

welcome to ah today's lecture on chemical kinetics  
if you remember yesterday what we were discussing was we were discussing the  
temperature dependence  
of reaction rates

so this is the topic we were discussing and when we you know started our  
chemical kinetics and we were progressing through the lectures we said that  
whatever rate laws  
and everything we were looking at or getting experimentally they were always  
done at a fixed  
temperature the reason being that temperature you know ah reaction rates do  
depend upon  
temperature that means temperature has influence on the rate of a reaction now  
then the

next step was is there a mathematical expression that can tell me how the rate  
varies as a function  
of temperature

so in that regard the you know the equation we are very familiar with is the  
arrhenius equation

so this is what we had started with yesterday you know at the last part when  
we  
were talking about the temperature dependence so the earliest equation goes as  
k which is the rate

constant is equal to a the pre exponential factor times exponential minus e a  
by r t right

and then in the next you know few minutes we talked about the relevance of  
this equation

and what the different terms out there mean now the last part of this last class  
we were focusing on or we

were trying to get an idea of how arrhenius came up with an expression like  
this right and  
doing

so what we said was we started with this vant of expression  
so we will just

write again we say that vantov in a famous book office use this  
expression c over del t at constant pre

so this k c is your equivalent constant expression  
in terms of concentrations which we saw before this is equal to delta u naught  
over r t square

right and we had given this an equation number of two after that we wrote down  
an equivalent

reaction a plus b going to p plus q and we said that ok k c can be written in  
the form

of k 1 over k minus 1 ok i am skipping all the intervening steps because we  
had done this in the  
last class

so please refer back to the last class lecture notes and discussion where  
what is k1

k1 is the rate constant for the reaction in the forward direction and k minus  
1 as the minus sign

is indicating is a change in direction that means k minus 1 is a rate constant  
for the reaction in  
the backward direction

so forward means a plus b going to p plus q and backward means p plus q u  
going back to a plus b

so now once we had this what we did was you see in this expression we had this  $k_c$

so this was a partial derivative because we are taking a constant pressure this

$\Delta u$  is the standard internal energy change based upon the reaction okay now what we can do

here is we can take this expression for  $k_c$  and put it back in this equation

so i will remove the

partial derivatives and then what i can write is  $d \ln k = \frac{1}{k} \frac{dk}{dt}$

right is equal to  $\frac{\Delta u^\ddagger}{R T^2}$  ok now vantov what he said was he argued what

he said was that ok this  $k_1$  and  $k_{-1}$  would be related to certain energies

$E_1$  and  $E_{-1}$

so then land of says or vantov i can say argued based on his proposal or based on

his proposed hypothesis that  $k_1$  and  $k_{-1}$  will be influenced will be influenced by two

different by two different energy factors which are  $E_1$  and  $E_{-1}$  ok

so these are the two energy factors and based on this he could then write that

$\ln k_1 = \frac{E_1}{R T} + \ln A_1$  this is  $k_1^2$  over sorry i will

not write  $k_2$  this is  $E_{-1}$

so please ah make sure that this is  $d \ln k_{-1}$  which

is the rate constant for the backward reaction over  $d t$  is equal to  $\frac{E_{-1}}{R T^2}$

square

so now again you can understand that this  $E_1$  is then energy factor associated with

the forward reaction and  $E_{-1}$  is the energy factor associated with the backward reaction ok

so after that what you know having said this what he then did was he said that ok based on

this if i you know if i am able to write this i should also be able to write that  $E_{-1}$

$E_{-1}$  is equal to  $\Delta u^\ddagger$  once you have all these set then it becomes

very clear

so if you would integrate one of these equations if you indicate one of these equations say for example if you would just say  $d \ln k$  over  $d t$  is

equal

to  $\frac{E}{R T^2}$  and if you would integrate this equation then what you will be

getting is  $\ln k$

so that means you can take  $d t$  over this side do the corresponding integration will be getting is equal to constant minus  $\frac{E}{R T}$  or now i can write

so this constant it is a constant this is logarithmic base e

so you should be able to understand how we can write the next step where i can write that  $k$

is equal to  $A e^{-\frac{E_a}{R T}}$  right

so this you should be able to figure out by yourself how

from here to here i can write the same but anyway what it tells you is it gives an idea of how this rna equation came about so let me see what the ah you know what the equation number was for this last one yesterday ok so then this one was i think equation nine which we gave right and then obviously this is the rns equation but then i am sure you are wondering right now if vantov had already proposed this then why is it said it is the arrhenius rate equation of the ironless expression for the temperature dependence of the rate constant on you know how the temperature how uh the rate constant depends on temperature why we call that equation as rns equation because vant have already given all these things now the importance of ardennes is here so what did it do is he generalized it so lets think about arrhenius right now see again from this hopefully you got a flavor that how this rns rate in rns expression for the dependence of temperature of a reaction rate or rate constant can be derived or can come into being but then as i was telling you since it was already proposed by vantov why would by call it to be an erroneous equation so rn is he accepted this approach by vantov right and he tried to generalize it he said that this is possibly applicable for any possible reaction but how does or how did he visualize the reaction happening now this is what he proposed so what he proposed was that this is a general concept this means the rna or the previous equation which is  $k = a e^{-\frac{e}{r t}}$  over r t so here you see i have replaces e by e a which is essentially our activation energy this is a general concept of how reactions occur ok it is a general concept and what he said was and equilibrium like chemical equilibrium equilibrium is established an equilibrium is established between normal and active reactant molecules ok so let me underline these two words so what rna has proposed was he said that this is indeed a general concept of the temperature dependence of a certain reaction or any given reaction say and in the process of giving an explanation for the expression you have seen he said that an equilibrium is achieved between two types of molecules reaction molecules one is a normal reactant molecule and the other one is an active reaction molecule now just merely by these two words normal and active you understand that he is creating a difference between the types of molecules which are present in your reaction system or the reaction vessel where you are carrying out the

reaction normal  
reactant molecules means they are normal out there active reactant molecules  
by the you  
know word active means they are more active towards a certain reaction now  
what we mean by  
that what we mean by this active reactor molecules we will soon see but you  
must be realizing right  
now that he has been able to make a distinction between the two groups of  
molecules that are  
present in a reaction vessel at any given moment one is a normal set of  
reactant molecules and the  
other one is an active set of reactor molecules and it goes without saying  
that this it is the  
active set of reactant molecules which would finally go over to the product  
side and actually  
give you the products right that's what that is why they are called the active  
reactor molecules  
because they are active enough  
so that they can give rise to products by whatever changes  
that happen in the reaction ok now see argenis you know he received his novel  
price is a  
nobel prize for ah his um you know theory of electrolytic dissociations right  
so  
he did not receive nobel prize for this this thing the temperature dependence  
of  
reaction rates and he was you know working on few reactions one of the  
reactions he was  
working on was the inversion of cane sugar ok  
so one of the reactions ardenius  
was working on was the inversion of cane sugar right and here he said that  
during the inversion process the inversion was not brought about the inversion  
was not brought about by a simple cane sugar molecule it was not it was not  
brought  
about by a simple cane sugar molecule but but a substance he referred to or he  
mentioned he mentioned as active cane sugar molecule but a substance but a  
substance he mentioned as active cane  
sugar molecule or active cancer and it goes without saying that the rate of  
this  
reaction or the rate of a reaction is proportional to the concentration of  
active molecules  
so if i write then he said that the rate of reaction is proportional  
proportional to this active cane sugar molecules right  
so this introduction  
of this word active was a key step taken by arrhenius in his proposition or  
in  
his generalization of that red expression  $k$  is equal or that expression  $k$  is  
equal to  
 $a e^{-E_a/RT}$  now let us try to draw a schematic profile you  
know to  
understand what we mean by this  
so start from a very simple schematic profile  
so here on the  
x axis i have something known as reaction coordinate on y axis  
so this is my reaction coordinate on y axis

what i have is something known as potential energy  
 so on the x axis i have the reaction  
 coordinate on the y axis at the potential energy  
 so if this is my reactant say this would be my reactants products right then  
 on my way from reactions to products this is how  
 the potential energy profile should look like ok  
 so this is how the potential  
 area profile should look like right  
 so what you seeing out here is i have my reactant  
 out here i have a product out here right and on my way from the reactant to  
 the product on my way  
 from the reactant to the product if you remember the equilibrium equation we  
 are talking about  
 what we can say is say if i take this maximum this one can be labeled as  $e_1$   
 right then if i extend this  
 line on the other side then i can say from here to here this is  $e_{-1}$  right  
 then the difference out here between the reactants and the products is your  
 $\Delta u_{naught}$  what is the general form  
 of this expression or rather this ah plot what does it say  
 so you have reactants you have product  
 so the relative energy level will depend upon what type of reaction you are  
 looking at right the  
 difference between the two potential energies that means the potential of the  
 reactant and  
 the potential of the product is equal to your change in internal energy that  
 is a standard  
 internal energy right now when the reactant has to go to the product when the  
 reaction  
 has to go to the product what the reactant what has what happens to the  
 potential energy  
 is you start from the production energy of the reactants then you slowly move  
 output right then  
 you reach a maximum once you reach the maximum once you go over to the other  
 side  
 so this is  
 the maximum right  
 so this is the maximum of the potential energy once you go to the other  
 side then you can again see that the potential started to decrease hence you  
 come down to the  
 products  
 so then for the reactants to go over to the product side they have to  
 surmount  
 an energy barrier which is given by  $e_1$  ok  
 so this this  $e_1$  is the energy barrier on  
 the other hand if the products have to come back to the reactants they have to  
 surmount  
 an energy barrier which is given by  $e_{-1}$  and as again i said before  
 that  $e_1$   
 is the energy associated with the forward reaction and  $e_{-1}$  is the  
 energy associated with  
 the backward reaction  
 so this  $e_1$  or  $e_{-1}$  one or you know let us say  $e_1$  because we  
 are more ah accustomed to looking at you know reactions going from reactants  
 to products

so this  $E_a$  one you know this  $E_a$  one is your  $E_a$  the activation energy ok  
so this  $E_a$  one can be equivalent to  $E_a$  the activation energy we will talk about this more when we go to the next topic which is about elementary reactions about looking at a schematic energy profile and see what information it gives us but for the time being it is enough for us to understand the bare essential features of a certain plot like this where if you have to go from the reactant to the broader side you have to go up in the potential energy right go to maximum once you reach the maximum once you reach the maximum then you make a transition over to the product side so this state out here this state out here is called the transition state so if I write if I say there is a state out here then I can say this is my transition state so what does this mean that means this is the state through which I transition from my reactants to products and that's why it's called the transition state and obviously the way it has been depicted on the diagram the transition state is the one which is at the top of your potential energy that means having the highest energy so the moment you move on two sides of the transition state what happens is your potential energy diminishes right so if you are going from here to here the potential it moves increases to the transition state now the moment you go to the other side of the transition state what is happening is now you are going to the product side so again the production starts decreasing because your products have started forming right but in between there is an energy barrier which the reactants will have to surmount to go over to the product site and this energy barrier essentially is given as your activation energy which is  $E_a$  right ok another thing is if you look at your books you know even a ncrd book or some other books you will see that this difference in reactants and products instead of  $\Delta U_{naught}$  being written it is all its many times written as  $\Delta H_{naught}$  but do not worry it is not a problem at all so let us look at what I mean so remember we are focusing on  $\Delta U_{naught}$  right now so you know think about this we know this from thermodynamics that  $H$  is equal to  $E$  plus  $PV$  right then once I have this I can write that if I have a finite change in  $\Delta H$  in the enthalpy  $H$  where  $H$  is enthalpy ok so I used another  $\Delta H$

so let  
 me let me rewrite this hold on just let me rewrite this let me  
 take a another sheet of paper you soon understand why i need to rewrite  
 so i am  
 saying  $\Delta H$  your enthalpy is equal to  $u + p v$  right  
 so your enthalpy  $h$  is equal to  $u + p v$   
 $ah$  in the you know sheet before i write an  $e$  but  $e$  is also  $ah$  you know used  
 for symbolizing  
 internal energy but then i was using  $e$  for my activation energy  
 so you might get confused so  
 i came back and used  $e$  because this was what i also used for depicting this  
 difference between  
 the reactants and the products the potential energy difference right ok now  
 remember what  
 we had started with what we have said was you should not be confused by the  
 fact that  
 there is whether  $\Delta u$  or  $\Delta h$  because now if i look for a  
 finite change in  $h$   
 then this would be equal to  $\Delta u + \Delta p v$  this can be rewritten as  
 $\Delta u + p \Delta v + v \Delta p$  right  
 so this is  $\Delta h$  ok now suppose now suppose if you would remember  
 that this  $d \ln k_c / dt$  which i had written i had written it as a partial  
 derivative right  
 initially  
 so it was  $\Delta \ln k_c / \Delta t$  at constant pressure  $p$   
 so because  
 it is constant pressure because it is constant pressure then  $\Delta p$   
 should be zero  
 so lets now rewrite this then  
 so i can write again  $\Delta h$  is equal  
 to  $\Delta u + p \Delta v + v \Delta p$  now at constant pressure at constant  
 pressure  $\Delta p$  is equal to  
 zero which means this is equal to zero  
 so the moment i write that then i have  $\Delta h$   
 $h$  is equal to  $\Delta u + p \Delta v$  right now for reactions for reactions in  
 condensed phases that means for reactions in in solids or solid state and  
 solutions the volume change is very small we know this right the volume change  
 is  
 very small  
 so we can write  $\Delta v$  is almost equal to zero hence  
 for solids and solutions right or liquid state we can write  
 that  $\Delta h$  is equal to  $\Delta u$   
 so now go back to what we had started discussing  
 this from or about  
 so we are talking of this  $\Delta u$  then for solids and liquids are  
 solutions  
 where reactions are happening in solutions then we straight away have this  
 $\Delta u$   
 $naught$  is equal to  $\Delta h$   $naught$  no problem right but what about gases gases  
 i cannot  
 say this ok  
 so let us talk about gas phase reactions right again we start from  $\Delta h$   
 $h$  is equal to  $\Delta u + p \Delta v$  right now remember we had said that  
 pressure

was a constant right let us consider ideal gas behavior for the gas molecules  
 ok now starting from the ideal gas equation  
 where  $pV$  is equal to  $nRT$  at fixed temperature and pressure at fixed  
 temperature and pressure i can write  $p \Delta V$  is equal to  $\Delta n RT$  is very  
 simple right i was looking at this  $p \Delta V$   
 factor out here right for ideal gas  $pV$  is equal to  $nRT$  now i have taken  
 the conditions where my  
 pressure is fixed and my temperature is also fixed  
 so if i am looking at a change in this equation  
 $p$  is not going to change because  $p$  is fixed  $T$  is not going to change because  $T$   
 is fixed  $R$   
 is a constant it is not going to change right  $V$  i have replaced  $V$  by  $\Delta V$  now  
 because  $\Delta V$   
 know volume can change obviously will change in case of gases then this change  
 in volume is equal  
 to  $\Delta n RT$  right  
 so what we can do now is we can take this  $p \Delta V$  is equal to  $\Delta n RT$   
 $T$  and use it back in this equation right using this what are going to get we  
 are going to get  
 $\Delta H$  is equal to  $\Delta U$  plus  $\Delta n RT$  what is  $\Delta n$   
 so  $\Delta n$  is the change in number of moles as you go from the reactant to the  
 product side  
 so under conditions where if  $\Delta n$  is equal to zero  
 so if  $\Delta n$  is equal to zero then immediately you  
 understand that  $\Delta H$  is equal to  $\Delta U$  right  
 so again going back to what we started  
 from remember  
 so for  $\Delta n$  is equal to zero this straight away comes out to be  $\Delta H$   
 naught  
 now even if  $\Delta n$  is not equal to zero even if  $\Delta n$  is not equal to zero  
 what will happen is  
 see  $R$  and  $T$  these are constants right  
 so then this  $\Delta n$  replace gets replaced by one two  
 whatever and still you will be having a working relation between what  $\Delta H$   
 and  $\Delta U$  so  
 that means if it is say  $\Delta n$  is equal to  $r$   $T$  then  $\Delta U$  can be replaced  
 by  $\Delta H$  minus  
 $rT$  and  
 so on  
 so that is why you do not have to be bothered by the terminology i used here  
 right  
 rather the you know thermodynamic parameter used here to describe the  
 potential energy difference  
 between the reactants and the products because for solids and liquids its no  
 problem for reactions  
 happening in the solid state or in a liquid state the solution state this is  
 always equal to  $\Delta H$   
 naught at constant pressure because first of all reactions are generally  
 observed at constant  
 pressure and secondly the volume change for these systems that solids and  
 liquids are  
 so low  
 that the  $\Delta V$  essentially is equal to zero right however in case of gases  
 as thats what

we are considering we can always say at fixed  $T$  and  $p$  we have  $p \Delta v$  is equal to  $\Delta n R T$  and then go forward and say that ok if  $\Delta n$  is equal to zero then  $\Delta h$  will be equal to  $\Delta u$  if  $\Delta n$  is not equal to zero then still i know that  $\Delta h$  is equal to  $\Delta u$  plus  $\Delta n R T$  which will be having some value times  $R T$  and then i can always replace  $\Delta u$  by this  $\Delta h$  ok

so thats how you you know relate these ah two things ok now based on our discussion of ah you know what we were doing out here let us try to look at this activation energy again from a different point of view

so the point of view is the following suppose there is a system having one mole of gaseous reactants ok one mole of gaseous reactants now one mole you know is avogadro's number its six point zero two three into ten to the power twenty three molecules now the question is at a certain temperature the molecules will be having their own kinetic energy you know go back to this kinetic theory of gases ok

so molecules will be having their kinetic energy but by you know think about this if i have a certain temperature say  $T$  is equal to 300 kelvin here which is close to room temperature what do you expect each and every molecule that means each of these six point you know this ten to the power twenty molecules would each molecule have the same kinetic energy probably not so what happens is that when at a certain temperature ah certain temperature and i am talking about

gaseous reactions it goes back to the kinetic theory of gases right you must have done this in some other class

so at a certain temperature what happens is that all molecules all molecules in the system do not have the same kinetic energy ok

so they do not have the same kinetic energy instead instead instead what happens is you have a distribution that is a distribution of kinetic energies a distribution of kinetic energies exist in the system and this distribution depends on temperature

so this is important this distribution depends upon temperature now even ah you know before showing you the distribution will not you know will not look at very much details of the distribution you know what the equation

the distribution is based on and

so on i will just show you the distribution

so that you have a feeling of what this you know arduous equation is all about what this activation is all about and

so on ok now this distribution it says it depends on temperature now this is obvious right

first let us not worry about the distribution if i have a certain temperature say three hundred kelvin the kinetic energy say is  $e$  one now if i increase the temperature to six hundred kelvin obviously the candidate is going to increase right but now the difference is that i am not talking about one molecule because we have i have made the statement in this previous sheet of paper that at a certain temperature a system having this many molecules or having so many molecules not every molecule would be having the same kinetic energy hence there will be distribution obviously now on the other hand if i increase my temperature that means i change my temperature i also change my kinetic energy if i change my kinetic energy then i am also going to affect my distribution of kinetic energies and how is that but first liquor let us you know take a look at the distribution of kinetic energy so this distribution was first proposed by maxwell and boltzmann the distribution was proposed by maxwell and boardsman yeah through a series of equations that they derived so this is how the distribution looks like so this is kinetic energy ok so this is kinetic energy so this on this side will be fraction of molecules ok and how is the distribution look so this should look like this so this is how the distribution looks like ok now so you have kinetic energy in the x axis i will just tell you what i mean by the fraction of molecules right tell you right now but see an important feature of the distribution one it is a distribution so there is a finite width its not a single line it is a finite width what does it mean that means you have a range of kinetic energy starting from almost zero to the other side right so this is the distribution somehow in between somehow somewhere in between the kinetic energy value peaks so that means there will be a fraction of molecules having the maximum kinetic energy right and that is where the fraction of molecules is peaking so which means there are this value so if i say this ok and i also extend on this side you can see that the fraction because there is a fraction the fraction is also high the highest out here the fraction is maximum and here the kinetic is also maximum right then we say that this value of kinetic energy corresponds to the most probable kinetic it corresponds to the most probable kinetic energy why is it most probable because you understand

that the maximum fraction of the molecules is having this kinetic energy and hence it is called the most probable kinetic energy right but again see that it is not one line but it is a distribution having a finite width that means at this temperature say this is  $t$  is equal to three hundred kelvin in my system having this many molecules not every molecule is having exactly the same kinetic energy there is a distribution of kinetic energies spread over this range not only that not only that the distribution also peaks at a certain point this peak to be read off from the y axis corresponds to the maximum fraction of molecules having this kinetic energy and because the maximum fraction of molecules is having this kinetic energy it is called the most probable kinetic energy because the maximum fraction of molecules is seen to have or possess this most probable kinetic energy ok we will come back to comparison again where we will you know take a higher temperature and see how this distribution changes because you know whatever we are doing is we are doing we are we are trying to understand this rna's equation right in a much better way trying to have much deeper insights as to what might be happening as you change the temperature okay what about this fraction so the fraction is this so that means you say that ok ah suppose the total number of molecules is  $n$  in the system if the total number molecule is  $n$  right then you have a certain fraction what is the fraction so the fraction is  $n_e$  by  $n$  the fraction is  $n_e$  by  $n$  so what is  $n_e$  say  $n_e$  is the number of molecules having kinetic energy  $e$  that's why it's called  $n_e$  and as we had seen before the peak the peak of the distribution the peak the peak of distribution it corresponds to the most probable kinetic energy okay which i am evading by  $k_e$  so the peak of the distribution corresponds to the most probable kinetic energy and this is any which is the number of molecules having certain kinetic energy  $e$  so again you go back and if you look at think about the fraction any by  $n$  then it just tells you that this point i have the maximum fraction that means i have the maximum number of molecules which is giving me this value of kinetic energy and because the maximum molecules is giving you that value of kinetic energy hence that kinetic energy being read off from the x axis corresponding to this fraction is called the most probable kinetic energy as simple as that great now having understood that there is a distribution of kinetic energies and that is that you know the distribution peaks at a

certain point which is called the most probable kinetic energy lets see how this distribution varies as a change temperature

so lets look at that now

so again out here i have the reaction coordinate and this again like before is my fraction of molecules now let us take two temperatures it does not matter what temperatures they are as long as the two temperatures are different

so for example let us take a temperature which is a distribution like this

so let this temperature be  $t$  is equal to three hundred kelvin

ok now lets take another temperature this time this temperature is higher than three hundred kelvin and say the temperature is you know say six hundred kelvin

so now what happens you see the

so let well let me take a higher temperature

so let this ah you know temperature be sure that this temperature be equal to say you know 900 kelvin now what has happened two things one is that from here to here when i change the temperature the distribution has become very broad not only that my peak which was here the most small value peak which was here has actually gone to somewhere here

so this is

so the most probable kinetic energy has increased at a higher temperature as compared to that of 300 kelvin

so 900 kelvin i have a higher value of most kinetic energy as compared to that of 300 kelvin again ah please realize that this ah you know has not been drawn to scale but just to make the point just to make the point now remember i had this activation energy ok so

let me draw a line where i say

so let me draw a line and i say that this this kinetic energy i did a mistake i am sorry this is not my reaction coordinate i am still you know in that mode

so this is you know as we had showed this is my kinetic energy extremely sorry for that please

make that change this is my kinetic energy right not my reaction corner ok anyway coming back to what i was telling you that here what does this line mean

this line corresponds to  $e_a$

so this is  $e_a$  my activation energy right now for the reaction to happen the molecules have to have this activation energy

so that they can go over the barrier that means the top of this potential energy surface or the potential energy and go to the product side

so the minimum energy the minimum energy that this molecules need to possess to go to the peroxide

is e a

so any energy which is higher than  $e_a$  so that means any molecule of an energy higher than

$e_a$  would be able to go to the product side right

so let me shed that portion

so for the first

curve 300 kelvin you see that the shaded region is the number of molecules right which are having

or the fraction total fraction converted to the number of molecules having energy higher than

$e_a$

so this point they would if they are having this energy higher than  $e_a$  then they would

definitely go over to the product side now for the same reaction considering the fact that

when i go to 900 kelvin the  $e_a$  has not changed that means the activation energy is say

temperature independent now for if you make the shade trying to make a different color you see

what will happen is the shade you see you will be having a much higher population

so when i was at 300 kelvin i was only

looking at this blue shaded region when i am at 900 kelvin i am looking at the shaded

region which is this plus obviously the blue ones right because they also fall under the

distribution and it immediately tells you that when i have increased my temperature i have gone

higher up the fraction of molecules having energy greater than  $e_a$  has also increased correspondingly

ok

so the few points that i should remember from this discussion is when i raise my temperature

from 309 kelvin my distribution becomes broad right when my distribution becomes

broad along with that there is a shift of the peak value which is the most probable

value of kinetic energy to a higher value now this is logical why as i was telling you before at

the start of the discussion of this distribution that if i increase my temperature then obviously

my kinetic energy is going to increase right and hence this is reflected by the shift of the peak

from here to a higher value right now we said that ok i know that based on our profile which

was you know let me see whether i can get that based on this potential energy profile we have

drawn before here

so based on this production energy profile for the reactants is to go to the product side they need to surround this energy barrier which is given by  $e_a$

the activation energy

so that means activation energy is the minimum energy that these reactant molecules

need to possess to go over to the product side right now when i take this and  
 come back here  
 and i say that ok say my activation energy is somewhere out here e a right  
 then any energy  
 greater than a means that all those molecules having that value of energy base  
 is greater than  
 e a must go over to the product side similarly when i increase my temperature  
 what happens is  
 the fraction of molecules having energy higher than ea has also increased  
 because my fraction of  
 molecules increased it immediately tells you that i have higher fraction of  
 molecules  
 and hence the rate will also be higher and this higher fraction is given by  
 what by the  
 shaded regions that i have under these individual distributions i hope i have  
 made myself clear i  
 just you know jot down the few points that i said  
 so then what happens to the distribution as temperature is increased what  
 happens if the distribution is increased  
 so one the distribution becomes broader to to the peak of distribution shifts  
 to higher value of kinetic energy right and three three this is possibly the  
 most important thing the shaded portion the shaded portion which shows the  
 fraction of molecules fraction of molecules having energy more than e a the  
 shaded portion which shows the  
 fraction of molecules having energy more than ea that area of shaded portion  
 increases increases as the temperature is increased as the temperature is  
 increased  
 and it can be shown it can be shown  
 so if i area increases as the temperature  
 is increase and it can be shown that fraction of molecules having excess energy  
 having excess energy that is energy in excess of e a is given by is given by  $e^{-e_a/RT}$   
 a over r t and then you can relate to the  
 arrhenius equation  $k = A e^{-E_a/RT}$  to the power minus e a over r t ok i will stop here  
 for today hopefully  
 by having this discussion i have been able to ah tell you or you know you know  
 show  
 you the insights of this arrhenius red expression or anionis expression for  
 temperature  
 dependence of rate constant and why it is called  
 so after rnas because he proposed all these  
 things and they do turn out to be very true ok  
 so in the next class what we will do is i will  
 finish off the rest of this chapter on ah i mean rest of this section on  
 temperature dependence  
 and move on to elementary reactions ok thank you you