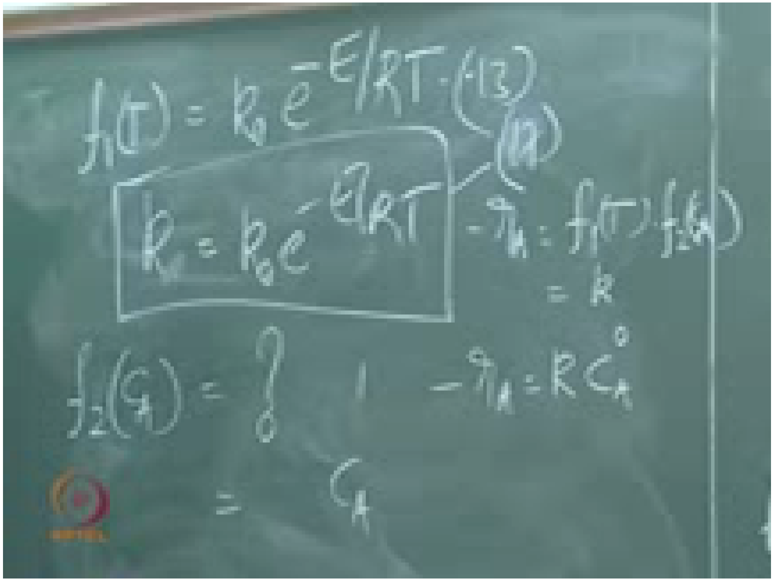

17 good.

So now this we are focusing, that can be either f 1, f 2 C A can be C A, or C A square or C A cube, C A cube or in general it may be C A to the power of n, where n can be zero to

(Professor – student conversation starts)
Student: 3
Professor: Zero to 3, it can also be negative. But negative orders we have not observed again, in nature.
(Professor – student conversation ends)

Ok, so that is why it can be, but it need not be integer.

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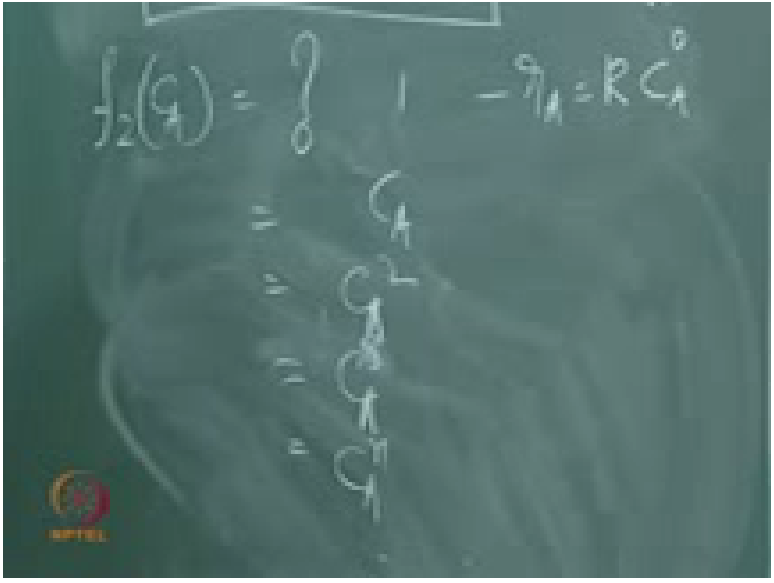

It can be even fraction also. So that is why I told you it is very, very difficult, the kinetics part in reaction engineering, if unfortunately if you want to design a reactor on your own from, from scratch, right.

So from scratch means you do not know how much you have to produce, that is very easy to get. Then you do not know what kind of, you know the kinetic, stoichiometric equation but you do not know what is the rate of reaction minus r A, what is the order and all that, so you have to conduct the rate, I mean you have to conduct the experiment to find out what is the rate, and what form you will get.

You need not get all the time k into C A. You may get any kind of you know, crazy equation. Like you may also have C A by k plus C A. Or Ok, some other form. K means again you may think rate constant. Yeah, so M plus C A,

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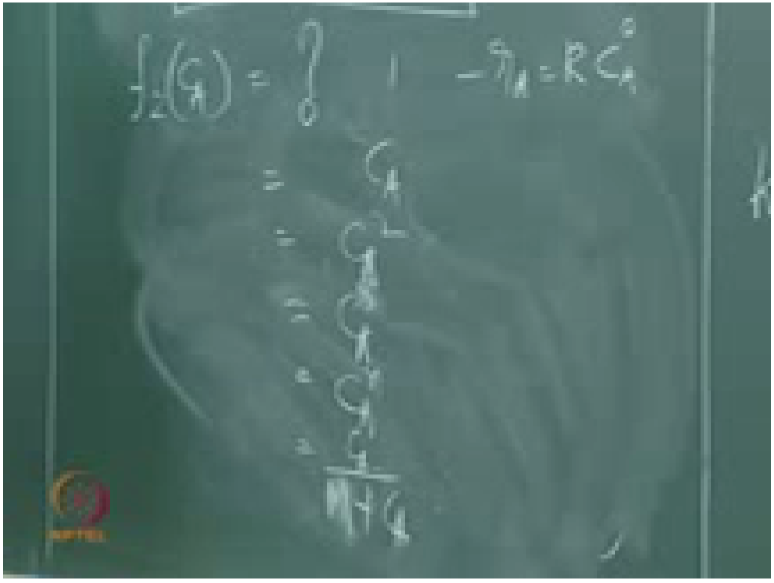

that format. So that is why absolutely you do not have any idea of you know what kind of thing you are going to get when you have this kind of 0:49:34.6, you know, in kinetics.

That is why that is much more difficult for us to deal with when compared to contacting. That is why I started contacting. But you know, I could have started this or that, does not matter but this time I started with contacting so that you will have 3 reactors and any of them you can use to find out minus r A, this one, minus r A, minus r A is f 1 T, f 2 C A. Need not be always batch reactor.

It can be even; in fact C S T R is the best reactor to find out kinetics. Ok. So now what we have to discuss is that, yes, if someone gives me I have a reaction stoichiometric equation, OK, A l plus B l giving me R l. Now

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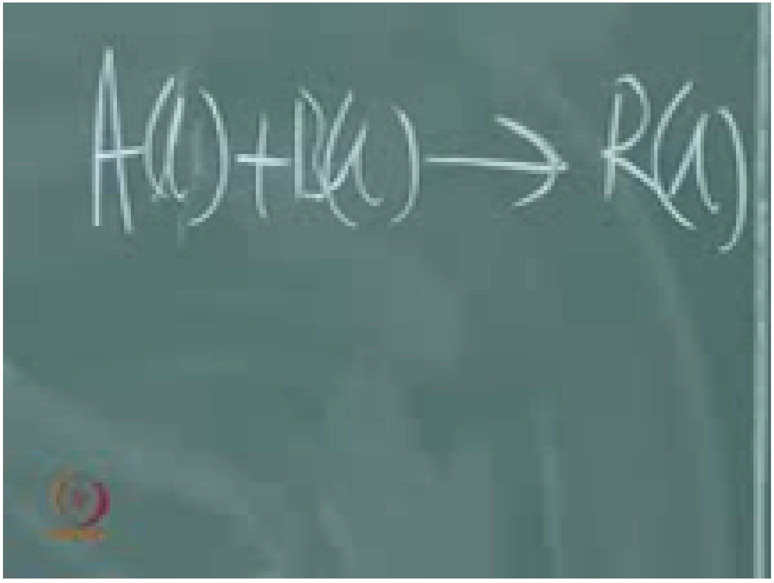

I have to find out the rate, minus r A. This minus r A I have decomposed into these two, f 1 T and f 2 C A. But this fellow I know very well. So this is nothing but minus E by R T.
But still I do not know C A. How do I do that?

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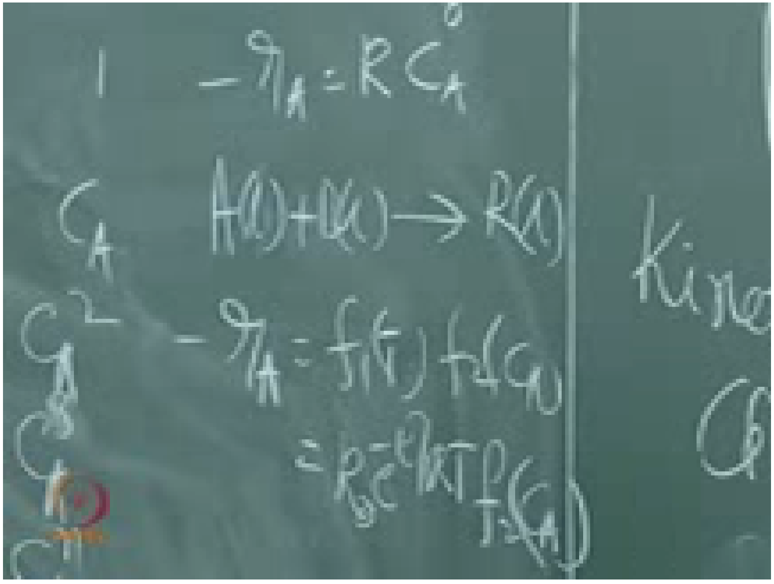

We have to do the experiment, Ok. Suppose if I give you this A plus B going to R how do you conduct the experiment? By the way what for are you conducting the experiment?

(Professor – student conversation starts)

Student: 0:51:09.6

Professor: To find out the

Student: 0:51:11.2

Professor: To find out the rate. You should have that

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minus r A.

(Professor – student conversation ends)

This is the problem with all our

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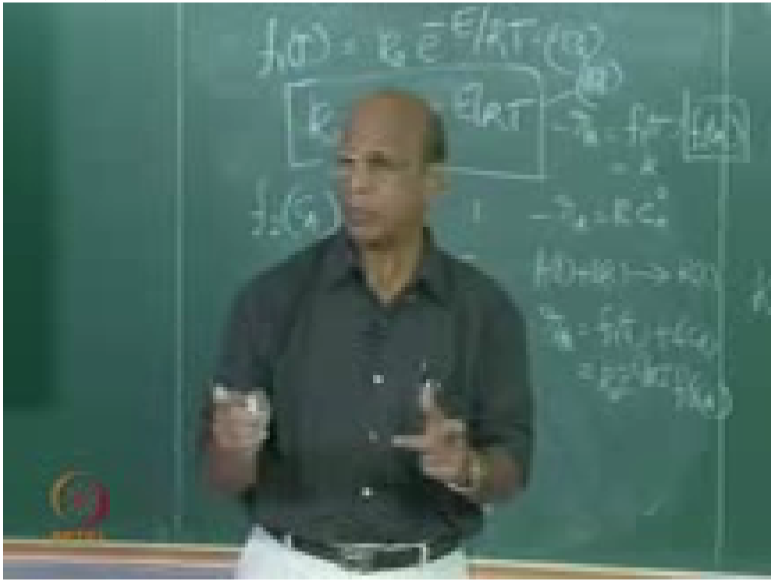

labs. You know without telling what is the exact aim, you know, without discussion much, we give that, you know to find A this much. Find kinetics. But we do not know, we do not explain to you why we have to find the kinetics and what are the problems in finding kinetics and all that. And then we will also tell that, Ok, go to lab, you have a reactor; you have reactant A, reactant what are the famous in the world, reactants?

(Professor – student conversation starts)

Student: Sodium hydroxide

Professor: Sodium hydroxide and?

Student: Ethyl

Professor: 90 percent of the labs in the world conduct sodium hydroxide and ethyl

Student: Acetate

Professor: Acetate. That is called esterification reaction? Yeah.

Student: It is very safe reactant...

Professor: Yeah, safe means what is going to kill you, is it going to kill you or what?

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Student: (laugh)

Student: well-behaved equation 0:52:20.1

Professor: Not only that. All that is apart,

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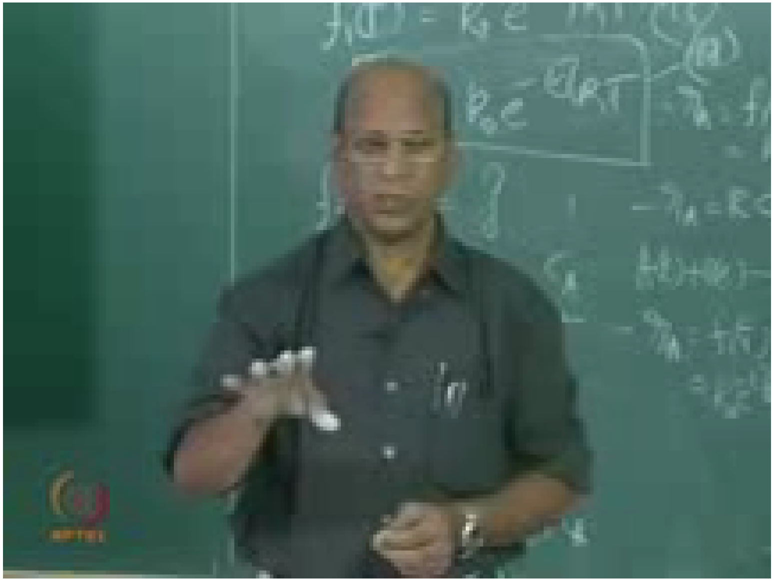

the kinetics are known to us. Whether you are right or wrong you should know. That is the reason why. I think well-behaved equation as he said, all those things are right but apart from that we know the kinetics. That is also one drawback. Ok because we know the kinetics, you somehow get the answer. Ok you do not really get the answer. Somehow...

Student: Analysis

Professor: Analysis is also very, but if you do it, no. Because you know K is this much at 30 degrees Centigrade, somehow you will get it.

(Professor – student conversation ends)

Yeah but if I do not know all that and then I am only talking about a totally new, new stoichiometric equation how do you go about that? Everything is a problem, I tell you. I can give straightaway M Tech or M S or P h D if I give you I think 2 components and then go to lab and then you conduct the experiment on your own. We do not tell anything. Everything you have to do it.

You have to choose what is the size of the container. You have to choose the temperature. You have to choose the concentration. You have to choose the analytical method. I will tell you, I think it is very, very, very difficult. In fact we are not training you in that way.

That is why at least you know I I T Madras, they may not listen to me when I say in our department, but I told in Amrita University Sir, for M tech students do not tell anything. Ask them to go and do some experiments in the lab. Let them define their own experiment.

I want to do only flow-through pipes. Ok, or... that means he has to choose the pipe, he has to choose the flow rate, he has to construct that you know all that connections, pump and all that, pumping and all that, then a distillation column, means a small distillation column he has to do it. Then you learn a lot.

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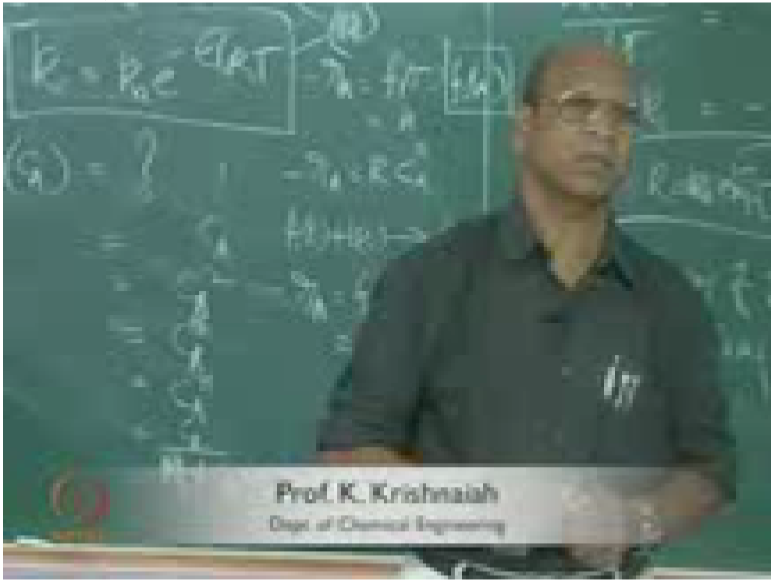

But unfortunately in no other educational institutions we are doing that, allowing you to do all that. We tried in our I I T Madras, experimentation. So we gave Fluid Mechanics labs for B Tech students long time back. I do not know still they are breaking?

So you know, there was a column like for example pipes were there, fluid mechanics, no. Or fluidized bed was there. So what they did was they removed all the pipes. They do not know how to put it back again. So they waited 2 days, 3 days, 4 days. Nothing is coming. Then mechanic has to come and then put it back.

Destroying is very easy. Creating entropy is very easy but decreasing entropy is very difficult, right? I do not know whether you understood what I said. Yeah creating entropy, we are all entropy generators. One small bomb here in this room, that is all, this will disappear and you will get the maximum disorder. When you have maximum disorder, what will be the entropy? Yeah, very high.

But now order comes if I ask you again, Ok, you have exploded that building, now you construct in the same way. Same shape you bring it. You know how much time it takes, how much energy required. That is what is the difficulty to go in that direction, you know. The decreasing entropy. The increasing entropy is very easy. That is what is happening throughout the world, increasing entropy.

Not only, I think that is why, the thermodynamics is a philosophical subject. It is not destroying building or increasing disorder by moving or by sending cars and you know all vehicles and all that. Not only that. It is philosophically also, our brain also goes for more and more disorder.

That is why 100 years back the sincerity, the kind of people what we had, all those people when you think at least you know, you would not seen them but at least we have some information on that. And how ethical they are, how good they are, how they were treating anyone when they come, you know, all our, anywhere on this planet I tell you.