Rate Processes
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Module No. #01
Lecture No. #14
Kinetics of Some Specific Reactions

Hello good morning everybody..

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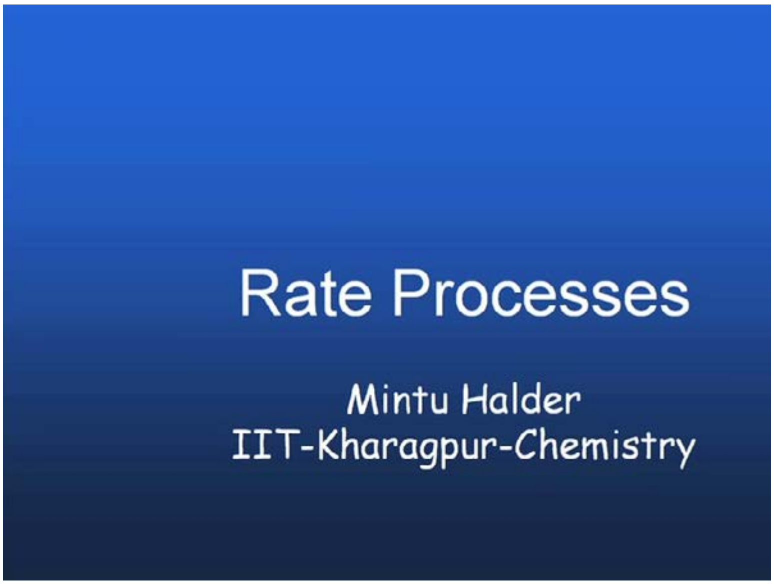

Rate Processes

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So, today we will continue to the topic rate process and under that we will take up kinetics of some specific reactions.

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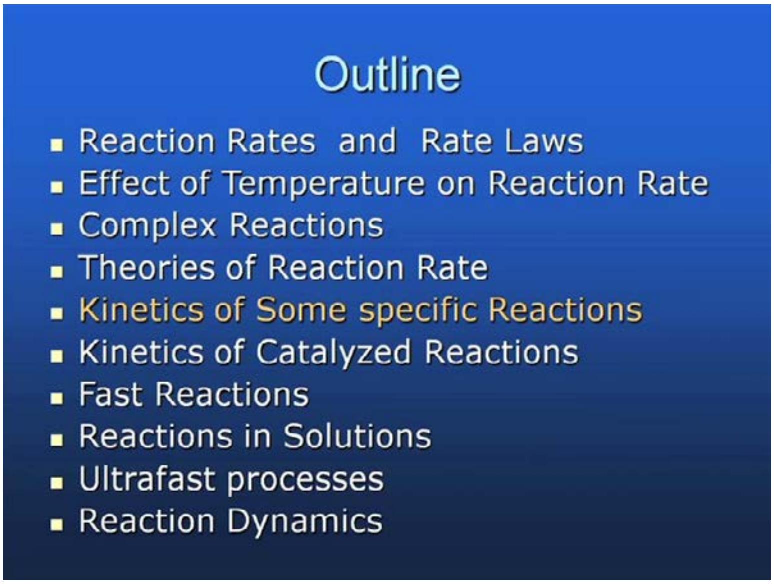

Outline

- Reaction Rates and Rate Laws
- Effect of Temperature on Reaction Rate
- Complex Reactions
- Theories of Reaction Rate
- Kinetics of Some specific Reactions
- Kinetics of Catalyzed Reactions
- Fast Reactions
- Reactions in Solutions
- Ultrafast processes
- Reaction Dynamics

In the last lecture we started with this diffusion controlled reactions.

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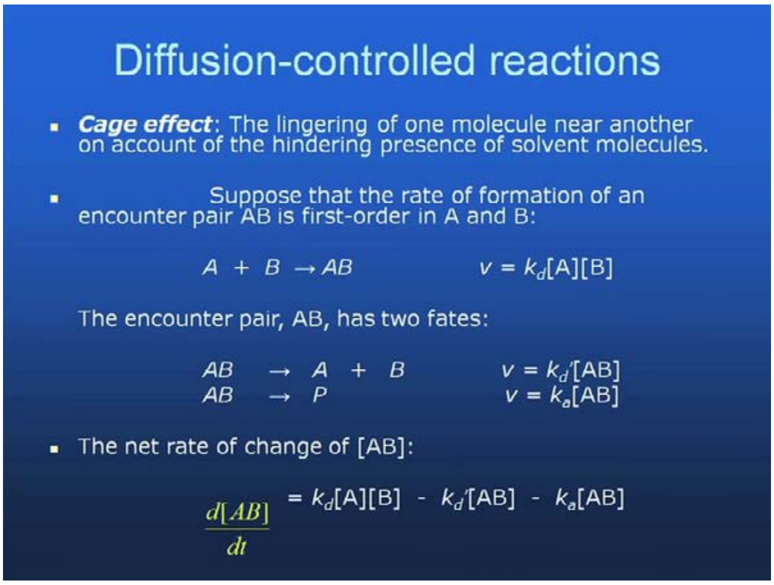

Diffusion-controlled reactions

- ***Cage effect***: The lingering of one molecule near another on account of the hindering presence of solvent molecules.
- Suppose that the rate of formation of an encounter pair AB is first-order in A and B:

$$A + B \rightarrow AB \qquad v = k_d[\mathrm{A}][\mathrm{B}]$$

The encounter pair, AB, has two fates:

$$AB \rightarrow A + B \qquad v = k_d'[\mathrm{AB}]$$
$$AB \rightarrow P \qquad v = k_a[\mathrm{AB}]$$

- The net rate of change of [AB]:

$$\frac{d[AB]}{dt} = k_d[\mathrm{A}][\mathrm{B}] - k_d'[\mathrm{AB}] - k_a[\mathrm{AB}]$$

Now, what is this diffusion controlled reaction now before that we should we should consider one thing the cage effect that is solvent cage. When a molecule is molecule or atom or an ion when it is in solvent phase then it is surrounded by a cage produced by this solvent molecules so; that means, you have got one molecule over here and you have got another molecule over here. So, like this two molecules or maybe two molecules one here another over here. So, they wanted to talk to each other,, but maybe maybe they are present in a crowded situation crowded bus that in between them there are too many crowds too many crowd means too many people are moving around in in them. So, they are not able to they are not able to talk to each other so; that means, as if this one and this one these two are caged within you know within cage that is cage found by the other people present within the bus.

So, lingering of one molecule near another on account of the hindering presence of solvent molecules it is called the cage effect that is they are inside cage. So, they will remain close to each other, but because of you know because of solvent molecule molecules in between they are not able to do any reaction. So, they they will stay for some time and then maybe when solvent molecules are moved apart then they will do do the reaction. Suppose that the rate of formation of an encounter pair A B is the first order in A and B. So, it is an encounter pair. So, first order it is a and this is an elementary process say and this is an elementary step. So, this is this rate of formation is dependent on this this concentration and that concentration. So, therefore, A plus B producing A B which is an encounter pair encounter complex. So, rate is k d times A and B encounter pair rate I mean formation of encounter that is that rate. So, the encounter pair has two fates either, it will disassociate to give you A and B or it will it will you know react to give you products.

So, forward rate is k d primed A B and the backward rate is k a sorry forward means dissociation rate is A B k d primed A B and the forward rate that is product formation is k d A B. So, net rate of change of A B because you have to apply the steady-state approximation; that means, rate of change of A B or maybe you can write the the rate of change of A B in terms of you know this forward rate of formation of A B. So, it i[s]- it is the production production step and these two are the you know it is expending I mean I mean these are expenditure step or these are used up so; that means, these two will be with negative signs therefore, k d A B minus k d primed A B for this one and also minus k a A B it is the overall rate of change of A B A B means the encounter complex.

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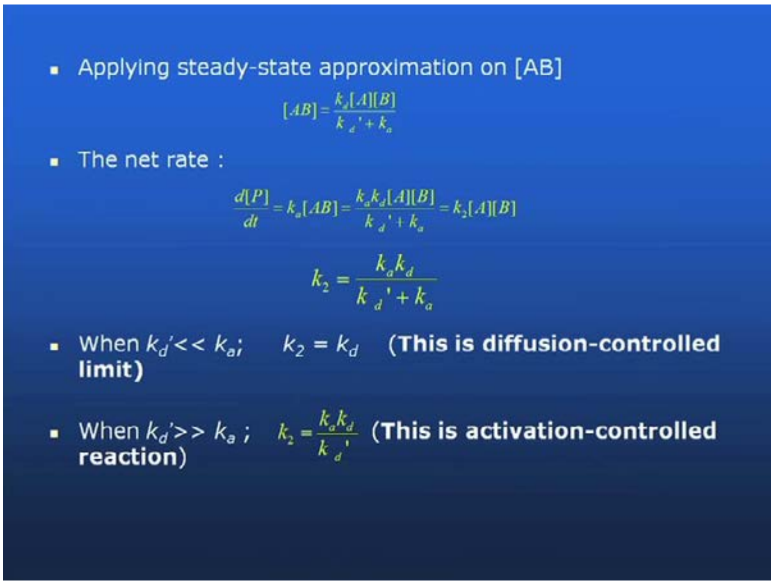

- Applying steady-state approximation on [AB]

$$[AB]=\frac{k_d[A][B]}{k_d'+k_a}$$

- The net rate :

$$\frac{d[P]}{dt}=k_a[AB]=\frac{k_ak_d[A][B]}{k_d'+k_a}=k_2[A][B]$$

$$k_2=\frac{k_ak_d}{k_d'+k_a}$$

- When $k_d' << k_a$; $k_2 = k_d$ **(This is diffusion-controlled limit)**
- When $k_d' >> k_a$; $k_2=\frac{k_ak_d}{k_d'}$ **(This is activation-controlled reaction)**

So; that means, we have to apply this steady-state approximation; that means, you should put this to be equal to 0. So, steady-state appr[oximation]- after applying steady-state approximation you get A B concentration of A B is k d A B divided by k d primed plus k a.

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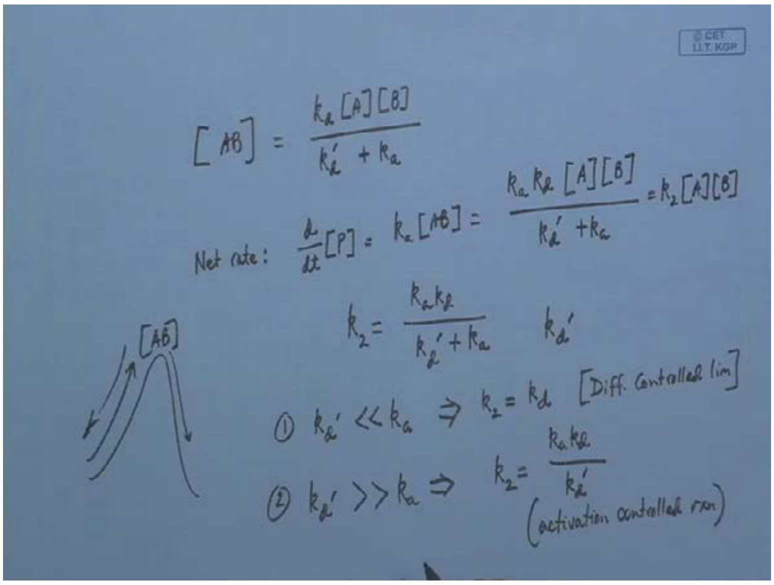

$$[AB]=\frac{k_d[A][B]}{k_d'+k_a}$$

Net rate : $\frac{d}{dt}[P]=k_a[AB]=\frac{k_ak_d[A][B]}{k_d'+k_a}=k_2[A][B]$

$$k_2=\frac{k_ak_d}{k_d'+k_a} \qquad k_d'$$

① $k_d' << k_a \Rightarrow k_2 = k_d$ [Diff. Controlled lim]

② $k_d' >> k_a \Rightarrow k_2=\frac{k_ak_d}{k_d'}$ (activation controlled rxn)

So, concentration of sorry concentration of concentration of A B because this is the species which is which is you know found and which is used up to give you products. So, therefore, we have to apply steady-state approximation on this basis. So, that will be equal to k d A B divided by k d primed plus k a. So, net rate net rate. So, product formation rate d d t of is equal to k a A B net product formation which is equal to k a then k d k a k d then A B divided by k d primed plus k a which is equal to. So, these two whole two altogether equal to k 2. So, k 2 A B therefore, k 2 will be equal to k a k d k a k d divided by k d primed plus k a situation one that when k d primed primed k d primed means which step let us go back k d primed means dissociation back to dissociation of A B back to A plus B. So, when k d primed is very very less than k a that is k a product formation this is very less then what you can write. So, situation 1 that k d primed is very very less than k a so; that means, you can just neglect it this this one.

So, this will give you k 2 is equal to k d k 2 is equal to k d k d means again the first step this encounter complex formation state k d and this is called your diffusion controlled limit diffusion controlled limit why diffusion controlled limit you can just explain from here that k d primed is very very less than k a means this this is negligibly small just once this encounter complex is found it will lead to product. So, this is basically a fast step very fast step and this is a slow slow step therefore, the the rate will be determined by the rate constant of this slowest step that is why it is k d and therefore, it is called the diffusion controlled level. So, reaction is under diffusion controlled controlled situation.

So, it is under diffusion controlled limit and what happens to the other situation that k d situation 2 primed is very very greater than k a then what happens then k a; that means, this is neglected therefore, your k 2 will be equal to k a k d divided by k d primed. So, this is called the activation controlled reaction activation controlled activation controlled reaction now again go back to the earlier slide that k d primed is very very greater than k a k d primed is very very greater than k a means ease of product formation. So, ease of product formation is ease of product formation is you know is a is a slow step so; that means, basically this step this step is very fast that; that means, diffusing out I mean once it is formed it will tend to disassociate. So, this is very fast. So, this formation and then you know this you know dissociation. So, this once it is found it will tend to dissociate the situation is you know it is similar to activation process as if the reaction is passing by an activation media; that means, you know you have got this A B once A B is formed.

So, this side is your formation of A B and going back is your you know dissociation and this is a slow process that is k a is low. So, this is similar to a chemical reaction that is which is occurring via you know via crossing of some activation barrier. So, what is k d k d is your 4 pi R star D N A where R star is the difference between the reactant molecule molecules and D is the sum of the diffusion coefficients of the two reactants reacting species where D A is k B T divided by 6 pi eta R A D B is similarly k v k T k v T divided by 6 pi eta R R B where eta is the viscosity of the medium R A R B are the hydrodynamic radius of A and B and if we assume that R A is equal to R B is equal to 1 by half R star R star is the distance between the reactant molecules then your k d will be 8 R T by 3 eta. So, what we get is that now a reaction can be called a diffusion controlled when your dissociation process dissociation process is very less. So, dissociation process is very less,, but like like this process dissociation I mean dissociation of your of your encounter complex two give you back this and it is less and the and the other option when k d primed is very very greater than k than it is called reactivation controlled; that means, here in this case in this case in the in the upper case this first case it is determined by how fast these these reacting molecules are coming close to each other for an an encounter complex that is the that is the you know bottleneck for the process if it is coming fast reaction will be fast if it is coming slow reaction will be slow that is why diffusion is the limit you cannot you know reduce it to that because at least the molecules or the atoms atoms have to diffuse close to each other close to each other to to do the reaction. So, that is why it is called the limiting situation.

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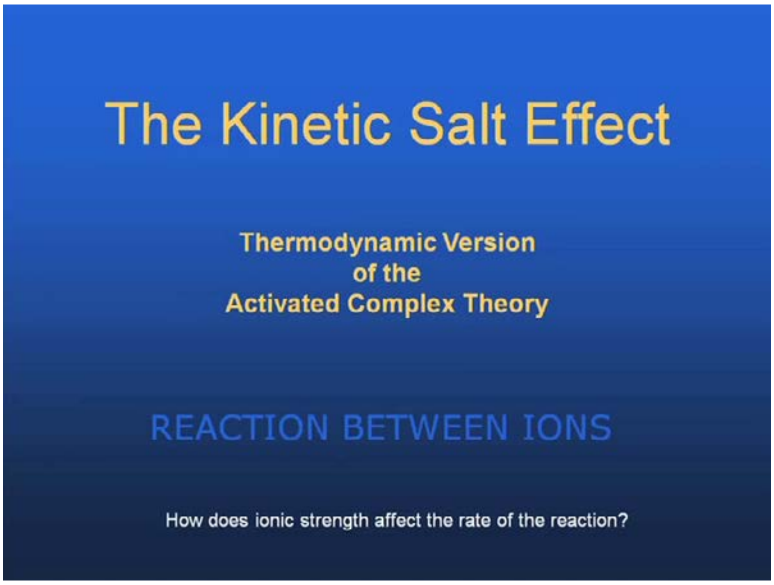

The Kinetic Salt Effect

Thermodynamic Version
of the
Activated Complex Theory

REACTION BETWEEN IONS

How does ionic strength affect the rate of the reaction?

Next we will move on to kinetic salt effect and it is a thermodynamic version of the activated complex theory it is it deals with deals with reaction between ions how does ionic strength affect the rate of a reaction does it really affect the the rate of rate of a chemical reaction and if it if it at all happens if it at all at all affects then how how does it affect. So, that is the question and it was first you know discussed it was first formulated by bronsted and bjerrum and it is called the kinetic salt effect that is the that is you know the effect of salt concentration or effect of salt on on rate of chemical reaction.

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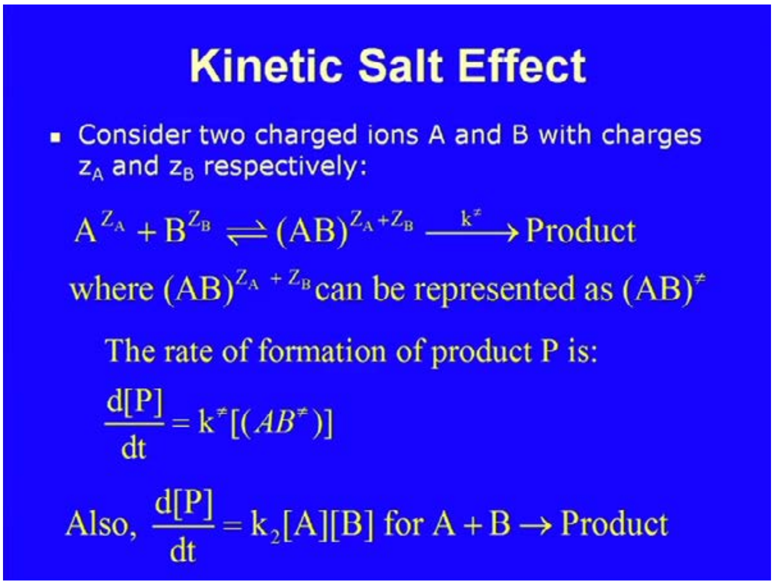

Kinetic Salt Effect

- Consider two charged ions A and B with charges z_A and z_B respectively:

$$A^{Z_A} + B^{Z_B} \rightleftharpoons (AB)^{Z_A+Z_B} \xrightarrow{k^{\neq}} \text{Product}$$

where $(AB)^{Z_A+Z_B}$ can be represented as $(AB)^{\neq}$

The rate of formation of product P is:

$$\frac{d[P]}{dt} = k^{\neq}[(AB^{\neq})]$$

Also, $\frac{d[P]}{dt} = k_2[A][B]$ for $A + B \rightarrow \text{Product}$

So, how to how to deal with this and of course, the question naturally comes if you have a reaction if you have a reaction between two two reactants which are uncharged then maybe you you will not possibly see any effect of salt possibly why it is not that why you you would not would not see I I will be coming to that point in later part of the discussion now what is the what does salt do when you add some salt into into a solution it is stated that ionic strength of the medium increases ionic strength means means it has got some relation to you know number of ions maybe, but the thing is if you have say from mono-positive ion to di-positive ion then you say that its ionic strength is more it is more because you know each ion contributes twice compared to the previous case therefore, ionic strength is more now it can be regarded this ionic strength can be regarded as the average electric field experienced by an ion due to the presence of other ions in solution it is a it is a qualitative way of understanding what do you mean by ionic strength of the medium. So, with this thing let us consider two charged ions A and B which charges Z A and Z B respectively and they are they are undergoing chemical transformation to give you some product so; that means, schematically we can write like this A Z A charged plus B Z B charged and it first it will first it will form A B A B means maybe it is a complex activated complex with charge total charge Z A plus Z B and then this activated complex will give rise to product give rise to product with you know equilibrium constant I mean with with the rate constant you know k k double dagger.

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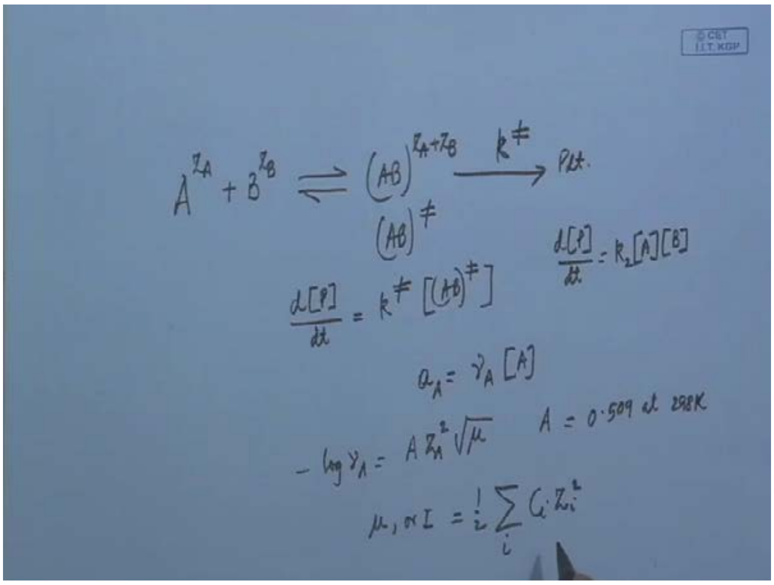

$$A^{Z_A} + B^{Z_B} \rightleftharpoons (AB)^{Z_A+Z_B} \xrightarrow{k^{\ddagger}} \text{Pdt.}$$

$$(AB)^{\ddagger}$$

$$\frac{d[P]}{dt} = k^{\ddagger}\left[(AB)^{\ddagger}\right] \qquad \frac{d[P]}{dt} = k_2[A][B]$$

$$a_A = \gamma_A [A]$$

$$-\log \gamma_A = A Z_A^2 \sqrt{\mu} \qquad A = 0.509 \text{ at } 298K$$

$$\mu, \text{ or } I = \frac{1}{2}\sum_i C_i Z_i^2$$

So, A Z A Z B equilibrium A B then products you can write this as this is the activated complex. So, rate of formation what is the rate of formation of your product of course,, it is this is your rate constant this is your rate constant. So, rate of formation d P d t will be equal to this is rate constant not the equilibrium constant k times concentration of this and also if it is a bimolecular process say if it is like it is having rate of formation of product that d P d t is equal to say k 2 A B then that is for A 2 A plus B 2 products.

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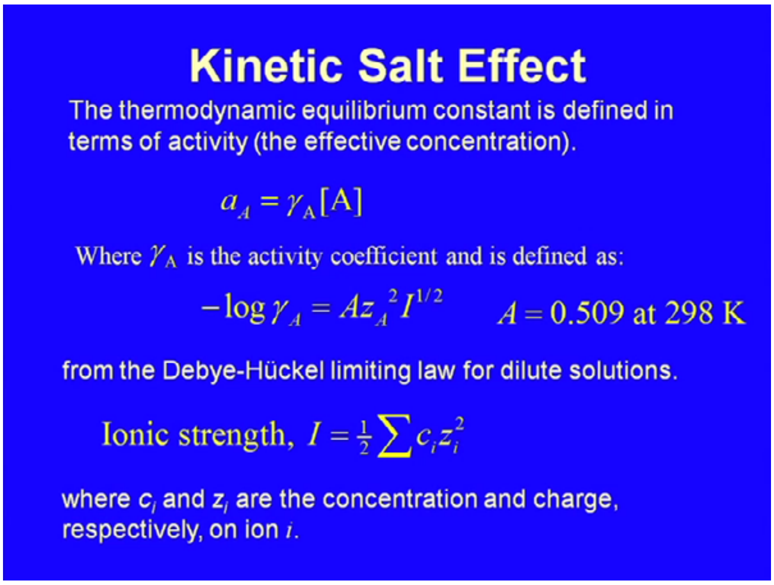

Kinetic Salt Effect

The thermodynamic equilibrium constant is defined in terms of activity (the effective concentration).

$$a_A = \gamma_A[\mathrm{A}]$$

Where γ_A is the activity coefficient and is defined as:

$$-\log \gamma_A = Az_A^{\,2} I^{1/2} \qquad A = 0.509 \text{ at } 298\ \mathrm{K}$$

from the Debye-Hückel limiting law for dilute solutions.

$$\text{Ionic strength, } I = \tfrac{1}{2}\sum c_i z_i^2$$

where c_i and z_i are the concentration and charge, respectively, on ion i.

Then then in terms of thermodynamic means the thermodynamic equilibrium constant means can be can be expressed with the help of your activity before that what is called activity let us try to understand means although for a dilute solution we replace conc[entration]- activity by concentration,, but it should be actually in true sense we should use activity in place of concentration. So, activity A of some species A is your concentration of A times gamma A. So, this is called your activity coefficient now this activity coefficient is has got a relation to ionic strength of the medium in the following way that minus log gamma A is equal to equal to A Z A square square root of mu mu means ionic strength of the medium or in some books it is written as square root of I mu or I where A is for water 0.509 at 298 kelvin. So, this is called the debye huckel limiting law for dilute solutions where ionic strength mu or or I is equal to half summation of C i Z i square over i C i is the concentration and Z i is the charge of the ith ion.

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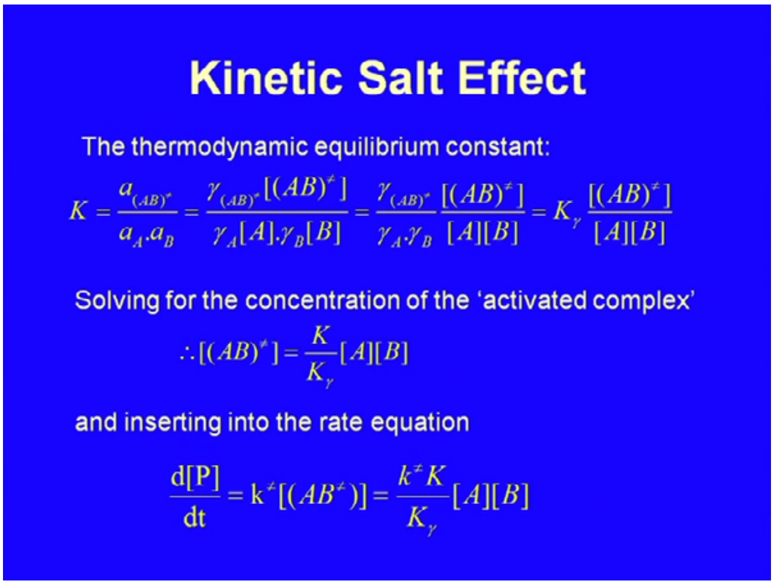

Kinetic Salt Effect

The thermodynamic equilibrium constant:

$$K = \frac{a_{(AB)^{\neq}}}{a_A . a_B} = \frac{\gamma_{(AB)^{\neq}}[(AB)^{\neq}]}{\gamma_A[A].\gamma_B[B]} = \frac{\gamma_{(AB)^{\neq}}}{\gamma_A.\gamma_B}\frac{[(AB)^{\neq}]}{[A][B]} = K_\gamma \frac{[(AB)^{\neq}]}{[A][B]}$$

Solving for the concentration of the 'activated complex'

$$\therefore [(AB)^{\neq}] = \frac{K}{K_\gamma}[A][B]$$

and inserting into the rate equation

$$\frac{d[P]}{dt} = k^{\neq}[(AB^{\neq})] = \frac{k^{\neq}K}{K_\gamma}[A][B]$$

So, thermodynamic equilibrium. So, for writing the thermodynamic equilibrium constant we should use this activity.

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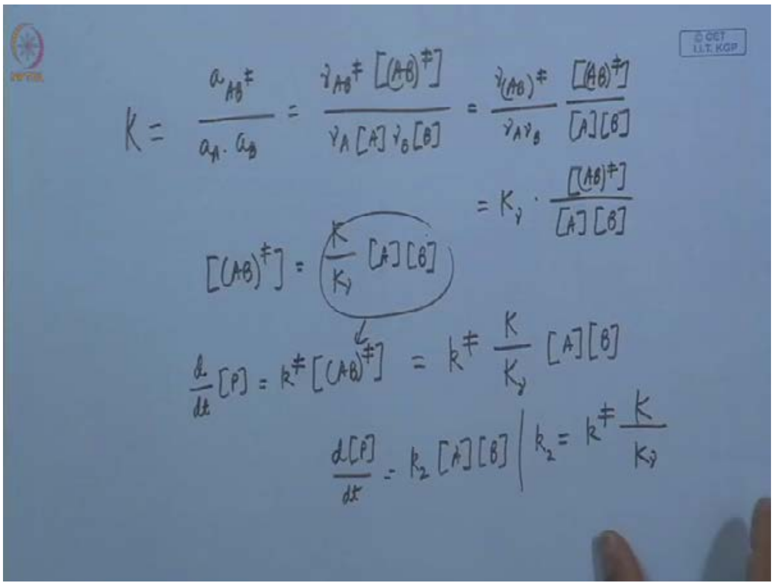

$$K = \frac{a_{AB^\ddagger}}{a_A \cdot a_B} = \frac{\gamma_{AB^\ddagger}[(AB)^\ddagger]}{\gamma_A[A]\gamma_B[B]} = \frac{\gamma_{(AB)^\ddagger}}{\gamma_A\gamma_B}\frac{[(AB)^\ddagger]}{[A][B]}$$

$$= K_\gamma \cdot \frac{[(AB)^\ddagger]}{[A][B]}$$

$$[(AB)^\ddagger] = \frac{K}{K_\gamma}[A][B]$$

$$\frac{d}{dt}[P] = k^\ddagger[(AB)^\ddagger] = k^\ddagger \frac{K}{K_\gamma}[A][B]$$

$$\frac{d[P]}{dt} = k_2[A][B] \quad \Big| \quad k_2 = k^\ddagger \frac{K}{K_\gamma}$$

So; that means K is equal to activity of A B divided by activity of A into activity of B which is equal to gamma A B activity coefficient A B or maybe A B and into concentration A B divided by gamma A A is equal to gamma A B divided by gamma A gamma B this is your gamma part this is your concentration part B which is equal to K gamma times this concentration equilibrium constant maybe. So, simplifying this we can write I mean rearranging K by K gamma times A times B see if we insert this into if we insert this into the into the rate equation what to we get d d t of product is A we just let us go back to this one that your k A B. So,. So, we just put this one this particular thing over here so; that means, k double dagger then K divided by K gamma A into B. So, rate of product formation can be written in this way. So, this is your equilibrium constant this is you you know ratio of the activity coefficients over here now since as I told you that for a for a you know second order process d P d t is equal to k 2 A B. So, overall I mean if you compare these two. So, experimentally absorbed rate constant k 2 has a connection with k double dagger K and K gamma in this way now we will first start with very dilute solution approximation.

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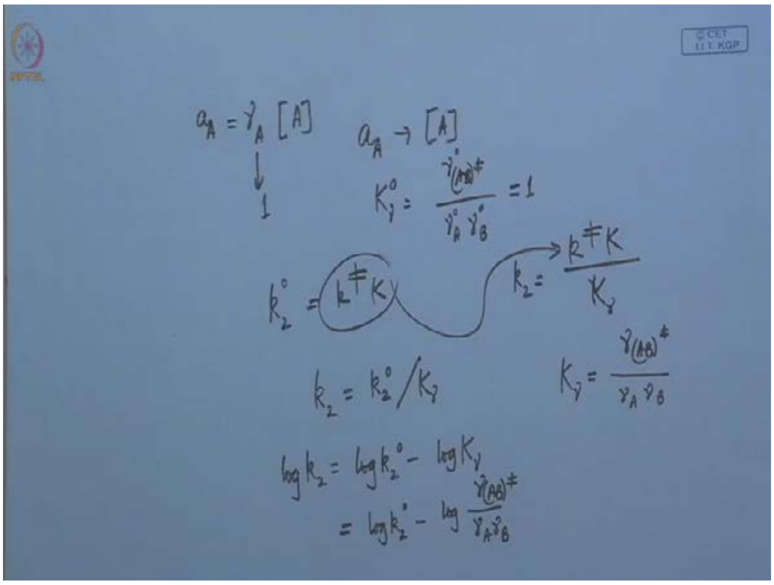

$a_A = \gamma_A [A]$ $\quad \gamma_A \downarrow 1$

$a_A \to [A]$

$K_\gamma^0 = \frac{\gamma^0_{(AB)^\ddagger}}{\gamma_A^0 \gamma_B^0} = 1$

$k_2^0 = k^\ddagger K$

$k_2 = \frac{k^\ddagger K}{K_\gamma}$

$k_2 = k_2^0 / K_\gamma$

$K_\gamma = \frac{\gamma_{(AB)^\ddagger}}{\gamma_A \gamma_B}$

$\log k_2 = \log k_2^0 - \log K_\gamma$

$= \log k_2^0 - \log \frac{\gamma_{(AB)^\ddagger}}{\gamma_A \gamma_B}$

Very dilute solution approximation means that activity A you know if you start with this expression into A and if it is very dilute then this will tend to unity so; that means, for all practical purposes you can write in place of a A you can just write A and therefore, your corresponding K gamma which is your you know gamma A B divided by gamma A gamma B. So, this one that will be that will be equal to 1 for infinitely dil[ute]- therefore, it is 0. So, for infinitely dilute solution solution your K gamma 0 is 1.

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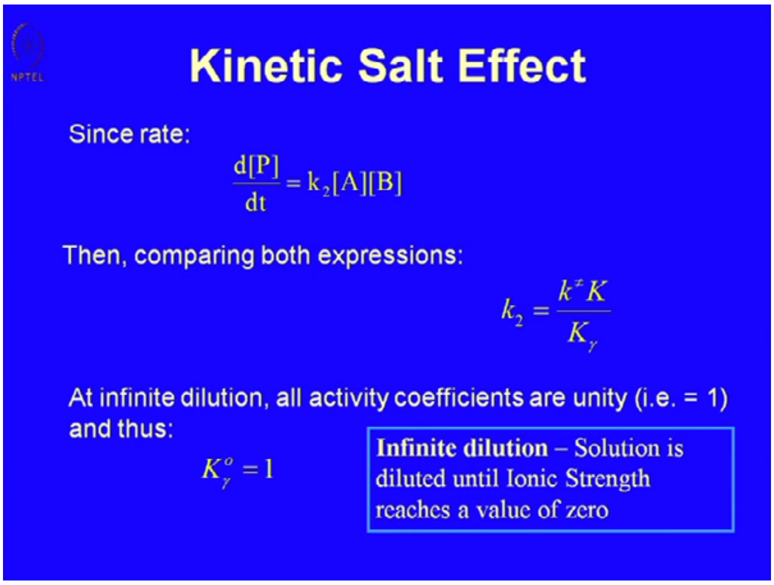

Kinetic Salt Effect

Since rate:

$$\frac{d[P]}{dt} = k_2[A][B]$$

Then, comparing both expressions:

$$k_2 = \frac{k^{\neq} K}{K_\gamma}$$

At infinite dilution, all activity coefficients are unity (i.e. = 1) and thus:

$$K_\gamma^o = 1$$

Infinite dilution – Solution is diluted until Ionic Strength reaches a value of zero

Now what is infinite dilution that is infinite dilution is a solution where your dilute in the solution until you reach until you reach the state of zero ionic strength practically there is no ions there is no ions at all that is average electric field experienced by an ion due to other ions. So, basically due to other ions means there is no other ion. So, it is. So, dilute or or the thing is that the solution is. So, dilute that the the average separation between between maybe two ions is very high. So, that practically one ion is not experiencing the influence of other ion because they are widely separated because of a hugely high dilution because of a huge dilution. So, therefore, you can write k 2 0 0 means infinite dilution is equal to k times K or or you know you can write you can write what you can write you know in place of in place of this you have got k 2 is equal to k K by K gamma. So,. So, your. So, your you know. So, you can write. So, from this you can write again what you do you take log of this. So, you have got and your this one is k 2 0 this one is k 2 0. So, you just replace this over here. So, therefore, your k 2 is equal to k 2 0 divided by K gamma now you take logarithm log 10 for both the sides. So, log k 2 is equal to log k 2 0 minus log K gamma. So, this one is your situation of infinitely dilute case.

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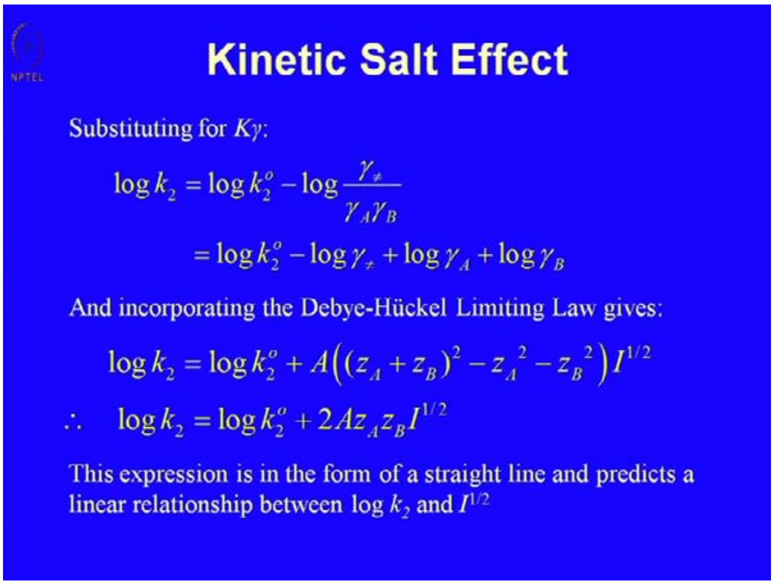

Kinetic Salt Effect

Substituting for $K\gamma$:

$$\log k_2 = \log k_2^o - \log \frac{\gamma_{\neq}}{\gamma_A \gamma_B}$$

$$= \log k_2^o - \log \gamma_{\neq} + \log \gamma_A + \log \gamma_B$$

And incorporating the Debye-Hückel Limiting Law gives:

$$\log k_2 = \log k_2^o + A\left((z_A + z_B)^2 - z_A{}^2 - z_B{}^2\right) I^{1/2}$$

$$\therefore \quad \log k_2 = \log k_2^o + 2Az_A z_B I^{1/2}$$

This expression is in the form of a straight line and predicts a linear relationship between log k_2 and $I^{1/2}$

Now you you put the expression for K gamma what is K gamma K gamma is this K gamma is your gamma A B here you should write 0 gamma A B divided by gamma A gamma B. So, you write log k 2 0 minus log gamma A B gamma A gamma B;

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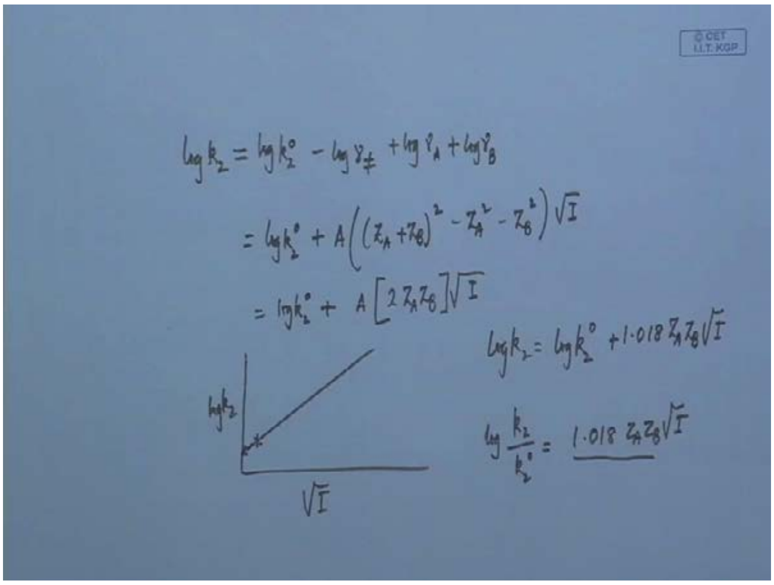

$$\log k_2 = \log k_2^o - \log \gamma_{\neq} + \log \gamma_A + \log \gamma_B$$

$$= \log k_2^o + A\left((Z_A + Z_B)^2 - Z_A^2 - Z_B^2\right)\sqrt{I}$$

$$= \log k_2^o + A\left[2 Z_A Z_B\right]\sqrt{I}$$

$$\log k_2 = \log k_2^o + 1.018\, Z_A Z_B \sqrt{I}$$

$$\log \frac{k_2}{k_2^o} = \underline{1.018\, Z_A Z_B} \sqrt{I}$$

That means, you can write from this you can write log k 2 is equal to log k 2 0 K 2 0 minus log gamma this plus log gamma A plus log gamma B. So, if we incorporate you know the respective expression of debye-huckel limitings law then we will be getting because log gamma gamma is minus A Z square square root of ionic strength therefore, in place of this you can write log k 2 0 plus you know A because A is constant. So, Z A plus Z B whole square minus Z A square because Z A plus Z B whole square because this is the overall charge of this This state this activated state minus Z B square square root of ionic strength. So, log k 2 0 minus A then this is Z A square plus Z B square. So, these two will get cancelled. So, 2 Z A Z B square root of ionic strength. So, this is the expression that relates your rate constant for the reaction at a given ionic strength rate constant when ionic strength is 0 and this is you know ionic strength of the medium. So, if we plot log k 2 what is the square root of ionic strength of the medium we should be getting a straight line we should be getting a straight line of this because there is a plus like this and your intercept slope will be giving you this one A 2 A Z plus Z minus an intercept will be giving you log k 2 0 that is when you; that means, when you extrapolate this to zero ionic strength. So, from here your extrapolating this up to this you are extrapolating maybe because you cannot in principle make a solution containing iron,, but ionic strength is zero because we are discussing ionic reactions. So, this is a you know a linear dependence linear dependence on this square root of ionic strength.

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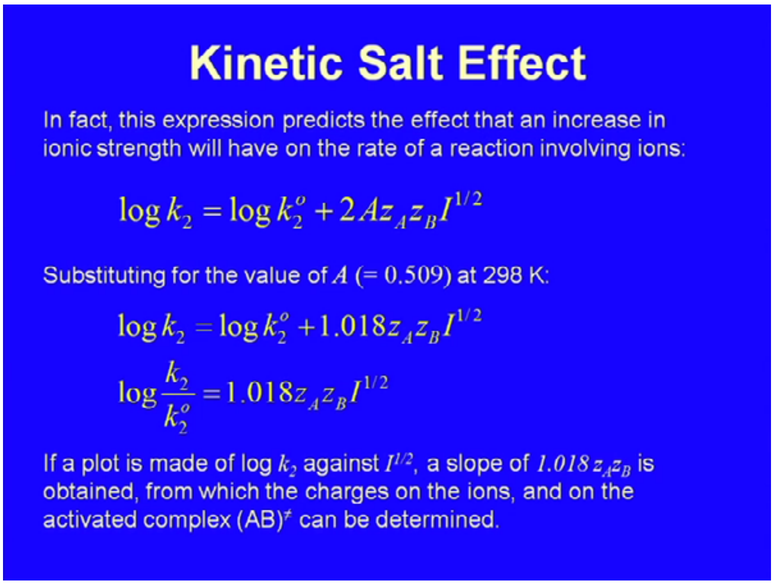

Kinetic Salt Effect

In fact, this expression predicts the effect that an increase in ionic strength will have on the rate of a reaction involving ions:

$$\log k_2 = \log k_2^o + 2Az_Az_BI^{1/2}$$

Substituting for the value of A (= 0.509) at 298 K:

$$\log k_2 = \log k_2^o + 1.018z_Az_BI^{1/2}$$

$$\log \frac{k_2}{k_2^o} = 1.018z_Az_BI^{1/2}$$

If a plot is made of log k_2 against $I^{1/2}$, a slope of $1.018\,z_Az_B$ is obtained, from which the charges on the ions, and on the activated complex $(AB)^{\neq}$ can be determined.

Now, in fact, this expression predicts the effect that an increase in ionic strength will have have on the rate of reaction involving ion. So, for ionic reactions if we if we increase the ionic strength then what is going to means what is going to happen to the overall of overall reaction rate or rate constant rather now for water at 25 degree centigrade 298 kelvin you know if we put the the numbers then log k 2 is equal to log k 2

0 plus 1.018 because 0.509 is a 2 into 0.509 means 1.018. So, Z A Z B square root of I. So, log k 2 by k 2 0 is equal to 1.018 Z A Z B square root of I. So, from this means if we plot log k 2 against square root of ionic strength the slope will be this and is this is obtained and from which the charge on ions and on the activated complex can be can be calculated can be determined experimentally.

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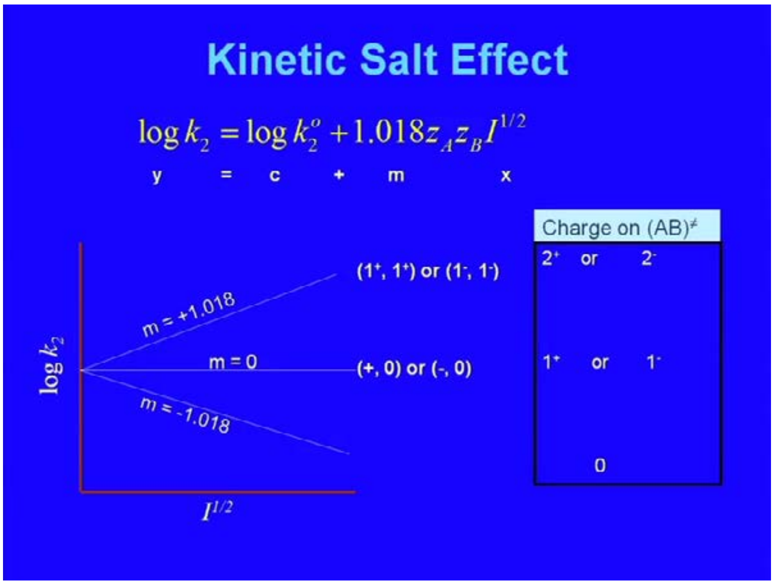

Kinetic Salt Effect

$$\log k_2 = \log k_2^o + 1.018 z_A z_B I^{1/2}$$

y = c + m x

So, this is you know this is you know a typical plot for you know that is showing the salt effect that log k 2 is log k 2 0 1.018 Z A Z B square root of ionic strength where log k 2 is c intercept and m is slope when m is equal to plus 1.018 it is the positive slope when it is the minus it is the negative slope for 1 1 case plus 1 or plus 1 or you know minus 1 minus 1. So, same type charge same type charge means plus plus means it is plus. So, it will increase minus minus it will increase,, but if it is opposite 1 plus 1 minus then it will be minus over here so; that means, this situation will come and when either of two ions is is having zero charge then it will have no effect. So, charge on this if this is this will be charge on A B here it is it is plus 2 or minus 2 plus 1 or minus 1 and it is 0 this this can be determined from you know whether this charge of A B is you know both plus or both minus or maybe one plu[s]- I mean overall charge whether overall charge is you know plus overall charge is a minus that you can determine from the overall nature of the plot because it is basically your it is the difference you know you see if you if you look into the derivation you see that it is Z A square Z B square and Z A Z B is the is the you know overall charge on the on this on the on the activated complex. So, you can find out in principle the charge on on A B from this particular plot. So, kinetic salt effect has got immense importance Let us again go back to another slide that you see that here.

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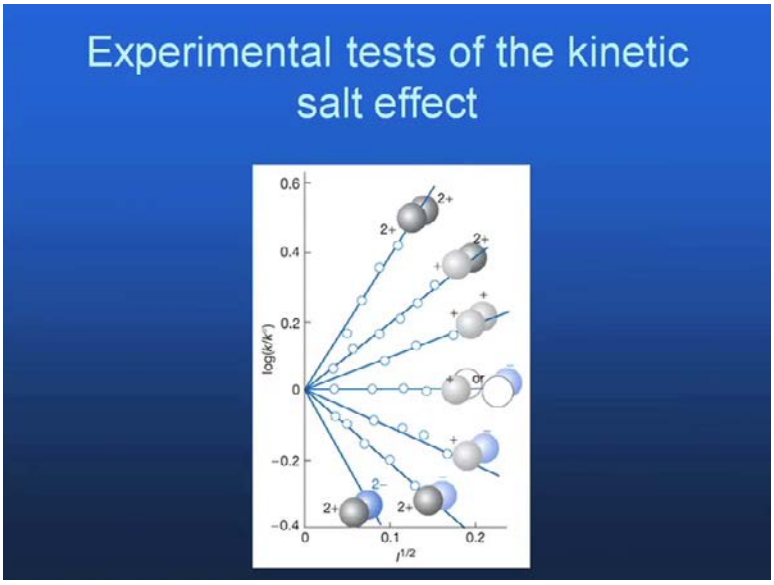

Experimental tests of the kinetic salt effect

You see if we plot log K by K 0 what I was trying to explain in last slide that is you know that is last slide means this one it is again demonstrated over here let us go back to to another slide this one it is a plot of log K by K 0. So, you see what is going to happen. So, if it is plus four that is 2 plus 2 plus that is plus 4 you see it is a huge you know slope positive slope 1 plus another 2 plus intermediate that is 2 overall 2 it is 4 plus plus means 1. So, less slope lesser slope then this is plus 0 or minus 0 0 again 1 plus 1 minus negative it is 2 plus 1 minus still negative 2 plus 2 minus minus 4 basically see you see that it is the test of test means you can test test that whether effect of salt is there in a in a kinetic process and specially when we when we consider ionic species in solution now what is happening here that if you increase if you increase your if you increase the ionic strength what is going to happen why your rate is increased I mean rate constant is increased rate constant means ultimately rate is increased because you know the the system is passing through A transition state that is transition state or an activated complex of this sort A B Z A plus Z B this one. So, it is the charged species. So, if this is a charged species say suppose this species does not have any any charge say for for example, suppose Z A is 0 Z B is also 0 then this species will not feel any electrostatic interaction that is its overall energy is not getting modified even say 1 is plus 1 another is minus 1. So, 1 is plus 1 means suppose we have got say one ion say here another ion here. So, 1 is you know plus 1 another is minus 1 say; that means, it is a it is a it is like a dipole. So, dipole is you know you are immersing a dipole where you are immersing a dipole in an ionic solution. So, there will be you know effect there will be there will be interaction between this dipole because it may act as a dipole this A B this species may act as a dipole because one one part is plus another part is minus. So, it is a plus minus case. So, its energy level will be affected so; that means, this transition state will be influenced in presence of ions if the transition state is influenced by ions then then what is going to happen what is going to happen that if transition state is influenced then you know if you look into this diagram.

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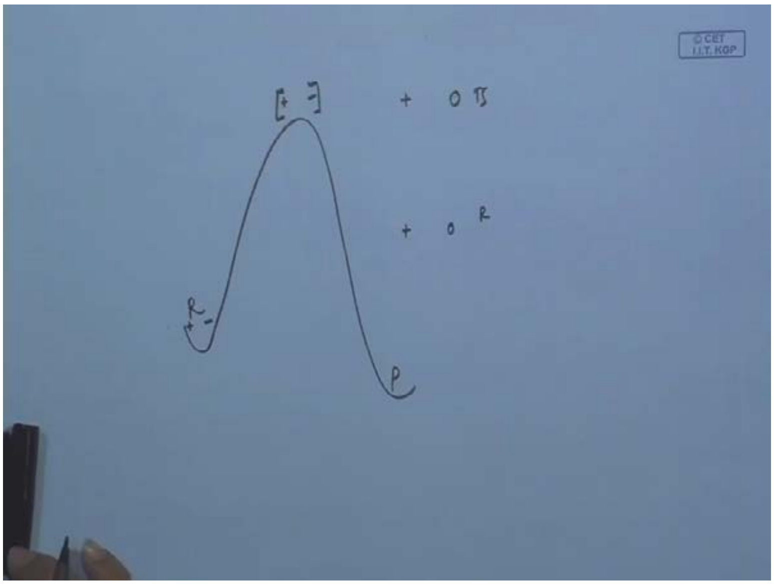

That like this your reactant this is your product and say this is your activated complex say one is plus another is minus. So, it is a dipole. So, its energy level will be modified and how much it will be modified it depends on you know whether means how this is also modified this state because this state is typically your 1 plus charge 1 minus charge they were initially separated. So,. So, this will be stabilized this will also be stabilized now it depends which one is more stabilized and or which one is more destabilized. So, therefore, that will determine the overall change in activation energy. So, it is it is because of your your because of the change in this state or may be this state that is responsible for changing your overall activation energy of the process and rate is hence it is it is modified suppose if if it is one is plus another is 0; that means, you started with one state of your starting state your reactant is plus 0 and your transition state is also plus

0. So, it is nothing new means nothing new means if you change the ionic strength of the medium then these two will be similarly affected compared to these two that is if you compare these two these two will be. So, this is your transition state and this is your reactant state. So, these two will be similarly affected if it is destabilized both will be destabilized to same extent if it is stabilized both will be stabilized to same extent. So, therefore, no net change in change in energy state between these two therefore, there will be there will be no effect that is why you see if you look into this one you see if it is plus or minus if it is plus or minus you will be seeing that no effect of ionic strength when it is plus plus it is increasing it is increasing when it is plus minus it is decreasing. So, this has got this has got a tremendous importance. So, when specially you consider ionic reactions when specially you consider ionic reactions. So, this is of of immense importance. So, you see that that how your ionic strength of the medium. So, as I told you ionic strength is a measure of average electric field experienced by the by by other by an ion due to the presence of other ions in solution. So, since it is a chemical reaction of ionic species. So, you know electric field experienced by ions that is reacting ions and your transition state could be similar or could be different depending on their charge and nature if they are similarly affected due to the presence of ions then we do not see any effect on rate constant,, but if they are differently affected say one is destabilized another is destabilized,, but to lesser a lesser extent or maybe in some other way then you see you will be seeing that the rate of reaction rate of reaction and the rate constant is is affected you know tremendously. So, it is the it is the basically consequence of electrostatic interaction between between the ions in solution and this 0.509 is A which is 0.509 this is for water at 298 kelvin if you take a different solvent then you have to you have to consider you know a that is you have to use the use a different value for that solvent and also temperature is a very important factor because temperature if temperature is increased. So, average thermal motion of ions and ions in solution will also be affected therefore, that may influence I mean for sure that will influence the overall rate of reaction. So, here we have we have we have made use of debye-huckel limiting law to to to find out this ionic strength in terms of concentration and the charge on ion and of course,, one one thing we must consider that this is this limiting law is for dilute solution it is not for concentrated solution. So, for concentrated solution this expression of ionic strength is different therefore, whatever kinetic salt effect on on ionic reactions I have discussed over here it is for moderately or maybe for dilute solution it is not applicable for concentrated solutions because for concentrated solution you cannot apply ionic

strength in this way that is I is equal to half summation of c i Z i square I mean an I mean not that one I mean log gamma plus gamma A is equal to A Z plus square square root of I that you cannot use; that means, the relation between log gamma and ionic strength will be different it is not you know linear so. So, therefore, this kinetic salt effect is for pretty much for dilute solutions. So, what we have learnt here in this particular part here we have you know particular part specially you know kinetic salt effect it is the thermodynamic version of activated complex theory that is the it is the it is the formation it deals with the formation of an activated complex due to interaction of two ions it may be similar charge or maybe differently charged similar I mean plus plus plus minus or maybe minus minus. So, and it it deals with reaction between ions and how does ionic strength affect the rate of of reaction is is is the is the main concern of this particular topic that is kinetic salt effect effect of salt on kinetics of a particular reaction. So, here what we have done is that we have taken two ions and we have formed the activated complex which is in in equilibrium with the ions constituent reactant ions and then this A B this activated complex that undergoes chemical reaction to produce your desired products and and in a in a separate way we have also used this formula that d P d t is k 2 A B. So, you have compared this rate and that rate because these two rates which must be equal because we are discussing the same reaction and from that we have used used you know the activity concept because activity concept is useful when the solution is concentrated,, but for dilute solution you can use at ease use concentration and then we have we have made use of the debye-huckel limiting law to find out you know to simplify this this equilibrium constant and it it turned out to be like this and finally, it gave this expression this simple expression that you know rate constant.

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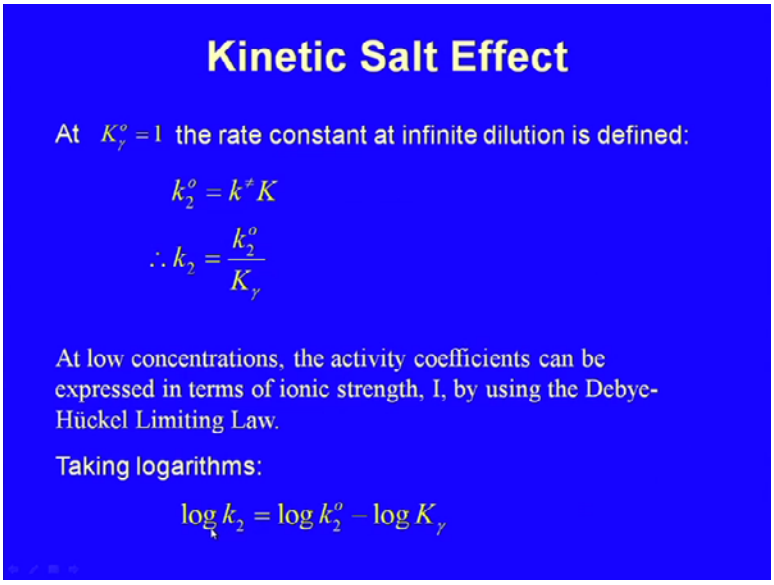

Kinetic Salt Effect

At $K_\gamma^o = 1$ the rate constant at infinite dilution is defined:

$$k_2^o = k^{\neq} K$$

$$\therefore k_2 = \frac{k_2^o}{K_\gamma}$$

At low concentrations, the activity coefficients can be expressed in terms of ionic strength, I, by using the Debye-Hückel Limiting Law.

Taking logarithms:

$$\log k_2 = \log k_2^o - \log K_\gamma$$

And rate constant at zero ionic strength and your log K gamma that is that is the ratio of the activity coefficient the ratio of the activity coefficient. So,. So, this is a very simple relation this is a very very simple elegant relation and if we simplify it then we will be finding that log k 2 is equal to log k 2 0 plus this factor. So, this factor is the factor that is responsible for the modification of your rate constant with with ionic strength this is responsible for this. So, therefore, and you see that since it is in plus sign. So, Z A plus Z B if these two are in same sign then it will be in plus sign. So, if your reacting ions are say both of them are positive or if both of them are negative then the rate constant will be increased rate constant will be increased as you increase the ionic strength of the medium as you increase as as you increase the average electric field you know experienced by ions due to the presence of other ions in solution. So, it will increase in a with a positive slope and if you have Z plus Z minus product of Z plus Z minus negative then it will reduce; that means, as if as if the increase of ionic strength has got an opposed effect it tends tend to you know slow down the process it does not you know favor somehow your activated complex is maybe destabilized and if it is destabilized. So, if activated complex is not formed. So, how does the reaction means how how can the reaction proceed ok. So, and if we plot from plot we can find out you know the type of you know what is the overall charge of the of the you know the activated state and this is a typical plot and if we take a take you know this plot this gives you a nice idea of two plus two plus or two plus plus or plus plus or plus minus or I mean plus zero or zero minus. So, in this particular section in this particular you know section where we we dealt with kinetics of some specific reaction some specific reaction specially this ionic reaction. So, how how these ionic reactions are affected due to presence of other ions in solution that is a very important part that we have taken up and we are we tried to explain and also we discussed this diffusion controlled reaction now diffusion controlled reaction means the reaction the rate which is dependent upon how easily or how fast these you know reacting species are diffusing and coming close to each other. So, that is the determining factor for you know for the for the process. So, that is a very important aspect which we also have talked about. So, diffusion controlled reaction falls under fast reaction and there are plenty of examples that you will be finding in literature that in connection with salt effect and that demonstrates that if you change the salt concentration ultimately there is enormous effect on overall rate of reaction overall rate of reaction means means how fast the products are formed. So, therefore, like temperature temperature is a very important parameter for chemical reaction if we increase the temperature since you know reactions which you already have talked about normal reactions or any reaction these are you know if if the reaction is you know energy barrier dependent then if you increase the temperature then rate will rate will change and rate will increase you will never find that rate to get you know reduces in the same way like temperature for for ionic reactions ionic strength is a very important factor that may you know in principle change the rate constant because you know states are modified in presence of ion in presence of ionic strength your starting state and then your activated state and your final state all are modified their relative positions are modified therefore, the system is no longer identical to the the initial situation when there was no no added salt that is why it is weaving in a different fashion and rates are modified I mean rate constants are also modified therefore, therefore, we will continue in the next lecture we will continue with kinetics of some specific reactions and then we will take up kinetics of catalyzed reactions especially enzyme catalyzed reaction we will take up. So, till then have nice time thank you.