

welcome to today's lecture

so we will ah start off

from where we left at the last class

so remember last class the we ended by posing a problem

so the

problem was this that you are given this reaction cyclic building getting transformed to betadine

right the activation energy for this reaction is 137 kilojoule per mole as written out here and the

question is if the temperature is changed from say 420 kelvin to 430 kelvin as a 10 degree change

by what factor will the rate of the reaction increase right that was a question

so for this

what you know the the way we approach this problem is very simple you remember we had derived this

equation number seven in the last class where what we have is the natural log of k_2 over k_1

which means the ratio of the two rate constants at two different temperatures is getting related

through the activation energy by this relation shift

so what we now do is if you look at this reaction again

so what do we not or what do we know we know what the value of E_a is it has been given to us it has been provided to us

so the value of E_a is 137 kilo joules per mole right we know what R is the gas constant 8.

314 with the appropriate units then we know what t_1 and t_2 are

so t_1 is four twenty kelvin and t_2 is four thirty kelvin right

so then

what we need to find is the ratio k_2 by k_1 and that will tell you by what factor the rate

has changed or increased ok

so let us do this then let us take this reaction as it is rather this equation as it is and plug in our values ok so based on this what we have then is you can write

natural log k_2 over k_1 is equal to E_a over R $\left(\frac{1}{t_1} - \frac{1}{t_2} \right)$.

so this was the equation

so now we will start plugging in values

so k_2 by k_1 is equal to

so what is the value of uh

our ah activation energy it is one thirty seven right kilo joules means ten to

the power three joules per mole now whatever R

so the value of R is eight

point three one four then joule per kelvin per mole and then i have one by t_1 minus one by t_2

so i can write

one by four two zero kelvin minus one by four three zero kelvin ok

so i will just since i am

moving out just write like this

so it is one by four twenty kelvin minus one by four thirty kelvin

right that's what it is that is t_1 this is t_2 ok
 so then natural log of k_2 over k_1
 again I did right as one thirty seven times ten to the power three joule per mole then
 eight point three one four joule per kelvin per mole or mole inverse then within
 brackets I write 430 minus 420 over over four twenty thirty ok
 so this is what I have and the unit for this one is kelvin inverse right
 so this is kelvin inverse now it is always good when you are doing any such mathematical calculations to write down the proper units right
 so you can always keep track of whether you are going the right direction or whether somewhere you have made a mistake
 so see this is $\ln k_2$ by k_1 this would be a pure number that means dimensionless no units
 so what are you going to have
 so this joule this joule will cancel out the small the small cancels out this kelvin this kelvin cancels out right hence we are left with the pure number
 ok
 so when we do the calculations you check the calculations by yourself should be getting
 natural log of k_2 over k_1 is equal to 0.
 913 right and then
 so you take anti log what you will get is k_2 over k_1 is equal to two point four nine this is your answer
 so now what you have seen is that for 10 kelvin rise in temperature right the rate increases by a factor of about 2.
 5
 so this is a rule of thumb this is a rule of thumb which says that we call it a general rule of thumb and what it says that the rate of a reaction will increase by a factor of 2 to 3 that means a factor between 2 to 3 for each 10 k rise in temperature
 so again what is the general rule of thumb as
 so this was the reason this problem was chosen as being discussed that the rate of reaction will increase by a factor between 2 to 3 for each 10 k rise in temperature
 and you can see this is 2.
 49 which is well between 2 to 3 okay
 so with this what we have done is you know come to the end of a discussion of how rates are affected as a function of or by temperature and what or how do we you know how can we have deeper insights into this insights not only from the arrhenius equation but then where the Arrhenius equation originated from

and what are the underlying assumptions in this and so on right so hopefully again having gone through this discussion of temperature dependence and reaction rates you would be able to better realize or appreciate what happens when the temperature is increased and how the reaction rate follows that increase in temperature right ok now we move on and come to something which is different a little bit different we say we will take a closer look at chemical reactions ok so what we are saying is that we are going to take a closer look at chemical reactions now when i say that what do i mean by that so what i mean is very simple what i mean is that suppose you are given a reaction right suppose you are given a reaction where say you have a plus b going to products so the reactants going to products the reactants been a and b so the moment you look at this reaction what are the different questions that can come to your mind right what are you trying to achieve what you know when you look at a reaction what do you think about the reaction at your first site so one is that based on this does the reaction occur in a single step right or does it involve multiple steps right so this is an important question you ask yourself is it a single step reaction or is it a multiple step reaction ok so single step means that in one step only a reacts with b to give us p if its multiple steps then it means that it is not happening in one step so there is at least two steps there is at least one step more than the one which is referred to as the single step so that means there should be at least two steps to make it a multiple step right next what happens when a reaction generally what happens when a reaction goes on to products you have bonds making bonds will break bonds will form right during the course of the reaction that means when the reactants go to the products so your next question is again very simple so this is your next question so the next question is which bonds are broken right which bonds are being formed not only that does the bond making that means bond formation and bond breaking does the bond making and bond breaking happen at the same time so again in one question you are asking too many things so what are the things you are asking which bonds are broken right which bonds are broken which bonds are being formed right and then do these two processes that is bond making and bond breaking are they happening at the same time

so see you are given a reaction the first question you ask is is it a single step or a multi-step process right the second question you are asking is ok i know that bonds are being formed ah and also bonds are being broken which are those bonds which having broken which are those bonds which are being formed are they being broken at the same time are they are they forming at the same time that means ah is the bond breakage and the bond you know formation happening together simultaneously and the other question the other question which you can ask is is also very relevant question the other question is can ask is what energy changes are involved in the reaction or reactions what energy changes are involved in the reactions so the three very important questions at least three very important questions you ask yourself a whether single step or multiple step two which bonds are going to break which bonds are going to form will the bond breaking and bond formation be taking place simultaneously three what are the energy changes that are involved as the reaction progresses towards the product side all these can be summed up in what we say is the reaction mechanism so the reaction mechanism will encompass all the informations that you have asked for that you are looking for right is it a single step is it a multiple step which bonds are being formed or being broken are they is you know are these processes happening at the same time then what are the energy changes involved these are the three questions you asked and these three questions are addressed together by the reaction mechanism of a certain reaction so what is the reaction mechanism so the reaction mechanism we can say so the reaction mechanism is if i write it again is providing you something what is it providing it is providing you a molecular description it is providing a molecular description it is proving a molecular description of how the reactants are being converted to products ok so it provides you a molecular description and please understand that chemistry is all about molecules and when you are talking about the reaction mechanism you are trying to understand at the molecular level that is at molecule by molecule how each molecule is reacting with the other to give rise to your products ok so this is why the reaction mechanism is so very important we can say the reaction mechanism again if you write is what so the reaction mechanism is a proposal is a proposed way or path of reactants going to products so it is a proposed v of

reactions of reactants going to products and that is why
so that means you
are proposing away based on what you are proposing a reaction you are
proposing
either a single step or multiple steps based on something
so what is something
something is the experiments you perform
so what are the experiments you perform
so the
experiments you perform
so you perform experiments that help you propose the reaction mechanism
so what are the experiments its very simple so
the experiment means you can say one you can vary concentrations of reactants
and then
the other one is very obvious can vary temperature right
so by doing these experiments by
doing these experiments we try to have an insight into how a specific reaction
is going
from the reactant side to the product side ok thats why the reaction mechanism
is so
important and is also fundamental significance in the branch of chemical
kinetics because
once you know the reaction mechanism you essentially know everything about
the
reaction as long as the reaction mechanism that you are proposing is a valid
one
right ok
so lets start with a few examples right
so lets take this first
example where we have ethyl bromide aqueous form okay reacting with OH^-
equals form to give you $\text{C}_2\text{H}_5\text{OH}$ $\text{C}_2\text{H}_5\text{Br}$ OH^- you know what it is equals one
plus Br^-
aqueous form
so let this be our reaction one
so it we i you know we can say
that it is very well established that this reaction happens in a single step
that means in a single step what happens is this molecule reacts with this
molecule to give
us the products such single step reactions such single step reactions are also
known as this is important elementary reactions ok
so this is a very
important concept in chemical kinetics so that means an elementary reaction is
what an
element reaction is one which proceeds through a single step there are no
other steps involved
one step its an elementary reaction moreover if you go back and take a look at
this equation if
you go back and take a look at this equation the balanced chemical equation
which is out here
gives you the message of how the reaction proceeds
so in this case the balanced chemical equation conveys conveys the one step
nature of the process right
so again the
balanced chemical equation conveys the one step nature of the process

what do you mean by that look at this this is a balanced reaction happening in a single step you know experiments have proved that is happening in a single step the balanced chemical equation is telling you is conveying the message that in one step what happens is if i go by molecule by molecule a molecule of ethyl bromide reacts with that of hydroxide ion OH^- give rise to ethanol and bromide ok that is the message that has been conveyed by this balanced chemical equation and this being a single step the balanced chemical equation provides you information about how the reaction is going and hence it is called an elementary reaction remember elementary reaction has to be of a single step right that is how an elementary reaction defined a single step is an elementary reaction right ok in order to think about this i can go ahead and write this that because the balanced chemical equation is conveying the one step nature of this process then i can write that the rate for this elementary reaction is given by k times the reactants which in this case $\text{C}_2\text{H}_5\text{Br}$ and OH^- i can straight away write from the equation that i started with so because what it is telling is because it is single step reaction the balanced chemical equation directly tells me that the rate will depend upon the molecule of ethyl bromide and the molecule of OH^- reacting with each other in a single step and that is why the rate can be written like this so this is something which is very important right the balanced chemical equation is conveying the message that this is how the reaction is going then it also gives rise to something known as molecularity and i will come to this thing so molecularity of a reaction i will discuss this later but what it essentially is saying is if it is a elementary reaction if the reaction is elementary then if you look at so this was equation right if the reaction is elementary that means happening in a single step then directly from this react you know this reaction i can write down the rate law because in a single step the overall order is equal to the molecularity of the reaction what does it mean you know just keep this in your mind we will discuss it later again so there is one molecule of reactant a ethyl bromide the reaction normal reactant b hydroxyl ion ok OH^- how many molecules one molecule of this one molecule of this so the total molecularity is two it is a bi molecular reaction and if you look at the rate law written what is the total order this is again one plus one which is equal to two which means in a single step which is elementary in nature right obviously elementary

single step then molecularity and order are equal
 so molecular is equal to order of the reaction
 just keep that in mind it will help our discussion during later times now let
 us take a very similar
 reaction but obviously different reactants
 so i have now C_6H_5Cl in aqueous form plus OH^- aqueous form giving me C_6H_5OH
 C_6H_5Cl in aqueous plus OH^- aqueous
 so they let this be reaction two all
 evidence all experimental evidences suggest that though this is a very similar
 reaction you can see
 i can show you the reaction again if you remember say this was reaction one
 right this was
 reaction one you see this was reaction one this was reaction one right and this
 is reaction
 two see how similar they are how similar they are only now the reactant the
 main reactant
 principle reactant has been changed from ethyl bromide to this one now once
 you have this all evidence tells you that this
 reaction is not elementary nature that means it happens in multiple steps
 and what are the steps the steps are C_6H_5Cl right giving you
 C_6H_5Cl plus OH^- say this is equation three the next step
 is C_6H_5Cl plus OH^- giving you C_6H_5OH
 this is four
 so what has happened is unlike the previous
 reaction where everything was happening in a single step this however we see
 is not
 happening in a single step the first step is going like this where this one
 decomposes
 into a benzyl cation and the corresponding chloride then this cation reacts
 with the hydroxyl
 ion to give rise to the corresponding alcohol
 so immediately when you have more than one step
 so now what you also see is before i move on if i take these two reactions if
 i take these
 two reactions and if i add these two reactions right if i add these two
 reactions what
 will you see you will see that this cation gets cancelled out from both the
 sides and you are
 left with the balanced chemical equation which you started with right
 so this is an important point
 of a multi step reaction that first the moment it is a multi step reaction
 then the reaction is not
 an elementary x second second when you add these two reactants ah you know
 these two steps up or
 whatever number of steps you have in a non single step reaction then that
 should give rise to your
 balanced chemical equation only exceptions being chain equations which we will
 not be discussing
 but chain equations are very very complicated in nature right ok
 so what can we say from this
 what we can say is that our reaction a reaction which precedes a reaction which
 proceeds by more than one step is known as a composite reaction or a complex
 reaction ok it is known as

a composite reaction or a complex reaction and hence the corresponding reaction mechanism is either referred to as a composite reaction mechanism or composite mechanism or a complex mechanism that means I have either a composite mechanism or a complex reaction mechanism. However, however, if I go back to this, please note that though this reaction is a composite reaction, it is made up of these two steps that is more than one step, hence composite or complex, but each step is elementary in nature. Each step is elementary in nature, so what we can say is that a composite reaction or a complex reaction is nothing but a sequence of elementary reactions. There can be two elementary reactions, there can be three elementary reactions, there can be four elementary reactions, depending upon the complexity of the reaction, right?

So let me say this again: a composite reaction is one or a complex reaction is one which happens by at least more than one step. The moment that happens, then each such step in a composite reaction is elementary in nature. For example, the first reaction here, reaction three is elementary, reaction four is elementary. These two different elementary reactions, when summed up, give us back the complex reaction or the reaction which is happening not in one step but in multiple steps. Now, this is something very important for you to understand, okay?

So as I said, so composite reaction is any reaction where the mechanism would involve the involve or would involve at least two steps that means definitely more than one step. Now, in general, in general, so some features you need to keep in mind for a composite reaction in general, for a composite reaction, for a composite or complex, so composite and complex can be used interchangeably. They, you know, they are kind of tell you they have the same meaning, they tell you the same thing, the number and nature of the steps, steps in the reaction mechanism, which is complex anyway, cannot be deduced from stoichiometry, okay, cannot be deduced, cannot be reduced from stoichiometry, right?

So why do we say this? So let us go back again to our the reaction we started with, so remember, so this was the first reaction we started with and we said that this is a single step elementary reaction. Look at the stoichiometry, one molecule of this, one molecule of this, and I said that the rate law for this can be written or the rate expression can be written by k times this concentration of this times the concentration of the other reactant, okay, and then you go back and take a look at the stoichiometry, you see that, oh, from the stoichiometry, I can

directly say or
write this rate expression for a single step or elementary reaction that is
where the molecularity
comes in and they say the molecule discussed later but the same thing you
cannot do for a complex
reaction you cannot write it down because you just do not know you just do not
know what the steps
are for you to be able to write it down ok
so that is what it meant or what i meant when i saying
you know by saying that for a composite reaction the number and nature of the
steps cannot be
written down see if i just tell you that this is a you know complex reaction
or composite
reaction without telling anything else you do not know whether it is going to
go ah you
know it is definitely going to go through by more than one step but do not
know what is going to
go through by two steps three steps or four steps it will totally depend upon
how complicated the
reaction is right
so for you just looking at the reaction if you do not know anything about
it you will not be able to say much except that because it is going by more
than one step
or through more than one step it has to be a complex or a composite reaction
thats it ok
so and you know when we were looking at this reaction you can you saw one
thing also this
complex reaction is that we were giving rise to a carbocation this c six h
right the benzyl cation
the carbocation
so c h five c h two plus
so this c six h five c h two plus carbocation in
this case is referred to as the intermediate is referred to as the intermediate
species or the intermediate in your reaction
so what is happening the
intermediate the intermediate is formed in one step and is being used up in
another ok it is being formed in one step and is being
used up in another
so just like this we go back to the reaction again you can see it is formed
in the
elementary reaction three and it is being used up in the elementary reaction
four
so in the
in
so thats why its called an intermediate it is something which is in between
the reactants
and the products it appears in between that it is formed through one
elementary step but it is
used up in the next elementary step
so that it does not appear in the final reaction that is
what an intimate is referred to by ok
so now the other problem is just
so that you know
is when i am saying its an intermediate the the most logical question that

will come to
your mind is can i observe an intermediate yes you can depending upon how the
or how stable
the intermediate is in the independent stable one you will be able to observe
it during your
reaction ok by some means but what happens is many reaction intermediates are
very short-lived
it is very hard to observe them and thats where proposing a reaction mechanism
becomes even
harder because see if you are going to propose a reaction mechanism if you are
going to propose
a reaction mechanism it has to follow the rate expression or the weight law
which we will see
later and to propose that you need to know what are the possible intermediates
that can happen
in a reaction now if you are able to see or identify the intermediates by some
means or
the other by some technique or the other then no problem but if you are not
able to identify
then it becomes that much more difficult for you to predict or to propose a
plausible a plausible
reaction mechanism that goes or follows the rate expression
so this is where the importance
of intermediates being able to be identified or not being identified comes
into play
so that
is why intermediates play a very important role in many many many chemical
reactions ok and i
had already mentioned this to you that i will not write this down an important
feature of such
composite reactions is that if you add up these elementary reactions which
make up the composite
or complex reaction mechanism then you should get back the final rate or the
final balanced chemical
equation which i started with the only exception being are chain reactions
so chain reactions are
much more complicated as i told you if you are not going to do that you are
not going to cover that
but
so in chain reactions you do not expect this to happen because as i said the
chain reactions
are too complicated before talking about reaction mechanisms because thats
what ah we are going for
lets think about the third question that you asked the third question was this
so what are the three
questions again let us ah try to recall a is it a single step a multiple step
two which bonds
have been broken which bonds have been formed are these things happening at
the same time two
process happening at the same time bond breaking bond making the third
question is what are the
energies involved what sort of energy diagram can i plot when i go from the
reactant side to the
product side

so let us try to do this energy thing or energy ah look at this energy diagram

so let us take a very simple ah plot i will tell you what the plots are so or the plot is

so on the horizontal x axis we have something known as the reaction coordinate right on the vertical axis of y axis we have potential energy ok

so this is potential energy on the y axis and this is the reaction coordinate now lets talk about a certain reaction okay

so let us talk about an elementary reaction let us talk about this elementary reaction

ah elementary reaction is an elementary reaction which is ah reaction which is

happening through a single step ok

so let this be our reactants let this be our products and this is typically what you would see being depicted in many books

so this then would be your reactants and this would be your products ok

so what is this diagram called

so this diagram is referred to as an energy profile

so ok

so i will draw it again later energy profile for a chemical reaction and here for this one we are just considering an elementary reaction right a single

step reaction now what do you see you have two things or aspects being plotted

one is the potential energy in the vertical axis and one is the reaction coordinate

let us try to understand a little bit more what these two mean these two axis that means the

potential energy axis and the reaction coordinate ok

so lets try to understand the potential energy the vertical axis

so the vertical axis the vertical axis is your potential energy axis right

so what does it represent it represents the potential energy

so what do you mean by that

so when i say that i say that this vertical axis which is the potential energy has contributions from the energy stored sorry the energy stored in chemical bonds as well as as well as that associated as well as that associated with interactions with interactions between each species and the surroundings ok again

so the vertical axis is what the vertical axis represents the potential energy and what is the potential energy composed of it is composed

of the contributions from the energy stored in chemical bonds

so remember here see if you have a bond which is being broken and the bond which is being formed then there is an energy stored in the bond

so that is what you are looking at right not only that

so then ah you know if two reactants are

coming and interacting with each other there is also interaction energy coming in

so that will be

here now suppose you have ions which are in water or some other neutral molecules which are in water

they would be having their respective interaction energies with the surroundings which is water the

reactants in water and else all those all those energy contributions are being clubbed into this

vertical axis which is your potential energy axis

so then you know what the vertical axis is the

vertical axis is your potential energy which is the contribution which is essentially the sum

of the contributions of all the energies that are stored and being changed when the reaction is

taking place that means you go from the reactants to the products hence when i am plotting this

potential energy i am looking at the change in that total energy which is the total potential

energy as i move from the reaction side to the product side ok then this leaves me with the

horizontal axis which is the reaction coordinate what does the reaction coordinate tell me then or the

so horizontal axis which is my reaction coordinate now the name might be a very fancy name

but it is very simple

so you see what does a reaction coordinate try to imply

so reaction called reaction means reaction coordinate means by looking at some coordinate

some sort like x y z coordinates and looking at some coordinate you understand how the reaction

is progressing

so that is typically what a reaction coordinate is

so we can write down

so we can write then the reaction coordinate summarizes the collection the collection of motions such as changes such as changes in inter atomic distances right and bond angles and bond angles that are directly involved that are directly involved in the formation of products ok

so again what it does it summarizes

that means it is a collective coordinate of the changes in inter atomic distances and or bond angles that are involved are directly involved as you move from the reactant side to the product side

so then what does it tell you

again then it tells you that it represents the path it represents the path that the system takes when it moves from the reactant side to the product side

so i can say then it is the path the system takes as a move from the reactant side to the product side so

now then having looked at both the axis the horizontal axis is the reaction coordinate and the vertical axis which is representing the potential energy you will

be able to now realize what it means

so along the reaction coordinate you are having

bond breaking bond angle changing and so on which bond is breaking the change

in the term distances and because of those changes because of the changes what is happening is your potential energy is changing because remember the potential energy is the contribution of all those things right your bond ah you know energy associated with the bond energy with interactions between the solid molecules because whenever these ah changes in bond angles or intermentations are happening all these energy are also changing as you go from the reactants to the products and this is what the energy profile is telling you so energy profile is telling you that as i move along the reaction coordinate which takes me from the reactant side to the product side how is my potential energy changing as i move along the reaction coordinate so that i move to the product side so this is what this is the information what the energy profile is giving you right when you look at a typical energy profile like this ok now as i said let us discuss this energy profile with respect to a very elementary reaction i mean respect to an elementary reaction so the elementary reaction we were looking at was what we are looking at $\text{C}_2\text{H}_6 + \text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{Br} + \text{HBr}$ reacting with OH^- so this is what we are looking at so we are looking at $\text{C}_2\text{H}_6 + \text{C}_2\text{H}_5\text{Br} + \text{OH}^-$ plus OH^- and this by definition is an elementary reaction so now go back to this plot let's go back to this plot so what are your reactants your reactants are your reactants are these two what are your products you know what your products are right your products are $\text{C}_2\text{H}_6 + \text{C}_2\text{H}_5\text{Br} + \text{OH}^-$ plus Br^- sorry this is minus a minus one i am a minus ok i am not writing the states you know that so what then is telling you is that so at the reactants at the reactant side you have what you have the $\text{C}_2\text{H}_6 + \text{Br}_2$ and OH^- at the product side you have the true product $\text{C}_2\text{H}_5\text{Br} + \text{Br}^-$ now lets consider or think about the reaction at the molecule level is molecule by molecule so one molecule of $\text{C}_2\text{H}_6 + \text{C}_2\text{H}_5\text{Br} + \text{Br}_2$ say three $\text{C}_2\text{H}_6 + \text{C}_2\text{H}_5\text{Br} + \text{Br}_2$ one molecule interacts with one of OH^- now when these two come and interact so when they are not interacting so this is your potential energy profile so when these two come and interact what is going to happen is changes are going to happen see what about your products your products what $\text{C}_2\text{H}_6 + \text{C}_2\text{H}_5\text{Br} + \text{OH}^-$ and Br^- that means the $\text{C}-\text{Br}$ bond has to break and the $\text{O}-\text{H}$ bond has

to form

so as the reaction proceeds you can think like this as the reaction proceeds you can think

like this that the c b r bond is slowly breaking and the c o h bond is being slowly formed

when that is happening because you have moved from a stable species that means which this was

stable now because your bond breaking and bond making is taking place the potential energy is

slowly increasing why because now your bonds have become distorted the cbr bond before breaking

becomes distorted say it increases in length say the cbr bond increase in length and finally snaps

right then the o h minus also the c o h minus was initially not there then the c o h bond forms

and slowly it comes close

so what you are saying is that as this thing is happening my potential energy is increasing it increases to a point up till here where my potential energy

is maximum right

so that means i have had breaking of bonds and i also have had making of bonds say taking place to almost equal extent and when i move there

so when i reach

this state or this species i reach a level which is at the highest point of my

potential energy curve or energy profile

so this is my point and this point would be referred to as the

so this this state would be referred to as the transition state

so once i reach the transition state which

is the highest point of my energy profile then more distortion

so it cannot be more

distorted than this this is my maximum energy

so a little more distortion would lead me

where will lead me to the product side

so this means that now the c o h bond is being formed more and more

so that i can go to the product side and the c b r bond is broken more and more so

that the b r minus comes out right and that is how typically a reaction is going to take

place in the next class i will start from here and i will give you another small example

so that

it helps you better understand the value of this energy profile what kind of information this is

energy profile have in store for you thank you you