Fundamentals Of Combustion (Part 1)
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Lecture – 24
Specific reaction rate and Arrhenius law

Let us start this lecture with a thought process from William Ramsay. He says the country which is in advance of the rest of the world in chemistry will also be the foremost in wealth and in general prosperity.

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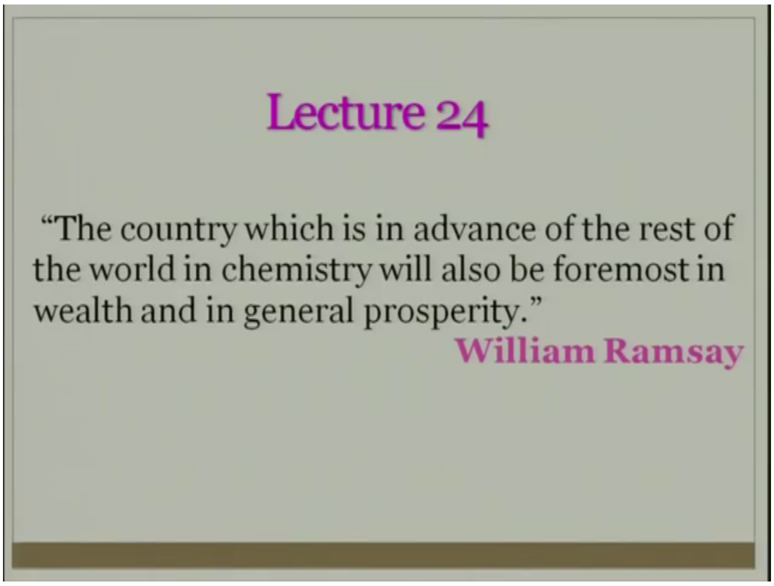

Lecture 24

"The country which is in advance of the rest of the world in chemistry will also be foremost in wealth and in general prosperity."
William Ramsay

I would like to draw your attention to a book which is basically known as Hindu chemistry by, it was written by P C Roy long time back right. If it is there in Google you can see and then look at it.

So, we are basically discussing about reaction rate coefficient or the specific reaction rate in the last lecture, and we have derived it and we have also looked at how one can use the collision theory to do that and it considering the molecular theory of gases. And we will now do on more on that that is basically what we look at the k. If you look at k; we have look at k, we have small k k is basically A e power to the RuT.

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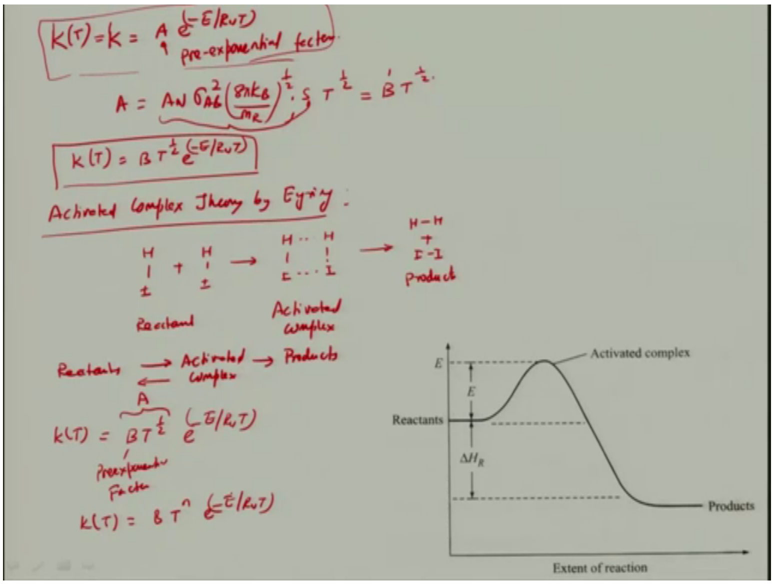

$$\boxed{k(T) = k = A\, e^{(-E/R_uT)}}$$

pre-exponential factor

$$A = \underbrace{A_N \sigma_{AB}^2 \left(\frac{8\pi k_B}{m_R}\right)^{\frac{1}{2}} \cdot S}\, T^{\frac{1}{2}} = B\, T^{\frac{1}{2}}.$$

$$\boxed{k(T) = B\, T^{\frac{1}{2}} e^{(-E/R_uT)}}$$

Activated Complex Theory by Eyring:

$$H\text{–}I + H\text{–}I \rightarrow H\cdots H,\ I\cdots I \rightarrow H\text{–}H + I\text{–}I$$

Reactant / Activated complex / Product

$$\text{Reactants} \rightleftarrows \text{Activated complex} \rightarrow \text{Products}$$

$$k(T) = \overbrace{B T^{\frac{1}{2}}}^{A}\, e^{(-E/R_uT)}$$

Preexponential Factor

$$k(T) = B\, T^{n}\, e^{(-E/R_uT)}$$

And k is not a constant k is a function of temperature right, and k is basically function of temperature I can write down k is a function of temperature right and A we call it as a sometime pre exponential factor is basically a constant, is it really a constant it is not ok. So, if you look at the this thing you will find out that it is basically A N, A if you recall A is A N sigma A B square 8 k B by there will be pi M relative into half into steric factor into T power to the half.

This you can consider till this ok. You can consider as what as a constant because steric factor is a constant for between molecule A and B and k B is Boltzmann constant and M R relative mass is also a constant right. And sigma A B already you know molecularly we are considering constant. But however, T is (Refer Time: 03:07). So, I can write down this basically B right which is a constant into T power to the half. So, therefore, I can write down k T is equal to B T power to the half e by RuT. We will be discussing little bit about this little later on I will show you how it can be.

But problem is this kind of expression for k what we have derived right, if you consider this portion it does not really tell us to how to evaluate the steric factor and how to evaluate the activation energy, right. So, these are the limitation of that. And for that of course, there is a very sophisticated theory what you have look at it using this quantum theories and people have talked about it. But I will not do much upon that , but I will just like to mention that people have talked about you know activated complex theory right, this is basically activated complex theory it is given by Eyring, right.

I will just touch upon it, it is a very complicated I will not get into. But what it says it assumes right there will be an intermediate activated complex which will lead to the product right. That means, there is a transient state of the reactants which can lead to decomposition of a you know product sorry of a molecule into its product right.

For example, if I consider that let us say hydrogen iodide right H this I plus I will consider another hydrogen iodide ok, it can go to this is basically reactant right. When they will collide each other right what will happen? This may coming like kind of things and I and this is the activated complex, it is leading to H H right 1 molecule plus I I, this is your product ; that means, this of course, gives a physical meaning to that of the activation energy. And if you look at if I can write down that reactants right is getting to activated complex. Keep in mind that even though it is going to activated complex it may return back to the reactant and then it will go to the product right. The activated complex can get into this side product side, but once it will get into product it cannot comeback unless there is another collision ok. Are you getting?

So, therefore, this is the way it can be really look at it that activation energy is required to take initial system to the activated complex. So, what I was telling that is basically reactants you know will be having it will having much higher energy level activation energy means, much higher energy level than the average energy a molecules will be possessing right. Then only it will be collision then it will get into activated complex and then it may return back I am like nothing (Refer Time: 07:34) fine.

But otherwise it will go to the product, and these kind of reaction is basically exothermic reaction endothermic reaction will be other way around the reactant will be here somewhere and product will be somewhere up like higher energy so that is the endothermic. So, it will be true for all the things right.

Now, if you look at this k values right I mean this is the reason I thought I will get into this. But some of you may be interest in that get into this activated complex theory by Erying, who is happens to be a novel (Refer Time: 08:10) and which is little complex I will not deal with that. This is the specific reaction rate constant. Keep in mind that generally people talk about this things in from arenas form of relationship, because from the experiment arenas really found out the values of e and R u right. So, what I was telling this k T is basically BT half into e power to the RuT.

And this you can get this values you know this is basic you know pre-exponential factor, factor. Generally this is in arenas form this a is known as pre-exponential factor. But for elementary reaction if you want to look at it and also take care of the T what you call coefficients this is a and this need not to be half of the time for elementary reactions right where you will conduct experiments and do that and this can be basically k T is equal to BT power to the let us say N T power to the RuT.

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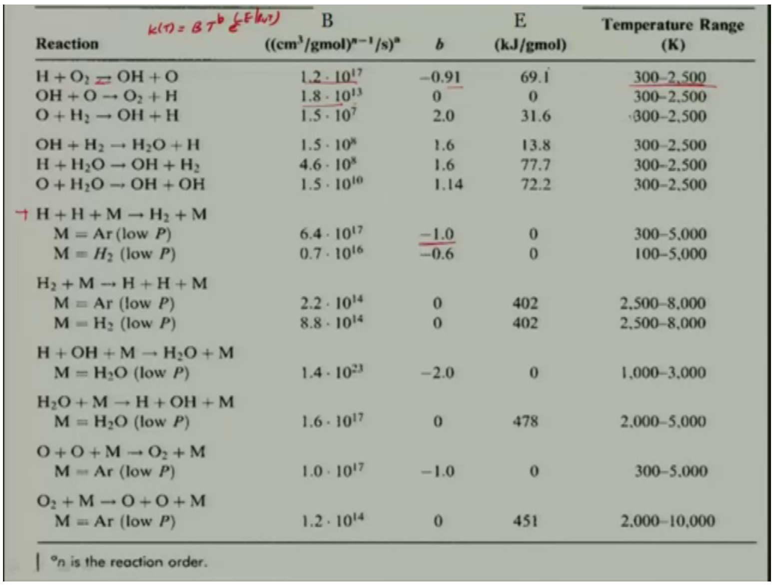

$k(T) = BT^b e^{-E/R_uT}$

Reaction	B $((cm^3/gmol)^{n-1}/s)^a$	b	E (kJ/gmol)	Temperature Range (K)
$H + O_2 \rightleftarrows OH + O$	$1.2 \cdot 10^{17}$	−0.91	69.1	300–2,500
$OH + O \rightarrow O_2 + H$	$1.8 \cdot 10^{13}$	0	0	300–2,500
$O + H_2 \rightarrow OH + H$	$1.5 \cdot 10^{7}$	2.0	31.6	300–2,500
$OH + H_2 \rightarrow H_2O + H$	$1.5 \cdot 10^{8}$	1.6	13.8	300–2,500
$H + H_2O \rightarrow OH + H_2$	$4.6 \cdot 10^{8}$	1.6	77.7	300–2,500
$O + H_2O \rightarrow OH + OH$	$1.5 \cdot 10^{10}$	1.14	72.2	300–2,500
$H + H + M \rightarrow H_2 + M$				
M = Ar (low P)	$6.4 \cdot 10^{17}$	−1.0	0	300–5,000
M = H_2 (low P)	$0.7 \cdot 10^{16}$	−0.6	0	100–5,000
$H_2 + M \rightarrow H + H + M$				
M = Ar (low P)	$2.2 \cdot 10^{14}$	0	402	2,500–8,000
M = H_2 (low P)	$8.8 \cdot 10^{14}$	0	402	2,500–8,000
$H + OH + M \rightarrow H_2O + M$				
M = H_2O (low P)	$1.4 \cdot 10^{23}$	−2.0	0	1,000–3,000
$H_2O + M \rightarrow H + OH + M$				
M = H_2O (low P)	$1.6 \cdot 10^{17}$	0	478	2,000–5,000
$O + O + M \rightarrow O_2 + M$				
M = Ar (low P)	$1.0 \cdot 10^{17}$	−1.0	0	300–5,000
$O_2 + M \rightarrow O + O + M$				
M = Ar (low P)	$1.2 \cdot 10^{14}$	0	451	2,000–10,000

[a] n is the reaction order.

I will show you some of the datas for hydrogen oxygen system right. If you look at this is what I will writing B right, this is nothing but your k T is equal to BT power to the I am sorry that will be B e power to the RuT. So, this datas are given, B is corresponding to this values let us say if I take HO 2, H reacting with oxygen getting into OH plus O, and B is basically 0.91, and e is your activation energy 69.1 kilo Joule per.

And this is in the range for 300 to 2500 Kelvin; that means, this will valid for that this people have got. Keep in mind that when you are reacting other around OH plus O going to the go O 2 plus O, basically this is the same reaction in the opposite direction of the first one, but however the B is different quite different of course, the capital B small b is 0 right, and this activation energy is 0 right and this again in the this range and of course, this are the various reactions I have shown here. Keep in mind that in this reaction particularly the M is the third body reactions, third body and it will be hold good for low pressure it will be organs right and hydrogen or any other stable basis.

And sometime this B also will be negative right ok, it will be also negative need not to be this thing. And of curse there are various reaction keep in mind that these all these values B and e, and generally people conduct experiments particularly for the forward reactions whenever possible and then they calculate from the equilibrium the backward reaction ok. Therefore, sometime e is coming 0 and this thing number one point I want to make.

The other things I will talk about is that this numbers you know if you look at two people are conducting experiments there might be 10 times different than the number. The error you know will be something 10 times, that why people jokingly oh this the things whatever you put and we do that for a global kinetics you know. What will do? We want to match the reaction rate or the heat release rate we will be playing with this B values or the A particularly free of (Refer Time: 12:18) factor and then try to match that is the another way.

Activation energy generally the error you know experimental error will be order of something 10 to 30 percent error. Sometimes you know if you look at that is the thing with which we are leaving today may be in future it will improving one, right. So, as I told although we related this pre exponential factor and exponential factors into the kinetic theory of gases or the collision theory, but people do conduct experiment and there is a arenas form of reaction, right.

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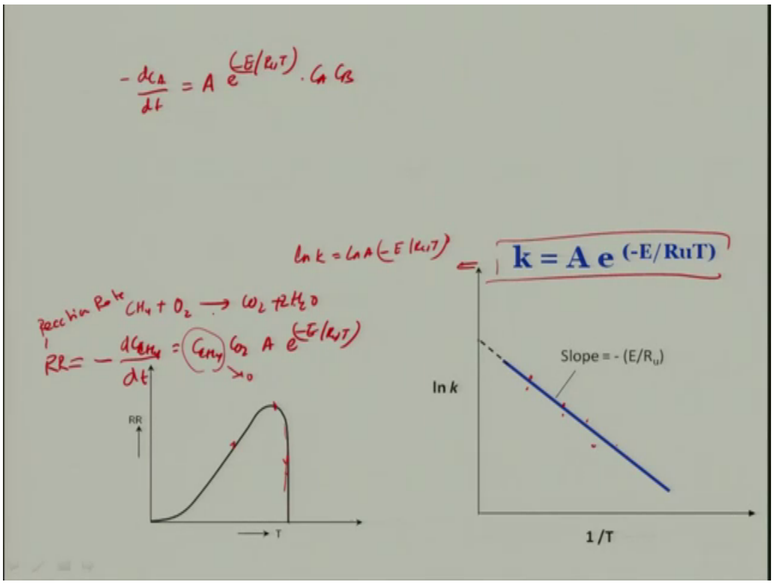

$$-\frac{dC_A}{dt} = A\, e^{(-E/R_uT)} \cdot C_A C_B$$

$$\ln k = \ln A\,(-E/R_uT)$$

$$k = A\, e^{(-E/R_uT)}$$

Reaction Rate $CH_4 + O_2 \rightarrow CO_2 + 2H_2O$

$$RR = -\frac{dC_{CH_4}}{dt} = C_{CH_4} C_{O_2} A\, e^{(-E/R_uT)}$$

What it is basically if I write down this is d C A by dt is nothing but A right e power to the RuT into C A, C B basically this portion is known as arenas form of reactions.

Now if I take the log of this right this, if I take a log what we will get? I will get ln k is equal to ln A minus e power to the E by RuT right. So, and if I will take this and plot this values ln by 1 over T right, I will get a slop E by R u right if you look at from this slop I can get E by H values right, and if I will get at this values here. What I will get? At this kind of things I will get basically A right. And from this one can really find out from experimental datas you can put it and get this values slop and then get this values A and then you will find out what it will be right, because this is corresponding to that.

Now, if there is a pre mixture like methane is reacting with oxygen is going to C O 2 and water right, then I can write down C H, C C H 4 is equal to C C H 4 C O 2 into A E by RuT right. Are you getting by dt, this is negative. Now, if I put this reaction rate and that is nothing, but your reaction rate, this is reaction rate and I will plot it I will get reaction rate versus temperatures because temperatures is the function right and particularly, but certain full air mixture right which is pre mixture I say then what will happen the reaction rate goes on increasing. Because temperature increasing that will increase right and once this methane or the oxygen any one of them right will be coming to the 0 what will happen, its moving to here and the reaction rate will be coming down graph and this is corresponding to the you know like your maximum activation energy what will be happen right.

So, this will be coming to 0 because why any one of them species is tending towards 0 tending toward 0 not 0 if it became 0 then it will come to the tensile even though temperature is higher, but reaction rate will be 0, because this is 0 getting into 0, right. So, that you can keep in mind and otherwise if the reaction rate is not the you know if it is not finite infinite full air mixture is there this will be reaction rate will be going up as the temperature increasing right, for a particular activation energy.

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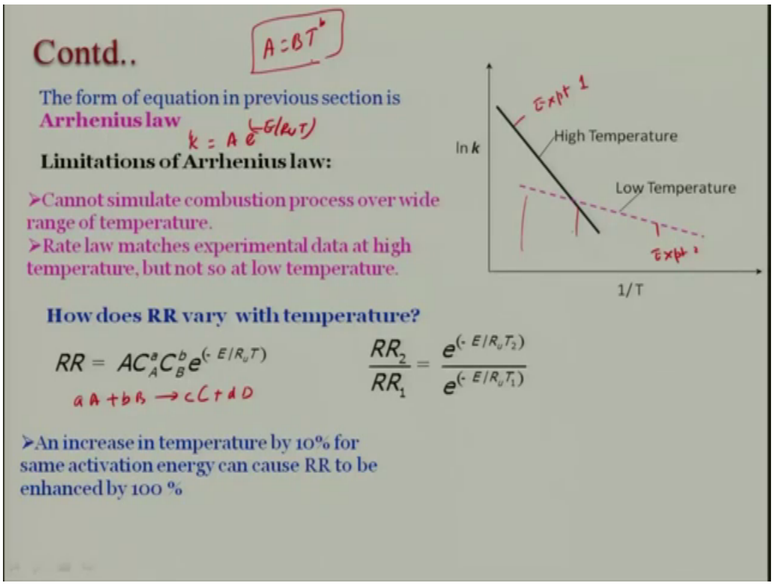

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$A = BT^b$

The form of equation in previous section is **Arrhenius law**

$k = A e^{(-E/R_u T)}$

Limitations of Arrhenius law:

- Cannot simulate combustion process over wide range of temperature.
- Rate law matches experimental data at high temperature, but not so at low temperature.

How does RR vary with temperature?

$$RR = A C_A^a C_B^b e^{(-E/R_u T)}$$

$aA + bB \rightarrow cC + dD$

$$\frac{RR_2}{RR_1} = \frac{e^{(-E/R_u T_2)}}{e^{(-E/R_u T_1)}}$$

- An increase in temperature by 10% for same activation energy can cause RR to be enhanced by 100 %

So, now this what you call the form of equation what we have seen is basically the Arrhenius law what they call that is k is equal to A RuT right. And this can be keep in mind that it is basically at a high temperature the slope will be higher and low temperature will be slope will be you know low right that is a reaction which will taking place.

Keep in mind that this is from one experiment right, and this may be you can get experiment number 2, means tie one you know this is experiment number 1, this is experiment number 2. There might be some common then which one is that you know that is the one you did not worry about because these are two different experiment from where you are getting data.

Now, let us look at how does this reaction rate vary with temperature right. If I consider this reaction rates C A of course, there is a coefficient and C B coefficient this is a you know in our case we have taken you know A as 1, B as 1 ok. Are you getting? If I write down as basically basically what we call if I write down a A plus b B going to c C plus d D then this will come into picture this a is the stoichiometric coefficient right.

And if I look at reaction two and reaction 1 corresponding to 2 different temperature T 1 T 2 I mean all are same for the same reaction this will cancel it out. So, you will getting E by RuT and keep in mind that there is a 10 percent increase for the same activation energy the reaction rate will enhance by almost 100 percent right, kind of things.

So, but their limitation of this Arrhenius is that it cannot stimulate combustion process over a wide range of temperature as I have explained right you know. And rate law matches well with experimental data with high temperature, but not at the low temperature right not are the in this low range this kind of things may not be look at it right. For the same experiment if you will do in the you know different temperature you will get a different slope.

So, therefore, one has to be little concern about that. But if it is just, if it is both the experiment at different then there is alright , but if it is the same reaction and you are only changing the temperature getting two different slope then therefore, one has to be careful. Yeah.

Student: Say timing also depending upon temperature.

A.

Student: A

A, here in this case Arrhenius form of reaction if does not recognize that as a temperature function temperature. But whereas, when you go to the elementary reactions right it will be recognizing T is function. See as I told this is a Arrhenius form, Arrhenius form does not as I told earlier A is equal to B, T power to the some coefficient right. But in this case Arrhenius does not recognize that as that because from experiment it will be difficult like then there is a put into a ballpark number that is a different between a Arrhenius and the elementary reaction rate coefficient. Are you getting?

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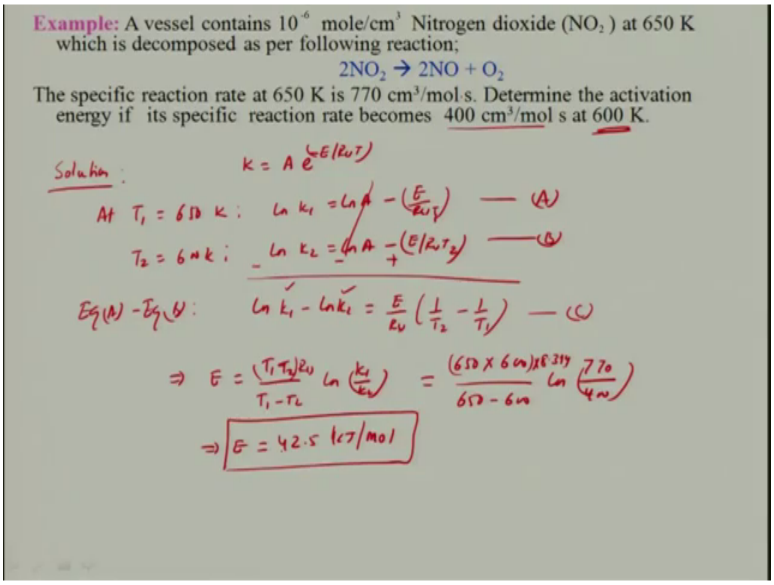

Example: A vessel contains 10^{-6} mole/cm^3 Nitrogen dioxide (NO_2) at 650 K which is decomposed as per following reaction;

$$2NO_2 \rightarrow 2NO + O_2$$

The specific reaction rate at 650 K is 770 cm^3/mol·s. Determine the activation energy if its specific reaction rate becomes 400 cm^3/mol s at 600 K.

Solution:

$$k = A e^{(-E/R_uT)}$$

At $T_1 = 650$ K: $\ln k_1 = \ln A - \left(\frac{E}{R_uT}\right)$ — (A)

$T_2 = 600$ K: $\underset{-}{}\ln k_2 = \underset{-}{\ln A}\ \underset{+}{-}(E/R_uT_2)$ — (B)

Eq(A) − Eq(B): $\ln k_1 - \ln k_2 = \frac{E}{R_u}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ — (C)

$$\Rightarrow E = \frac{(T_1T_2)R_u}{T_1 - T_2}\ln\left(\frac{k_1}{k_2}\right) = \frac{(650 \times 600) \times 8.314}{650 - 600}\ln\left(\frac{770}{400}\right)$$

$$\Rightarrow \boxed{E = 42.5\ \text{kJ/mol}}$$

So, let us take an example right. A vessel contains 10 power to minus 6 moles per meter cube of nitrogen oxide at 650 Kelvin and which is decomposed as for the following reaction 2 N O 2, is going to 2 N O plus O 2. And specific reaction rate at 650 Kelvin is 770 centimeter cube mole per second right and we will have to determine basically activation energy if its specific reaction rate becomes 400 cube at 600 Kelvin. Basically what is given? At two different temperature the reaction rate is given right.

So, we know that we know that k 1 right, at temperature T 1 right, at temperature T 1 is 650 Kelvin right. We know the what is that reaction rate k is equal to A T right this is the reaction rate. And at this one I give if take log this will be ln k 1 is equal to ln A minus E by RuT.

So, at T is equal to you know 600 Kelvin the reaction specific a reaction rate you know I can take it as a k 2 is equal to ln A minus E this is by RuT 2 right and in this case this will be 1. See if I say this is equation A and this is equation B right. So, if I will take just you know minus that one that will be this and this will be plus this will cancel it out and that I will get right if I say equation A minus equation B as ln k 1 minus ln k 2 is equal to what you call E by R u if I take this will be 1 by 2 minus 1 by T 1 right.

So, if you look at in this, this I can say this is equation 3. k 1 is known right, k 1 is given k 2 is given E is given, is given or not, E is not given we will have to find out. R u is known T is given right, T T 2 is given T 1 is given. So, you can find out activation energy. So, activation energy becomes T 1 T 2, T 1 minus T 2 R u ln k 1 by k 2, right.

If I substitute this values I will get T 1 is what? 650, into T 2 is 600 into 88.314 divided by T 1 is 650 minus 600 ln 770 divided by the 400. You will get something E is equal to 42.5 kilo Joule by mole. So, you can get very easily this activation energy and keep in mind that people do this things routine man at to find out at two different temperature what will be the activation energy right. And as I told the slope will be the your activation energy you can plot several data you can get.

Student: (Refer Time: 24:39).

So, with this I will stop over and then we will see in the next lecture about more about the elementary reactants.