Rate Processes

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Module No. # 01

Lecture No. # 02

Reaction Rates and Rate Laws

Hello in our last lecture, we have learnt various rate laws, then concentration time equations, then their half life's like for 0 order reaction, rate was found to be equal to k I mean just for 0 order rate equal to k.

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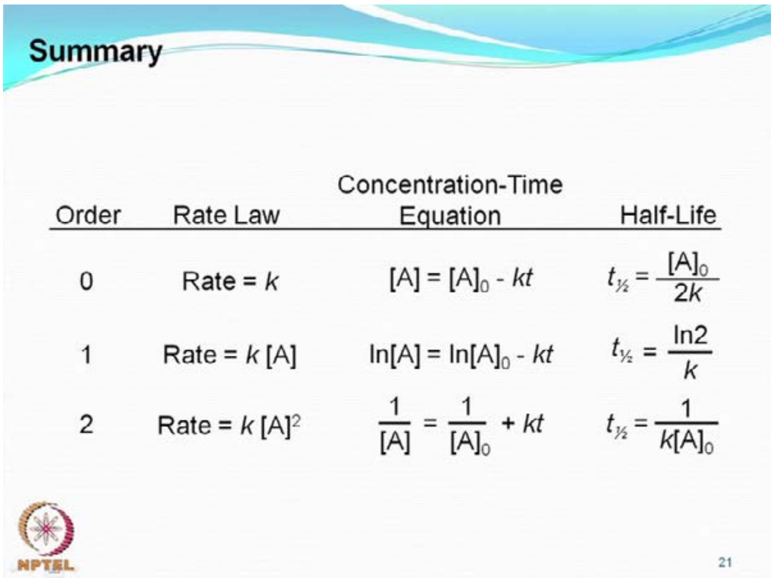

Summary

Order	Rate Law	Concentration-Time Equation	Half-Life
0	Rate = k	$[A] = [A]_0 - kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1	Rate = k [A]	$\ln[A] = \ln[A]_0 - kt$	$t_{1/2} = \frac{\ln 2}{k}$
2	Rate = $k\,[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{1/2} = \frac{1}{k[A]_0}$

Then for first order, rate is equal to k times A; for the second order, rate is k times A to the power 2 and corresponding half life's are like this (Refer Slide Time: 00:53); where you see that, for the first order reaction t half is independent of the initial concentration of the reactant.

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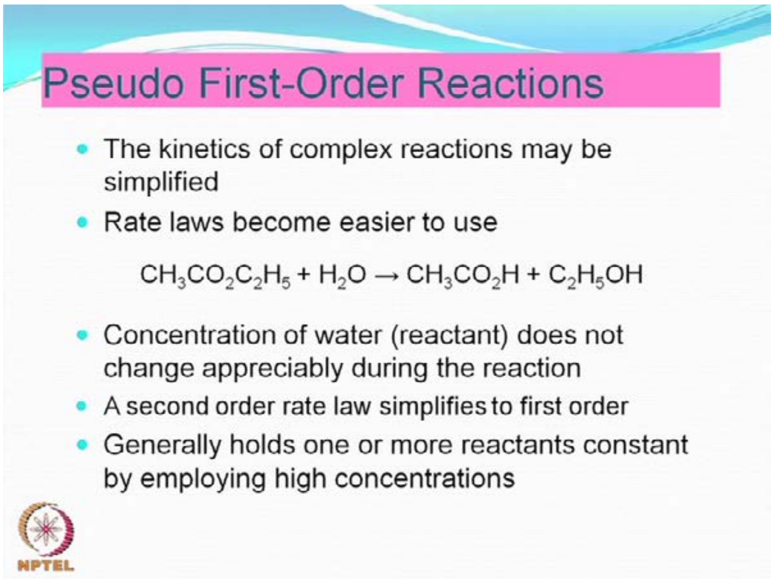

Pseudo First-Order Reactions

- The kinetics of complex reactions may be simplified
- Rate laws become easier to use

$$CH_3CO_2C_2H_5 + H_2O \rightarrow CH_3CO_2H + C_2H_5OH$$

- Concentration of water (reactant) does not change appreciably during the reaction
- A second order rate law simplifies to first order
- Generally holds one or more reactants constant by employing high concentrations

Now, next we will move on to a special kind of reaction which is called the pseudo-first-order reaction.

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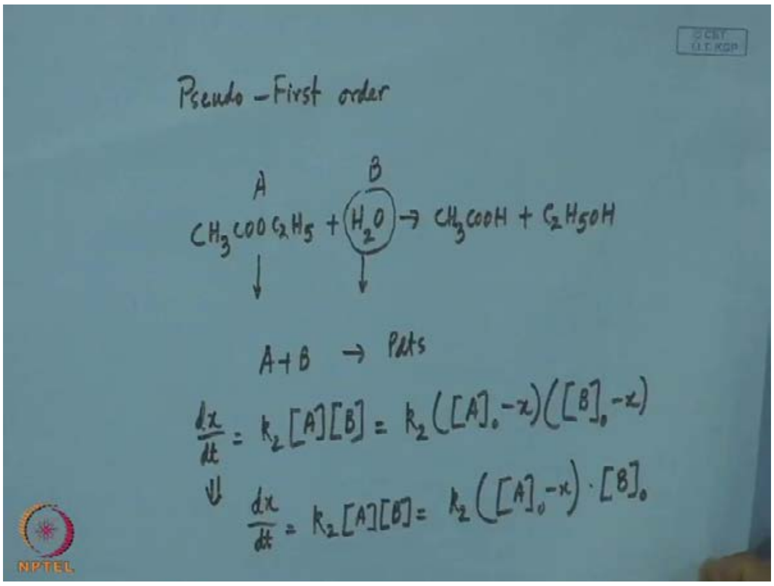

Pseudo-First order

$$\overset{A}{CH_3COOC_2H_5} + \boxed{\overset{B}{H_2O}} \rightarrow CH_3COOH + C_2H_5OH$$

$$A + B \rightarrow Pdts$$

$$\frac{dx}{dt} = k_2[A][B] = k_2([A]_0 - x)([B]_0 - x)$$

$$\Downarrow \quad \frac{dx}{dt} = k_2[A][B] = k_2([A]_0 - x)\cdot[B]_0$$

Pseudo-first-order reaction pseudo-first order, so the kinetics of complex reactions may be simplified. And rate laws become easier to use, although in certain cases some complicated rate laws may happen, but under certain simplification those rate laws may be reduced down to some usable form.

Suppose, we are we are having reaction of this sort, C H 3 C O O C 2 H 5 that is ethyl acetate in water in presence of may be little trace amount of acid producing acetic acid and ethyl alcohol, C 2 H 5 O H. So, it is in true sense, a second order reaction that is rate is proportional to the concentration of this and also concentration of water. Now, this reaction is carried out in water that is you put a measured amount of ethyl acetate in given volume of water, then you add a trace amount of little amount of acid say H C L and then, allow the reaction to you know proceed.

So, in that case ethyl alcohol and acetic acid will be (( )) along with water I mean water will remain as it is that is suppose, you have used say say 100 m l of water and we have put say 1 m l of ethyl acetate; so, all 100 m l of water will virtually remain you know remain 100 m l, although very little amount of water will be used used up to you know decompose this one, but virtually the water concentration will not change. That means, since the water concentration that is the one of the reactants is kept at high value then virtually it does not change appreciably.

So, now in that case the second order rate law may be simplified, and this will reduce to a first order reaction I mean first order kinetics. And this generally holds one or more reactants constant by employing high concentration. So, if we put this one high concentration then, throughout the reaction we may think that this is virtually constant.

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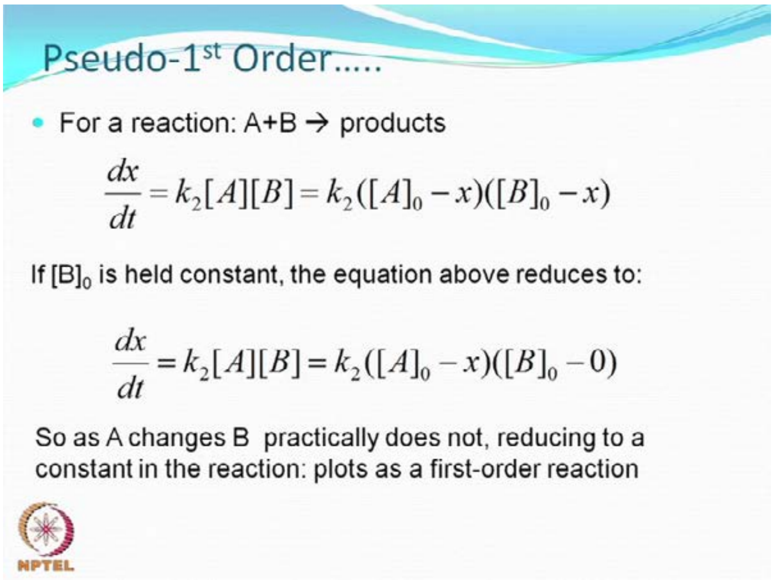

Pseudo-1st Order.....

- For a reaction: A+B → products

$$\frac{dx}{dt} = k_2[A][B] = k_2([A]_0 - x)([B]_0 - x)$$

If $[B]_0$ is held constant, the equation above reduces to:

$$\frac{dx}{dt} = k_2[A][B] = k_2([A]_0 - x)([B]_0 - 0)$$

So as A changes B practically does not, reducing to a constant in the reaction: plots as a first-order reaction

So, pseudo-first order reaction say general start from the general second order reaction that is you know A plus B say this is A and this is B, A plus B producing products. So, your rate expression will be d x d t is equal to k 2, 2 is for the second order (( )) is equal to I already have talked about this expression, it is a general second order expression minus x times B naught minus x.

So, now if B is held constant then, if this is held constant or may be if it is kept at some high value then, for all practical purposes we can think that this one that is this second quantity bracketed second quantity is constant. So, that means in that case, this expression reduces to d x d t is equal to k 2 A B is equal to k 2 A naught minus x times B naught, because it is in high I mean high concentration or in large excess.

So, during the course of reaction A reduces, but B remains almost constant almost constant (Refer Slide Time: 05:47). So, now if we plot this one, the plot will look like a like a first order one that means rate will now be written as your k 2 then B naught times A naught minus x. So, the plot will look like a first order plot. So, now we will move on to certain examples simple examples (Refer Slide Time: 06:43).

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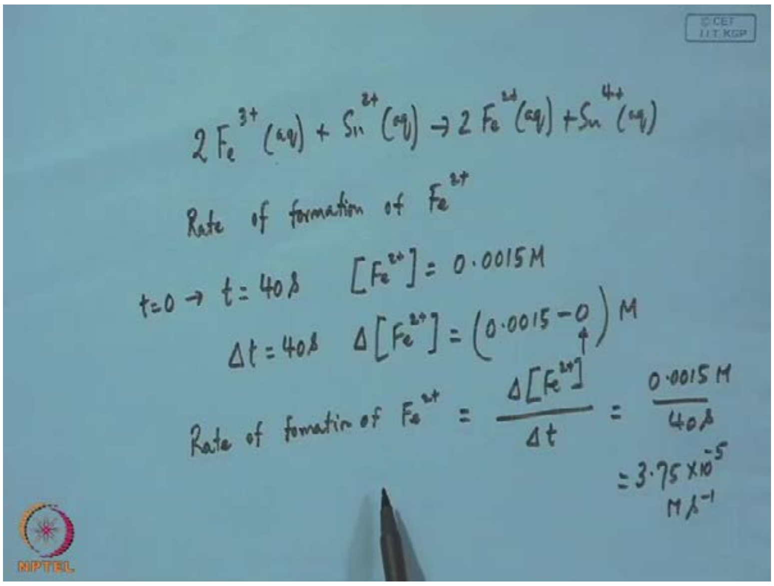

$$2\,Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow 2\,Fe^{2+}(aq) + Sn^{4+}(aq)$$

Rate of formation of Fe^{2+}

$t=0 \rightarrow t = 40\,s \quad [Fe^{2+}] = 0.0015\,M$

$\Delta t = 40\,s \quad \Delta[Fe^{2+}] = (0.0015 - \underset{\uparrow}{0})\,M$

$$\text{Rate of formation of } Fe^{2+} = \frac{\Delta[Fe^{2+}]}{\Delta t} = \frac{0.0015\,M}{40\,s}$$

$$= 3.75 \times 10^{-5}\ M\,s^{-1}$$

So, let us concentrate on to concentrate on to a reaction of this kind say 2 F e 3 plus aqueous means aquated (( )) plus S n 2 plus, this is also aqueous producing 2 F e 2 plus aqueous plus S n 4 plus aqueous. And we would like to know the rate of formation rate of formation of F e 2 plus that is the ferrous iron.

So, we need some time information, so say let us put t is equal to say 40 second and say concentration of F e 2 plus say this is equal to 0.015 molar; we can measure by various means may be spectro photometrically or may be some other analytic method we can measure the concentration. And t is equal to 0 to t is equal to 40, so delta t is equal to 40 second.

And so, delta F e 2 plus is equal to 0.0015 minus 0 because, why this is 0? Because, at the start there was no F e 2 plus, so this much of molar. So, rate of formation formation of F e 2 plus is equal to delta divided by delta t, which is equal to 0.0015 divided by 40 second and this is molar; and this gives you 3.75 into 10 to the power minus 5 mol second inverse. So, this way we can find out the rate of formation of F e 2 plus.

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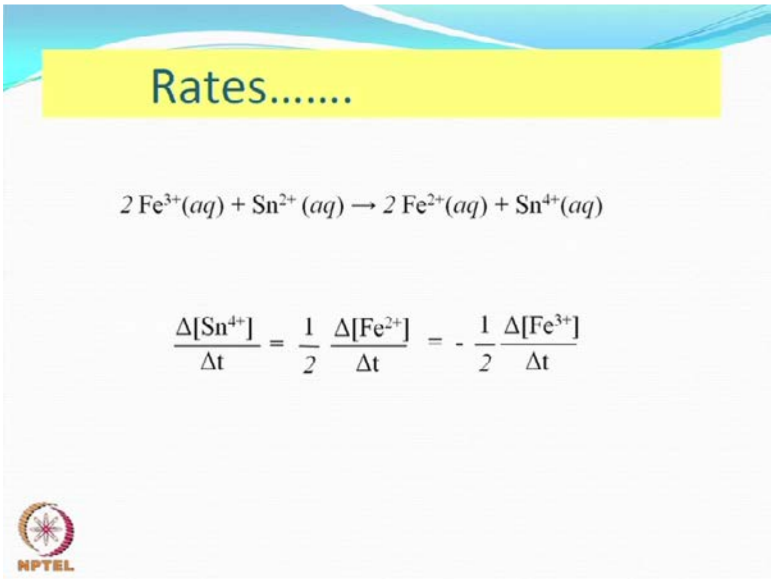

Rates.......

$$2\,Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow 2\,Fe^{2+}(aq) + Sn^{4+}(aq)$$

$$\frac{\Delta[Sn^{4+}]}{\Delta t} = \frac{1}{2}\frac{\Delta[Fe^{2+}]}{\Delta t} = -\frac{1}{2}\frac{\Delta[Fe^{3+}]}{\Delta t}$$

Next is about the stoichiometric equation say let us have a concrete example.

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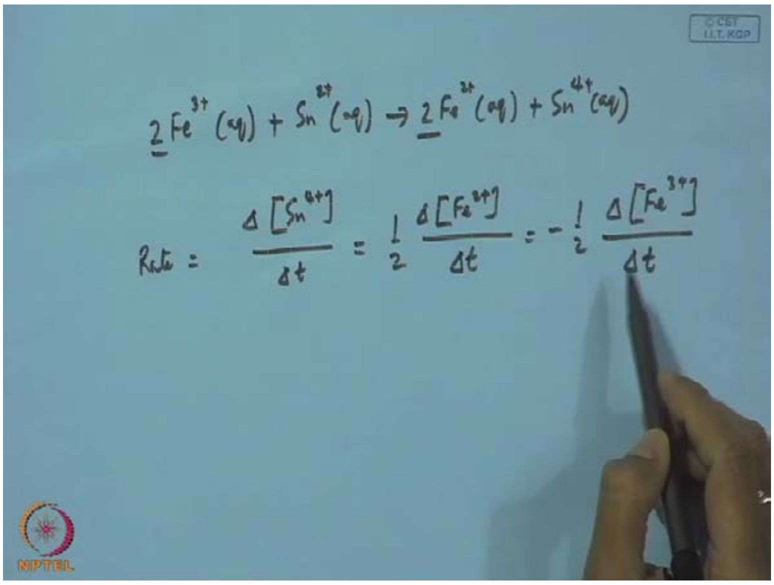

$$\underline{2}Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow \underline{2}Fe^{2+}(aq) + Sn^{4+}(aq)$$

$$Rate = \frac{\Delta[Sn^{4+}]}{\Delta t} = \frac{1}{2}\frac{\Delta[Fe^{2+}]}{\Delta t} = -\frac{1}{2}\frac{\Delta[Fe^{3+}]}{\Delta t}$$

2 F e 3 plus aqueous S n 2 plus aqueous giving rise to 2 F e 2 plus aqueous plus S n 4 plus aqueous. Then the rate will be will be equal to delta of concentration of S n 4 plus by delta t, which is equal to half delta of concentration of F e 2 plus by delta t, which is equal to minus half because it is 2, this stoichiometric coefficient half; therefore, delta of F e 3 plus divided by delta of t. So, this way we can write. Because, we can express rate in this way that, time rate of change of concentration of S n 4 plus because at 0 time, there was no S n 4 plus.

Therefore, whatever S n 4 plus is form is the net S n 4 plus form. So, from that we can we can find out the rate in the same way; we started with with F e 3 plus, but initially there was no F e 2 plus. So, again in the same way, your initial F e 2 plus is 0, so from that we can find out the rate of formation of F e 2 plus or the rate of formation of F e 3 plus and from that, overall rate of reaction.

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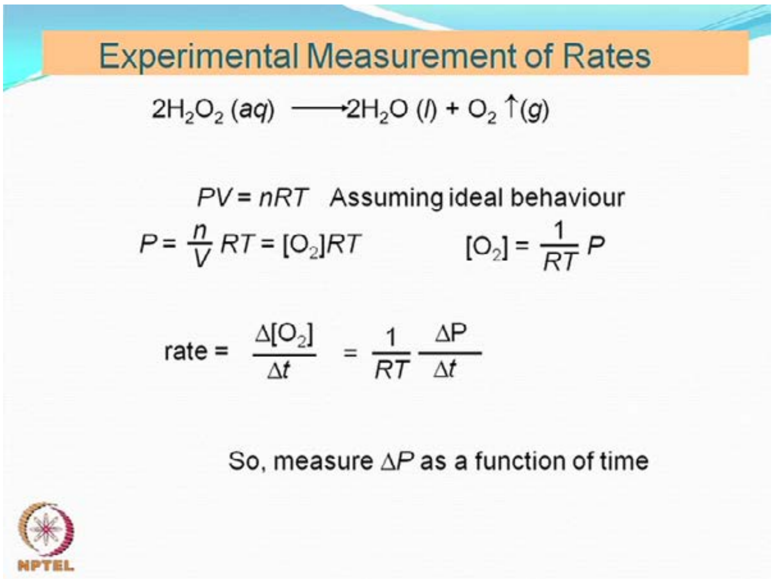

Experimental Measurement of Rates

$2H_2O_2\,(aq) \longrightarrow 2H_2O\,(l) + O_2\uparrow(g)$

$PV = nRT$ Assuming ideal behaviour

$P = \frac{n}{V}RT = [O_2]RT \qquad [O_2] = \frac{1}{RT}P$

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{1}{RT}\frac{\Delta P}{\Delta t}$$

So, measure ΔP as a function of time

Next, we will move on to experimental measurement of chemical reaction rates.

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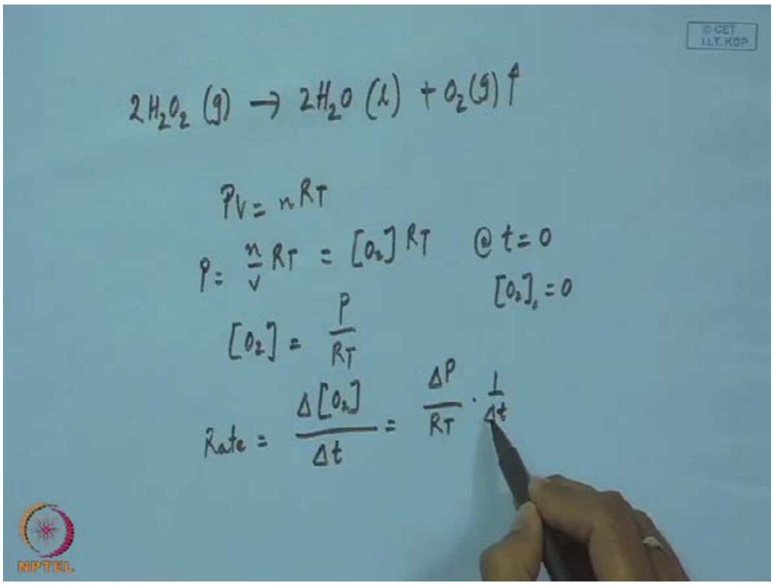

$2H_2O_2\,(g) \rightarrow 2H_2O\,(l) + O_2(g)\uparrow$

$PV = nRT$

$P = \frac{n}{V}RT = [O_2]RT \qquad @\, t=0$

$[O_2]_0 = 0$

$[O_2] = \frac{P}{RT}$

$$\text{Rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta P}{RT}\cdot\frac{1}{\Delta t}$$

So, let us start with let us start with a simple example that, decomposition of H 2 O 2 producing 2 H 2 O liquid, because it happens in aqueous H 2 O 2 plus O 2 gas, gas is evolved. So, how to find out the rate? Now, in this case, suppose that this gas, so evolved is behaving (( )) ideally. So, in that case we can use the ideal gas equation that, P V is equal to n RT that is P is equal to n by V R T. So, n by V means it is basically concentration of O 2, because no gases species is there in on the left hand side.

So, only on the right hand side, this oxygen is the gases species, O 2 then R T. So, that means concentration of O 2 is equal to P by R T. So, rate will be equal to will be equal to delta O 2, delta of concentration of O 2, because delta O 2 means how much of change in concentration of O 2 is there divided by delta t.

So, basically delta O 2 is nothing but, O 2 because at the very start, there was no O 2. So, at t is equal to 0, concentration of O 2 is equal to 0 that is why it is it will be you know delta P by R T into 1 by delta t, delta P means change in pressure change in pressure. So, if we measure change in pressure as a function of time, we should be able to find out the rate of reaction and the corresponding other parameters involved; other parameters means you know rate then, rate constant although it is a constant quantity.

So, these things and also we should be able to find out you know the (( )) plots and etcetera so on, and so forth. So, just by you know measuring the delta P and delta t, we should be able to find out the rate of these particular reaction.

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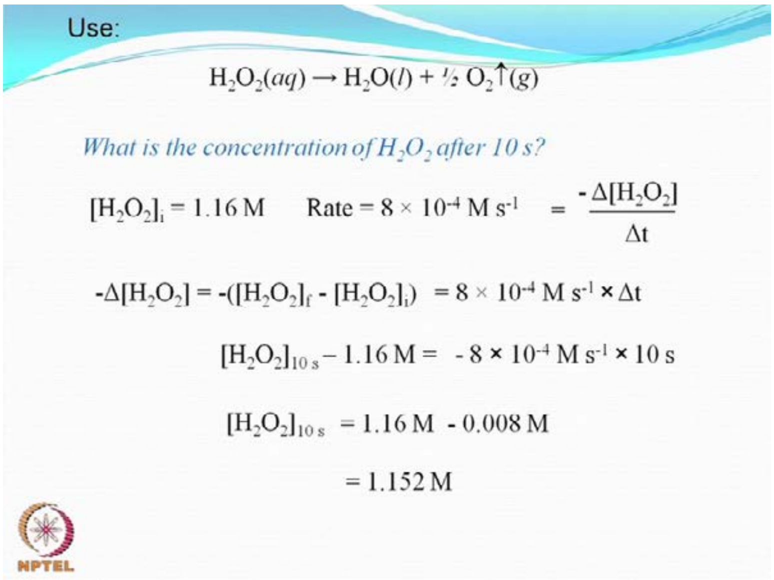

Use:

$$H_2O_2(aq) \rightarrow H_2O(l) + \tfrac{1}{2}\, O_2\uparrow(g)$$

What is the concentration of H_2O_2 after 10 s?

$$[H_2O_2]_i = 1.16\ \mathrm{M} \qquad \text{Rate} = 8 \times 10^{-4}\ \mathrm{M\ s^{-1}} \quad = \frac{-\Delta[H_2O_2]}{\Delta t}$$

$$-\Delta[H_2O_2] = -([H_2O_2]_f - [H_2O_2]_i) \ = 8 \times 10^{-4}\ \mathrm{M\ s^{-1}} \times \Delta t$$

$$[H_2O_2]_{10\,s} - 1.16\ \mathrm{M} = \ -8 \times 10^{-4}\ \mathrm{M\ s^{-1}} \times 10\ \mathrm{s}$$

$$[H_2O_2]_{10\,s} \ = 1.16\ \mathrm{M}\ - 0.008\ \mathrm{M}$$

$$= 1.152\ \mathrm{M}$$

Now, if you would like to know the concentration of H 2 O 2 after the reaction has elapsed say 10 seconds how to find out, how to find out the concentration if we if we are given the initial concentration?

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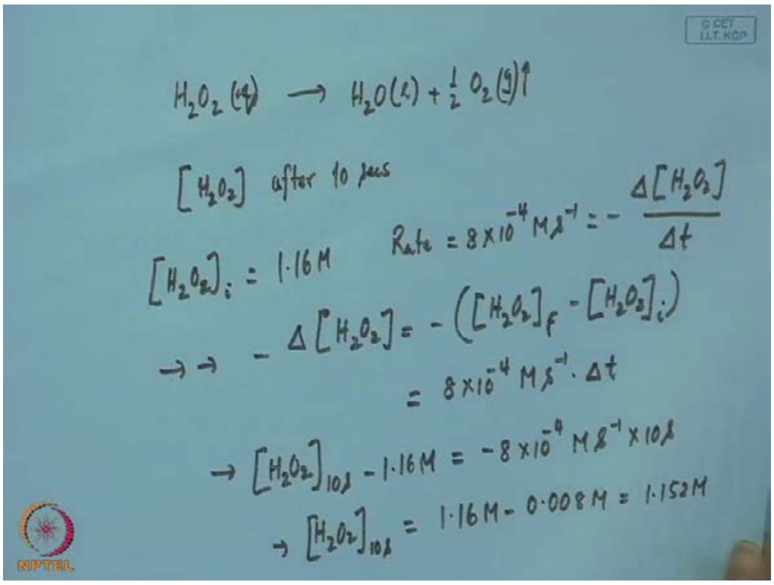

$H_2O_2(aq) \rightarrow H_2O(l) + \frac{1}{2}O_2(g)\uparrow$

$[H_2O_2]$ after 10 secs

$[H_2O_2]_i = 1.16\,M$ Rate $= 8\times10^{-4}\,M s^{-1} = -\frac{\Delta[H_2O_2]}{\Delta t}$

$\rightarrow\rightarrow -\Delta[H_2O_2] = -([H_2O_2]_f - [H_2O_2]_i)$

$= 8\times10^{-4}\,M s^{-1}\cdot\Delta t$

$\rightarrow [H_2O_2]_{10s} - 1.16\,M = -8\times10^{-4}\,M s^{-1}\times10s$

$\rightarrow [H_2O_2]_{10s} = 1.16\,M - 0.008\,M = 1.152\,M$

So, again we start with the same reaction H 2 O 2 liquid reducing H 2 O liquid or it is better to say aqueous liquid plus half O 2 gas. So, in that case, we would like to find out the concentration of H 2 O 2 after 10 seconds. So, let us think that, initial concentration is given to be is equal to say 1.16 molar and also given that, rate is equal to 8 into 10 to the power minus 4 mol second inverse; so, which is equal to minus of delta H 2 O 2 divided by delta t, why minus? Because, it is it is depleting.

So, we can write from this we can write minus of delta H 2 O 2 is equal to minus of H 2 O 2 final minus H 2 O 2 initial, which is equal to 8 into 10 to the power minus 4 mol second inverse inverse into delta t time's delta t. So, from this again we can write H 2 O 2 O 2 10 second minus 1.16 molar is equal to minus 8 into 10 to the power minus 4 mol second inverse into 10 second.

So, this gives you H 2 O 2 10 second is equal to 1.16 molar minus 0.008 molar, which is equal to 1.152 molar. So, that means after 10 seconds, the concentration of H 2 O 2 which is remaining in the solution that is which has which has has not taken place you know you know which has not taken part into into this decomposition reaction is 1.152 molar. So, that means it has reduced, in 10 seconds it has reduced to a little bit, but it has reduced, because of this chemical you know reaction which is nothing but, the decomposition process.

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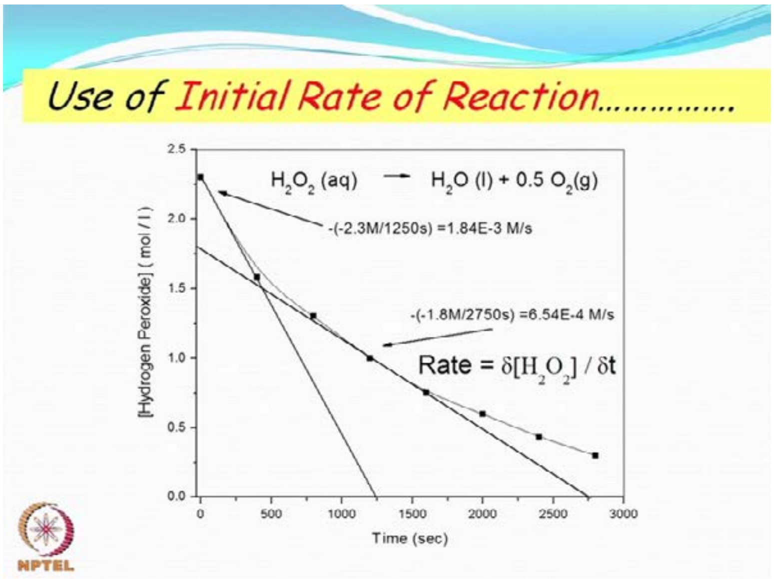

Use of Initial Rate of Reaction……………

Now, there is another method, which is called the initial rate method; initial rate method method to find out the rate of reaction.

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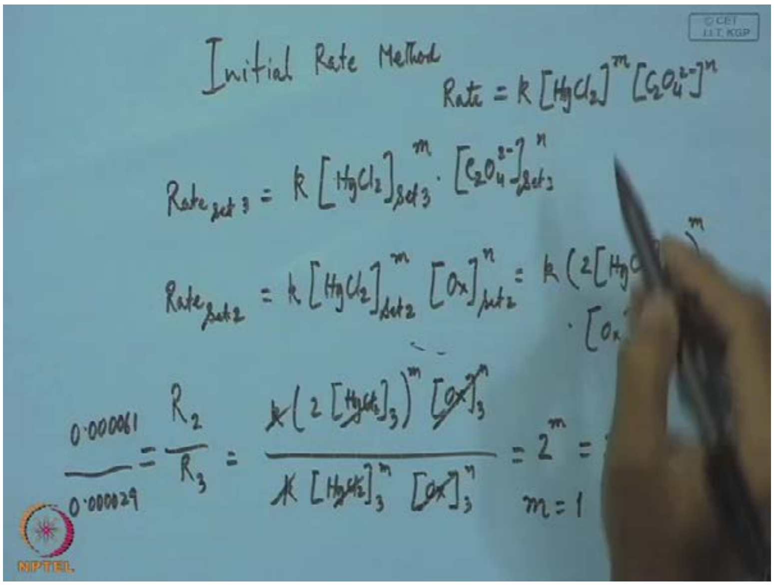

Initial Rate Method

$$Rate = k[HgCl_2]^m[C_2O_4^{2-}]^n$$

$$Rate_{set\,3} = k[HgCl_2]^m_{set\,3} \cdot [C_2O_4^{2-}]^n_{set\,3}$$

$$Rate_{set\,2} = k[HgCl_2]^m_{set\,2}\,[Ox]^n_{set\,2} = k(2[Hg$$

$$\cdot\,[O_x$$

$$\frac{0.000061}{0.000029} = \frac{R_2}{R_3} = \frac{\cancel{k}(2[HgCl_2]_3)^m\,\cancel{[Ox]}^n_3}{\cancel{k}[HgCl_2]^m_3\,[Ox]^n_3} = 2^m =$$

$$m = 1$$

Now, let us look into this slide that here, we are using the same reaction that is H 2 O 2 aqueous producing H 2 O liquid and 0.5 O 2 gas. Now, and this is the you know concentration of hydrogen peroxide as a function of time. So, these dotted points I mean this this this one is one data, this is another data point, this is another data, these are the data points. This square you know black squares are your data points. So, you see that it is reducing with time.

Now, if we draw a tangent at some specific point say at this point and then another tangent at this point (Refer Slide Time: 18:15). So, this tangent is basically you know the rate that is rate of you know delta H 2 O 2 divided by delta t, it is giving you this one. So, basically this this slope, this is the slope. So, this slope is basically how much this slope is basically this you know 2.3, this value is 2.3.

And this value is about 1250, so if you divide this divided by 1250 then, you will be getting some number, which is 1.84 into 10 to the power minus 3 mol per second. So, this number at this particular the tangent, the tangent has the magnitude 1.84 into 10 to the power minus 3 mol per second at this point. And here, it is 6.54 into 10 to the power minus 4 mol per second at this point.

So, we are just looking into we are looking at the the concentration versus time plot and the corresponding slopes. And rate is nothing but, your del del t of concentration of H 2 O 2, so we would like to find out that. So, basically we have this plot and on top of that, we have got this slope. So, for this one this value is 1. 1.8 8, and this value is about 2750; so, that is why 1.8 by 2.2750.

So, so how to employ this method, in finding out your your you know rate of reaction along with the order of a reaction. So, we are just interested to, interested in finding out the order of reaction (( )) the initial rate method. So, from this initial rate, we just wanted to know, what is the rate at that particular instant? So, at this instant, the rate is this much I mean this much (Refer Slide Time: 20:16); at this instant, this rate is this much. Because as we move on towards you know longer time scale, you know reactant amount of reactant is reducing therefore, the reaction rate become (( )) therefore, you know this slope is reducing.

So, we would like to use this information in in in finding out the order of reaction. So, we are using say, this reaction mercuric chloride oxalate producing chlorine gas and then carbon dioxide and mercuric chloride. So, we are using 3 sets for this particular you know example.

So, set 1 where mercuric chloride is 0.1 molar oxalate is 0.1 molar. Set 2, it is mercuric chloride is 0.1, oxalate is double of set 1 it is 0.2. And the third set is mercuric chloride is 0.05 and the oxalate is 0.2; and the corresponding initial rate I mean slope, slope of the you know concentration versus time plot. It is like for this set 1, it is this much 4 naught 15, here it is 4 naught 61 for the set 2; and for the set 3, it is 4 naught 29. You see that, there is a definitive change of the initial rate, as we move on to different sets consisting of different composition of mercuric chloride and oxalate.

So, again we use this expression (Refer Slide Time: 21:55), rate for set 3 is equal to rate constant then, basically this this reaction rate we do not know exactly, the rate with respect to mercuric chloride and the rate with respect to oxalate. So, we have to write like this, rate is equal to k into H g C l 2 to the power m and C 2 O 4 2 minus to the power n. So, that means the reaction is m th order with respect to mercuric chloride, and n th order with respect to oxalate. So, let us use set 3.

So, set 3 is k is k into H g C l 2 set 3 to the power m times C 2 O 4 2 minus set 3 n. Set 2 for set 2, rate set 2 is equal to again k the same rate constant H g C l 2 set 2 to the power m then, this is ox means oxalate set 2 to the power n; which is equal to you know now we will use the information about different you know composition and compare their relative you know proportion.

So, you see that for set 3 and set 2, we are looking into set 3 and set 2. So, for set 2, the mercuric chloride is how much? It is twice set 2, it is twice set 3 sorry it is twice set 3. So, that means 2 times H g c l 2 set 3 to the power m times oxalate set 3 set 3 to the power n. So, now we divide this by this or set 2 by set 3. So, R 2 by R 3 that means R for rate for set 2, rate for set 3 which is equal to k times 2 H g C l 2 3, 3 means set 3 to the power m then, oxalate ox 3 to the power n divided by same k then, H g C l 2 3 to the power m ox n 3. So, this two will cancel, again this two will cancel, k will cancel. So, this will be giving you this will be giving you 2 to the power m.

Now, we know what are the values of these initial rates, you see that R 2 is equal to 0.4 naught 61; and R 3 is 0.000029, so it is approximately 2 that means equal to 2, approximately very close to 2. So, therefore, we can write from these we can write m is equal to 1.

So, now we we are now able to find out the value of m, that is the order with respect to H g C l 2, we we see that it is the first order with respect to H g C l 2. So, the reaction which we are talking about that is the, that is the reaction between H g C l 2 and oxalate; in this case, this reaction is first order with respect to H g C l 2.

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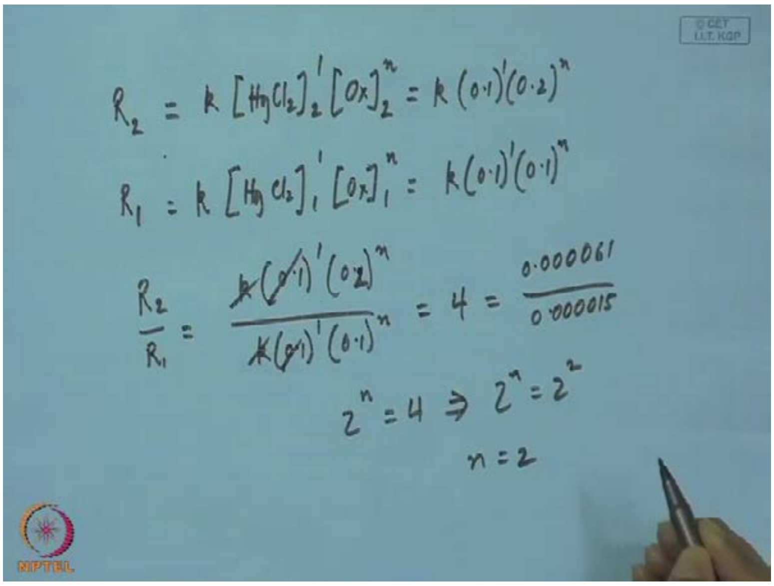

$$R_2 = k\,[HgCl_2]_2^{1}\,[Ox]_2^{n} = k\,(0.1)^1(0.2)^n$$

$$R_1 = k\,[HgCl_2]_1^{1}\,[Ox]_1^{n} = k\,(0.1)^1(0.1)^n$$

$$\frac{R_2}{R_1} = \frac{\cancel{k}\,\cancel{(0.1)^1}\,(0.2)^n}{\cancel{k}\,\cancel{(0.1)^1}\,(0.1)^n} = 4 = \frac{0.000061}{0.000015}$$

$$2^n = 4 \Rightarrow 2^n = 2^2$$

$$n = 2$$

Now, we have to find out the order with respect to the other reactant. So, in that case we have to use other two option like, say R 2 which is equal to k then, H g C l 2 2 to the power 1; because, now you are writing 1 because, you already have found out that the, it is first order with respect to H g C l 2; then O x 2 to the power n, which is equal to k into 0.1 into 0.2 to the power n, because it is 1.

In the same way, R 1 is equal to k H g C l 2 1 to the power 1 then, oxalate 1 to the power n which is equal to k into 0.1 to the power of 1 and 0.1 to the power n. So, if we divide R 2 by R 1, we will be getting k into 0.1 to the power 1 0.1 to the power n sorry 0.2 to the power n divided by k 0.1 to the power 1 and 0.1 to the power n.

And this is basically how much, if we look into the ratio for 2 and 1, it comes out to be equal to 4; because, this is 0.000061 divided by 0.000015 that means it is it is basically 4. So, that means we cross out this two, so that means it is 2 to the power n. 2 to the power n is equal to 4 implies 2 to the power n is equal to 2 to the power 2 that means n is equal to 2.

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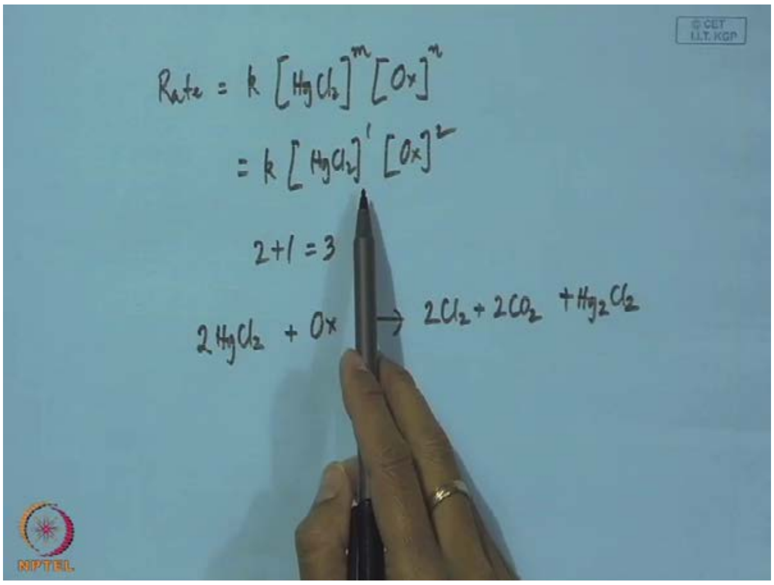

$$\text{Rate} = k\,[HgCl_2]^m\,[Ox]^n$$

$$= k\,[HgCl_2]^1\,[Ox]^2$$

$$2+1=3$$

$$2\,HgCl_2 + Ox \rightarrow 2Cl_2 + 2CO_2 + Hg_2Cl_2$$

So, what we got at the end is very simple and is very informative that, your reaction rate which is equal to k into H g C l 2 to the power m and oxalate n is equal to we can write H g C l 2 to the power 1 and ox to the power 2. So, it is first order with respect to mercuric chloride and second order with respect to oxalate.

So, therefore, what is the overall order? Overall order is 2 plus 1 is equal to 3. Again you see that, although your chemical reaction was like 2 H g C l 2 plus oxalate producing 2 C l 2 plus 2 C O 2 plus H g 2 C l 2. But, you see that, your rate equation it is first order, here it is stoichiometry 2, it is second order stoichiometry. So, there is no there is no direct correlation between this stoichiometry and the order of reaction, order of you know with respect to order with respect to a certain component.

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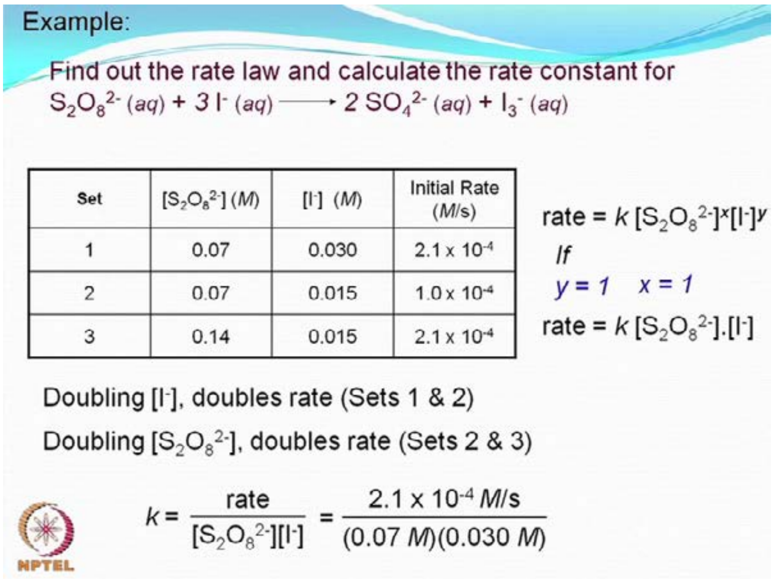

Example:

Find out the rate law and calculate the rate constant for

$S_2O_8^{2-}(aq) + 3\,I^-(aq) \longrightarrow 2\,SO_4^{2-}(aq) + I_3^-(aq)$

Set	$[S_2O_8^{2-}]$ (M)	$[I^-]$ (M)	Initial Rate (M/s)
1	0.07	0.030	2.1×10^{-4}
2	0.07	0.015	1.0×10^{-4}
3	0.14	0.015	2.1×10^{-4}

rate = $k\,[S_2O_8^{2-}]^x[I^-]^y$

If

$y = 1 \quad x = 1$

rate = $k\,[S_2O_8^{2-}].[I^-]$

Doubling $[I^-]$, doubles rate (Sets 1 & 2)

Doubling $[S_2O_8^{2-}]$, doubles rate (Sets 2 & 3)

$$k = \frac{\text{rate}}{[S_2O_8^{2-}][I^-]} = \frac{2.1 \times 10^{-4}\ M/s}{(0.07\ M)(0.030\ M)}$$

Next, we are looking at another example to find out x and y I mean say, it is a persulfate iodide reaction, where persulfate is an oxidizing agent and it oxidizes iodide to iodine and producing k I 3.

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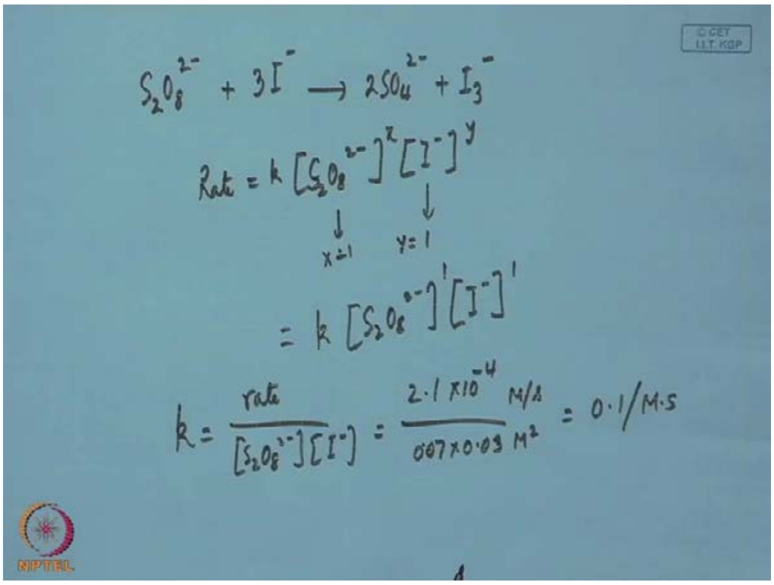

$$S_2O_8^{2-} + 3I^- \longrightarrow 2SO_4^{2-} + I_3^-$$

$$Rate = k\,[S_2O_8^{2-}]^x[I^-]^y$$

$$x = 1 \qquad y = 1$$

$$= k\,[S_2O_8^{2-}]^1[I^-]^1$$

$$k = \frac{rate}{[S_2O_8^{2-}][I^-]} = \frac{2.1 \times 10^{-4}\ M/s}{0.07 \times 0.03\ M^2} = 0.1/M\cdot s$$

So, it is a reaction S 2 O 8 2 minus plus 3 I minus producing 2 S O 4 2 minus plus I 3 minus all are in equated form. So, we have got, if we look into your various set you see that, set 1 where persulfate is 0.07 molar and iodide is 0.03, and initial rate is 2.1 into 10 to the power minus 4. For set 2, it is 0.07 for persulfate 0.07 and it is 0.015 for iodide, and 1 into 10 to the power minus 4 for initial rate. And therefore, the last one it is for for persulfate it is 0.14, for iodide it is 0.015 and the initial rate is 2.1 into 10 to the power minus 4.

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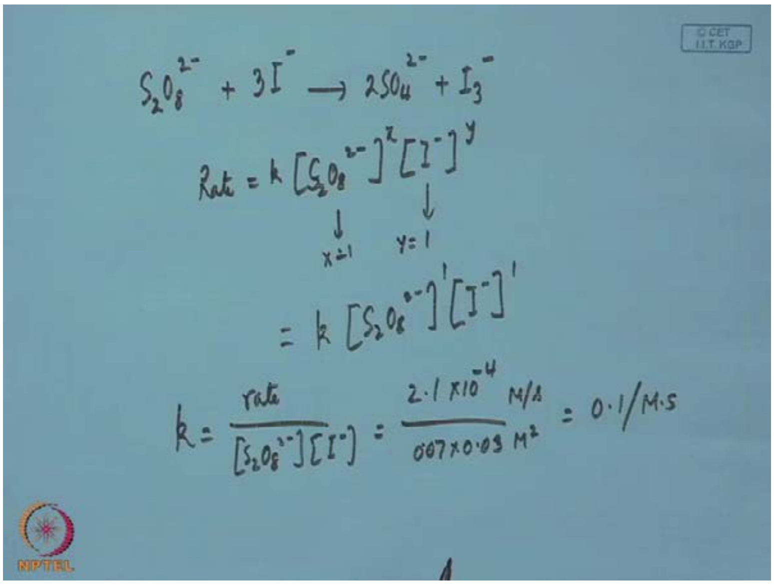

$$S_2O_8^{2-} + 3I^- \longrightarrow 2SO_4^{2-} + I_3^-$$

$$Rate = k\underset{\substack{\downarrow \\ x=1}}{[S_2O_8^{2-}]^x}\underset{\substack{\downarrow \\ y=1}}{[I^-]^y}$$

$$= k[S_2O_8^{2-}]^1[I^-]^1$$

$$k = \frac{rate}{[S_2O_8^{2-}][I^-]} = \frac{2.1\times10^{-4}\ M/s}{007\times0.03\ M^2} = 0.1/M.s$$

So, rate we can write in general equal to k into S 2 2 minus to the power x and I minus to the power y. So, if we look into the data you see that, doubling I minus doubles the rate; if we double I minus you see, if we double I minus from here to here, you see the rate is doubled (Refer Slide Time: 31:51). So, from from set 2 and 1 we see like this; so, that means we are keeping the concentration of persulfate fixed.

And we are just looking into the dependence; how it is depending whether it is linearly dependent or it it depends in in some non-linear way. You see that, it is doubled, it is also doubled that means we can see for sure that, this power should be power should be 1; otherwise, if it is more than 1 or something else than 1, then it should not have increased to the to the same extent like it is double, it is also doubled. So, that is one thing.

So, we we are now able to find out that, y is equal to 1. Now, what about x? You see here, in this two cases 2 and 3, these two are remaining same. So, we are now looking at the effect of change of concentration of persulfate it is that, you see that it is 0.07 it is double to 0.14 and you see that, the initial rate is initial rate is doubled. That means again in the same way, we can say that for persulfate this y I mean x is x is 1. So, that means, it is nothing but, k into S 2 O 8 2 minus to the power of 1 and I minus also to the power 1.

So, and also you know k will be equal to rate divided by S 2 O 8 2 minus times I minus, it is basically basically 2.1 into 10 to the power minus 4 divided by 0.07 times 0.03 mol square and this is mol second; so, this gives you 0.1 per mol second. So, this way we can find out we can look into the rate law, we can find out the rate law and also, the rate constant for a given reaction.

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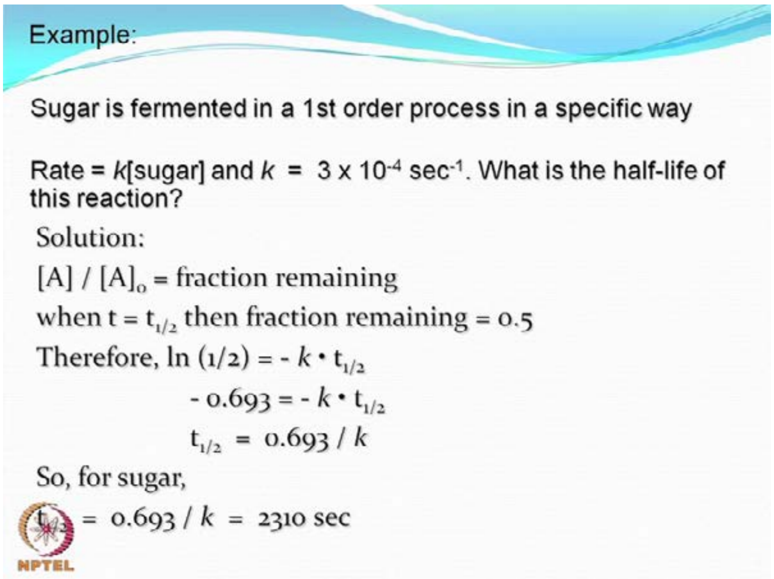

Example:

Sugar is fermented in a 1st order process in a specific way

Rate = k[sugar] and $k = 3 \times 10^{-4}$ $\sec^{-1}$. What is the half-life of this reaction?

Solution:

$[A] / [A]_0$ = fraction remaining

when $t = t_{1/2}$ then fraction remaining = 0.5

Therefore, $\ln (1/2) = - k \cdot t_{1/2}$

$$- 0.693 = - k \cdot t_{1/2}$$

$$t_{1/2} = 0.693 / k$$

So, for sugar,

$$t_{1/2} = 0.693 / k = 2310 \text{ sec}$$

There is another example of of t half that, sugar is fermented in a first order process in a specific way, where it has been found that, the rate sugar reaction is fermentation producing other other you know other chemicals.

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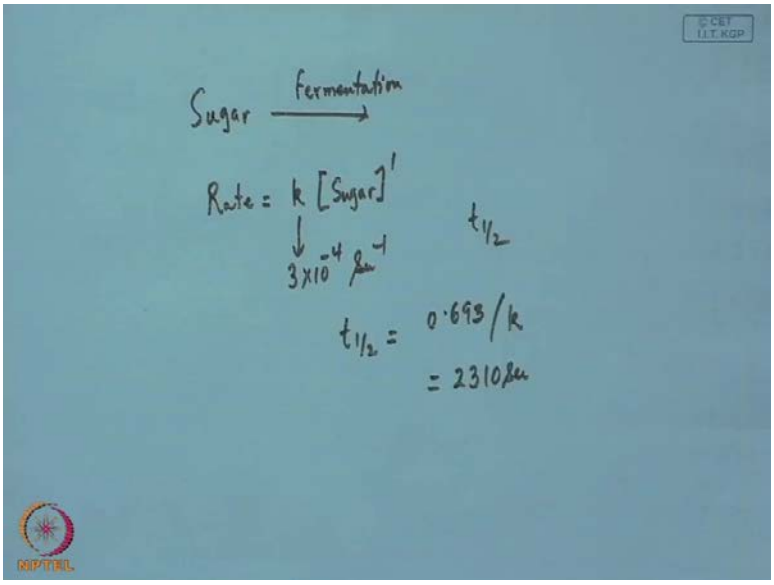

$$\text{Sugar} \xrightarrow{\text{Fermentation}}$$

$$\text{Rate} = k\,[\text{Sugar}]^1$$

$$k \downarrow 3\times10^{-4}\ \text{sec}^{-1}$$

$t_{1/2}$

$$t_{1/2} = 0.693/k$$

$$= 2310\ \text{sec}$$

So, rate is equal to k times sugar to the power 1 it is known to to proceed via first order kinetics, and where k is equal to 3 into 10 to the power minus 4 second inverse. So, what is the half life of the reaction t half? So, since it is the first order process therefore, t half will be equal to 0.693 by k, which is equal to if we put if we plug in the appropriate number; so, you will be getting 2310 second, (( )) like is 2310 second.

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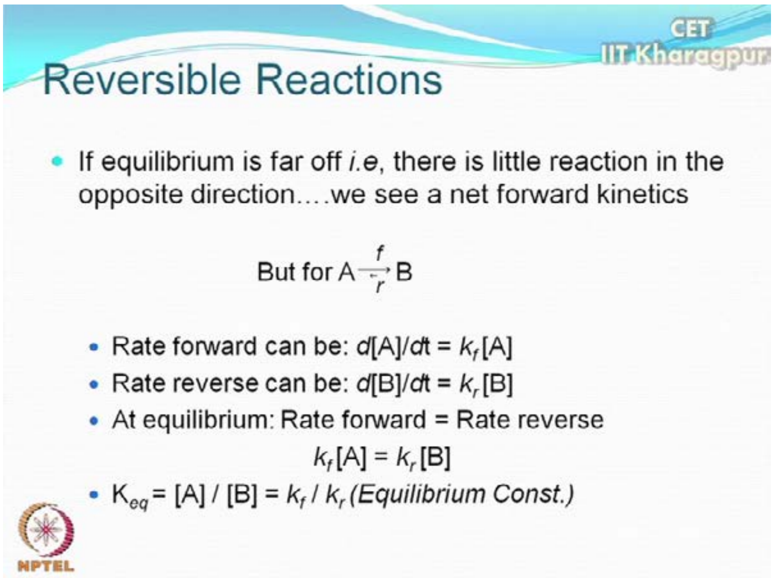

Reversible Reactions

- If equilibrium is far off *i.e*, there is little reaction in the opposite direction....we see a net forward kinetics

But for $A \underset{r}{\overset{f}{\rightleftarrows}} B$

- Rate forward can be: $d[A]/dt = k_f[A]$
- Rate reverse can be: $d[B]/dt = k_r[B]$
- At equilibrium: Rate forward = Rate reverse

  $k_f[A] = k_r[B]$
- $K_{eq} = [A] / [B] = k_f / k_r$ *(Equilibrium Const.)*

So, our next slide is reversible reactions. So, if equilibrium is far off that is there is a little reaction in the opposite direction, that is very little reaction in the back direction then, we see a net forward kinetics; that means there is no effect of the back reaction. Even, if there is a very little back reaction, but we do not see any effect of that. So, so that means we see that the equilibrium is far off, and the reaction is you know forward direction shifted that is forward shifted or the right hand direction shifted.

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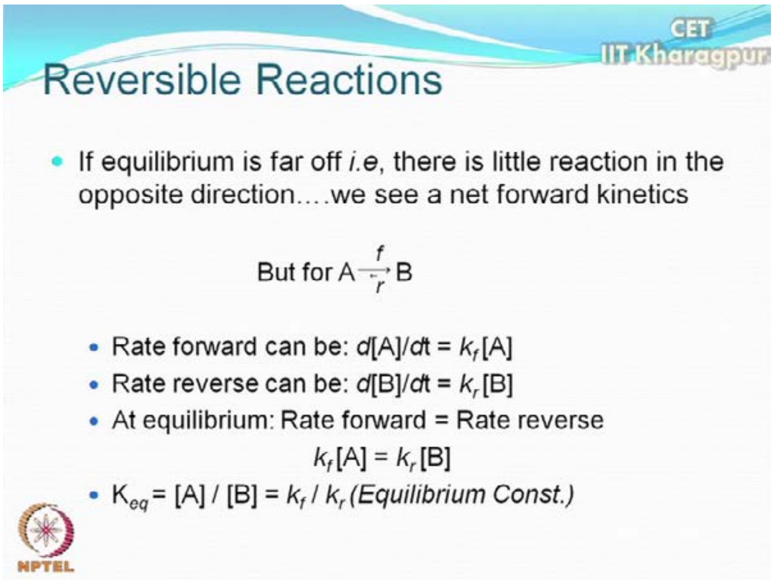

Reversible Reactions

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- If equilibrium is far off *i.e*, there is little reaction in the opposite direction….we see a net forward kinetics

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- Rate reverse can be: $d[B]/dt = k_r[B]$
- At equilibrium: Rate forward = Rate reverse

$$k_f[A] = k_r[B]$$

- $K_{eq} = [A] / [B] = k_f / k_r$ *(Equilibrium Const.)*

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But, if we think of a reaction like this (Refer Slide Time: 36:26), where it is not far from equilibrium may be close to equilibrium there is a there is a net you know back reaction and if both the directions are in in both the directions, the reaction is of first order kinetics; that is it is a forward reaction and say, this is your reverse reaction and corresponding rate constant k f and this is k r.

Then what can you write that, forward reaction rate of forward reaction rate of forward reaction rate of forward reaction, this can be written as d d t d d t of A is equal to k f into A. In the same way, the rate of reverse reaction it is d d t of B is equal to k r into B, since I already have told you that, in both the directions you know kinetics is first order kinetics.

It may be in other cases, may be complicated situation situations are there, where you know forward reaction is a is a is following a second order kinetics, and back reaction is a first order kinetics or may be second order is opposed by a second order like that; opposed means in the in the reverse reaction is also second order reaction.

So, what is happening at equilibrium? At equilibrium, virtually there is no change in concentration; that means means if you if we consider a particular concentration like say A or may be B; so, with time there is no change in concentration of A or may be the concentration of B, if equilibrium has reached has been has been attained. So, at equilibrium what you can write? So, equilibrium at equilibrium forward rate, rate forward is equal to rate reverse.

So, we can write k f into A is equal to k r into B. So, equilibrium constant equilibrium constant there is a you know in this slide, there is a little typo actually k equilibrium will be concentration of B divided by concentration of A this one; actually there is a typo this one should be here and B should be here anyway, so just correct it.

So, so basically let me do it here. So, B concentration of B divided by concentration of A is equal to k f by k r, which is equal to k equilibrium concentration, equilibrium constant of course, at a given temperature; because, it is very much sensitive to temperature. Why as I you know I I will be coming to that later on, the effect of temperature; because, you will be seeing that, if you change the temperature of a reaction it enormously affects the overall rate. So, that is why it is a it is a very much temperature dependent (( )) this equilibrium constant.

So, reversible kinetics if like for a simple first order opposed by first order kinetics then, you can write kinetics of reversible reaction you know in that case, requires a back reaction I mean back reaction means it is a considerable amount of back reaction; otherwise, if the back reaction is not in in considerable extent then, you will be seeing a net you know forward kinetics. So, that means for reversible reaction you need to have a considerable amount of back reaction. So, there is a definite role that approach to equilibrium plays on overall forward reaction kinetics.

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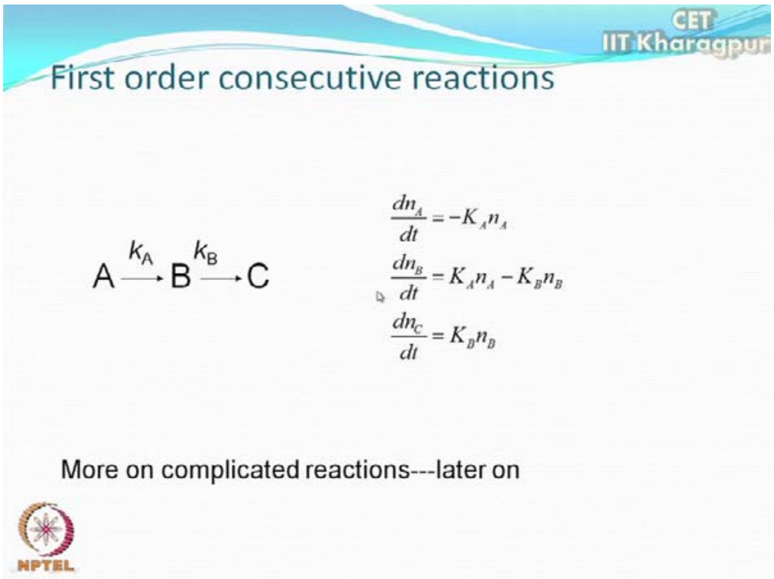

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First order consecutive reactions

$$A \xrightarrow{k_A} B \xrightarrow{k_B} C$$

$$\frac{dn_A}{dt} = -K_A n_A$$

$$\frac{dn_B}{dt} = K_A n_A - K_B n_B$$

$$\frac{dn_C}{dt} = K_B n_B$$

More on complicated reactions---later on

Next, little more complicated situation that is first order consecutive reactions that is A to B to C that is A producing B then, B is producing C. So, here it is generated B is generated and then from B, C is produced, produced means C is depleted. So, it is an increasing function basically with time builds up and with time it depletes; that means you will be seeing may be I will come to that may be later on.

That you will be finding that, this B will pass through and a situation of maximum concentration with at at a specific time and then, again it will deplete, because it is an increasing decreasing kind of thing; so, it should pass through an (( )) anyway. So, that is a that is a some some you know more involved description.

So, you see that, for the for the first of that is (( )) d n A d t that is number of mols of A changing with time is minus K A n A; d n B d t means it is produced and it is depleted, so that is why it is a negative sign. And d n C d t it is you know rate of change I mean rate of change of rate of depletion or whatever, rate of change of C with time is k B n B, because this this is a state which is responsible for the I mean formation of formation of C. This is basically formation of C not depletion it is a formation of C.

So, complications may come into action, if we keep on adding adding more steps like this was the simplest situation we started with; then we have added another component then B will be converted to C. You see that, your description becomes more complicated. So, so more complicated reaction we will we will talk about in later time.

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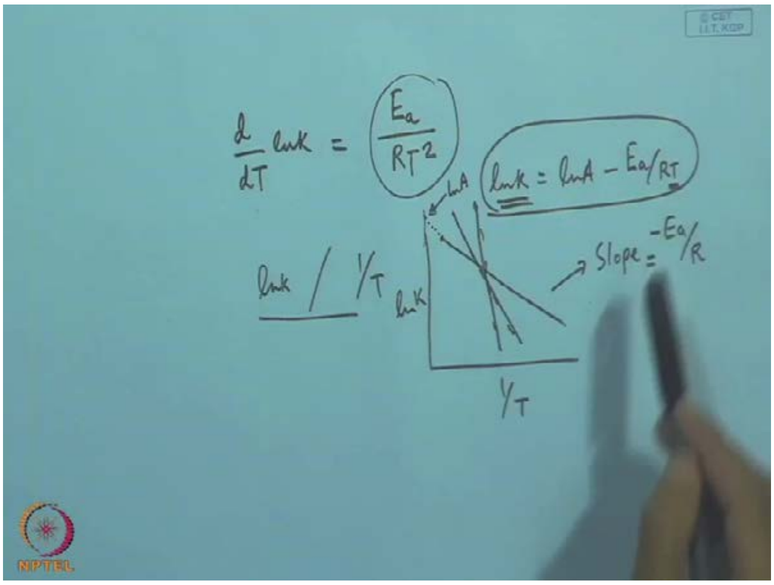

$$\frac{d}{dT}\ln k = \boxed{\frac{E_a}{RT^2}}$$

$$\boxed{\ln k = \ln A - E_a/RT}$$

$\ln k \,/\, 1/T$

Slope $= -E_a/R$

Like, it is a it is a consecutive reaction may be parallel reaction like there could be another situation say A to B to C it is a consecutive. It may so happen that, this A is doing another reaction A to P to Q. So, this is a parallel reaction, this reaction this is a reaction, this is another reaction that parallelly this two are happening. So, this is again this puts you know further complication. So, these parts this complicated complex reactions we will take up later on.

Now, we will come to as I told you that, temperature has got enormous importance in chemical kinetics in in rate processes; because, if you change temperature little bit, it changes many thing. So, the rate constant of which we are very much interested in chemical kinetics. So, rate constant is very much very much temperature dependent.

And this relation between rate constant and temperature was has got you know this relation has a you know very famous citation that it is called Arrhenius expression. And where k is equal to A into exponential minus E A by R T, so it is an exponential function of temperature. So, E A is an energy term, T is the absolute temperature, A is a pre-exponential term.

So, you see with increase of temperature k increases exponential I mean k rises exponentially. And you see from this that, k is dependent on temperature, it is from from experience. So, from experience we have been able to means peoples or scientist have been able to arrive at this expression; and this has been tested for all the cases and found to be true that, k follows an exponential dependence with temperature.

So, it always I mean temperature always increases the rate constant, if you increase the temperature rate constant also increases. So, and this pre-exponential term, so it is generally independent of temperature, now it is also called the frequency factor; frequency means I mean it came from the from the reaction I mean theory of reaction rate based on collision theory. So, collision theory we will talk about theory of reaction rates later on ok.

Now, if we differentiate this expression I mean k is equal to A exponential minus E A by R T, if we differentiate then it comes out to be like (Refer Slide Time: 46:09), d d T of l n k is equal to E A by R T square. So, if you take logarithm of rate constant and then, if do derivative it will give you this quantity (Refer Slide Time: 46:25).

Therefore, if you plot l n k versus 1 by T like, if you take the logarithm of your original expression then, l n k is equal to l n A minus E A by R T. So, if you do this plot I mean plot of this versus this then, then it will be giving you a straight line with a negative slope. So, in a y axis there will be an l n k, x axis 1 upon T. So, slope will be slope will be minus E a with a negative, so it is a negative slope E a by R, slope will be minus E A by R.

And intersect this is the intersect; intersect this way means 1 by T 0 means it is a huge temperature, which you cannot do experimentally. So, you can go may be up to certain temperature, this is your may be highest temperature that you can do the experiment in the laboratory. So, these are the values corresponding to different temperatures; and in this side, temperature is minimum.

And then you do extra collision, because you need to extra collate otherwise, you cannot get (( )), because you cannot do real experiment with a with a very high temperature. So, after extra collision, you will be getting l n A. So, l n A will be giving you I mean this will give you the pre-exponential time or which is also called the frequency factor.

So, from this introduction it is clear that, if you change the temperature it changes the rate constant significantly; but, whether it will be significant or insignificant that is determined by the slope; that means that is determined by this activation energy. So, when higher activation energy is high then, your slope will be steeper like like this; that means like this may be this (Refer Slide Time: 48:37), so steeper slope, when E a is more. So, that means this slope whether there will be a significant there will be a significant you know effect of temperature on rate constant that will be decided by the magnitude of activation energy.

So, this is a very important quantity energetic quantity that, determines you know when you increase the temperature whether you will have a significant change in rate constant of the process. So, that is why we need to have a careful you know careful observation of observation on this E a value. This is very important carefully we have to observe every time for any reaction when you study any reaction then, you have to be careful you have to be careful in in in finding out this this is a very important quantity; careful means, why careful I am telling you that, this determines the very nature of your temperature variation experiment (( )) if you change the temperature then, your your k value will be modified. So, how it will be modified that is written decided by E a.

Next is, let us have a look at typical range of you know this activation energy (Refer Slide Time: 50:05), that is I have I have tabulated you know a number of processes reactions with their typical range of activation energies. So, physical absorption, physical absorption means absorption physical absorption means a a basically absorption is a surface phenomena.

So, physical absorption means you know there is no chemical linkage there is no chemical linkage that happen between you know (( )) and adsorbent, but there may be a physical force may be Van der Waals force or may be something else. So, that is that has got typical range of E A, 2 to 6 kilocalorie per mol.

Aqueous diffusion means say you put some sugar in water and you do not agitate the the water then, may be may be after sometime you will be you will be finding after sometime may be after a day, you will be seeing that the whole water is now sweet sweetened. So, this is basically because of the aqueous diffusion. So, that aqueous diffusion has got a typical range of activation energy less than 5 kilocalorie per mol less than 5 kilocalorie per mol.

Then, biotic reaction it is 5 to 20 kilocalorie per mol then mineral dissolution or precipitation, mineral dissolution means say you are having some (( )) of mineral and then you leach with water then, may be some of the minerals will get dissolved. So, this dissolution sorry this dissolution has got typical you know range of activation energy 8 to 36 kilocalories per mol.

Then dissolution controlled by surface reaction, surface reaction means it is not a not a typical surface reaction, it is a you know I mean the reaction which we generally do is typical bulk reaction. Surface reaction means those reactions like you know zero order reaction like, dissociation of ammonia on (( )) surface that is a surface reaction. So, this dissolution controlled by surface reaction has got 10 to 20 kilocalorie per mol. So, surface reaction is different from the bulk reaction. So, and that requires about 10 to 20 kilocalories per mol.

Isotopic exchange in solution in solution phase, suppose you have got say R OH alcohol per hydrogen is you know hydrogen and if you want to exchange that hydrogen with deuterium then, that isotopic exchange would require 18 to 48 kilocalorie per mol. Solid state diffusion in mineral, because it this diffusion occurs in a solid phase. So, that requires more activation energy and it is 20 to 120 kilocalories per mol.

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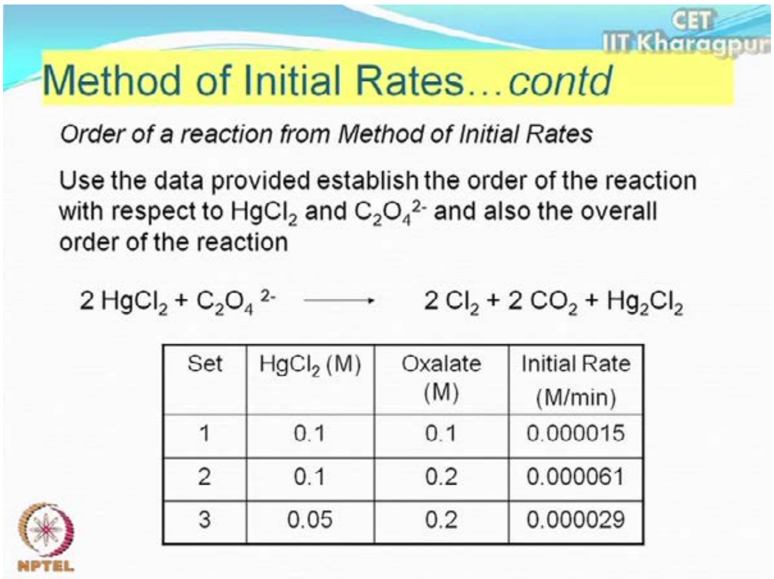

Method of Initial Rates…*contd*

Order of a reaction from Method of Initial Rates

Use the data provided establish the order of the reaction with respect to $HgCl_2$ and $C_2O_4^{2-}$ and also the overall order of the reaction

$$2\,HgCl_2 + C_2O_4^{2-} \longrightarrow 2\,Cl_2 + 2\,CO_2 + Hg_2Cl_2$$

Set	$HgCl_2$ (M)	Oxalate (M)	Initial Rate (M/min)
1	0.1	0.1	0.000015
2	0.1	0.2	0.000061
3	0.05	0.2	0.000029

So, what we have learnt in this particular part of discussion? That we have learnt various, we have learnt like how to use initial rate method to find out the rate equations that is you have got say (Refer Slide Time: 53:48), rate is equal to k into say A to the power alpha B to the power beta. So, what is the value of alpha and beta, and to find out the overall order of the reaction; so that, you can do by by by making use of initial rate method.

And also we have studied various types of you know various types of kinetics like zero order, first order, second order, third order and also n th order. Also we talked about the pseudo unimolecular reaction, where you have kept one of the reactant in reactants in large excess. So, that virtually during the course of reaction, it is not changing.

So, the whole rate equation is now you know simplified to one order less or may be a second order one is transformed to a first order one. And also we have talked a little about this reversible reaction; and and also you know consecutive reaction I gave a you know very brief introduction of consecutive reaction.

So, in the in the next class in the next class we will talk about we will talk about in in talk about the temperature effect in details. And also we take up this Arrhenius equation, how this can be used, what is the utility, what is the significance of activation energy, what is the significance of you know this pre-exponential term all will be taken up may be in next 2 lectures on the effect of temperature on chemical reaction rate. So, till then I have nice time, so see you in next lecture with this effect of temperature on chemical reactions, thank you.