

Aspects of Biochemical Engineering
Prof. Debabrata Das
Department of Biotechnology
Indian Institute of Technology, Kharagpur

Lecture – 13
Kinetics of Homogeneous Chemical Reactions – III

Welcome back to me course Aspect of Biochemical Engineering. Now we are discussing this Kinetics of Homogeneous Chemical Reaction and last lectures couple of lectures we try to concentrate that how to write the mathematical expression for the irreversible chemical reaction, how to write the expression for the reversible chemical reaction, how we write the expression for the chain reaction and I by mention that most of the biochemical reaction their chain reaction and they are reversible in nature.

Now in case of chain reaction our main emphasize is that how if you look at the profile of the different component present in the reaction mixture that we find that first component it will keep on decreasing with respect to time and last component will be keep on increasing with respect to time, but all intermediate compounds they will increased and then decrease.

So, our intention was that how to find out that at what time we will get the maximum amount of this intermediate product form intermediate product formation that to take place in the system. So, in the last lectures we tried to derive the equation for the different component in present in the reaction mixture then also we tried to discuss this reversible; reversible chemical reaction and I told you at equilibrium condition rate of forward reaction should be equal to rate of backward reaction and equilibrium constant is equal to concentration of product divided by concentration of substrate.

Now in case of the reversible reaction that question comes what should be our strategy to maximize the product formation. The our strategy will be that I try to mention that as soon as the product form that when the product if you take out from the system, then what will happen that more substrate will converted to product to maintain the k_c constant k_c is the equilibrium constant. So, this is how talk how we can increase the product yield of the process or product concentration of the project yield of the process. Another approach through, which we can increase the product formation because if we add more substrate because since it is the ratio of concentration of product defects the

concentration of substrate. So, if you add more substrate we will get more product in the in the process. So, through this approach we can we can increase the product I can keep a typical example that in case of ethanol fermentation process ethanol is a volatile component if we applied some vacuum we can we can we can we can vaporize this out. So, your product concentration decreases. So, more substrate will be converted into product.

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Problem

A first order reaction $A \rightarrow B$

If $-r_A = -(dC_A/dt) = 0.2 \text{ mol/(L.s)}$ when $C_A = 1 \text{ mol/L}$, what is the rate of reaction when $C_A = 10 \text{ mol/L}$?

Solution

the rate equation $-r_A = kC_A$

When $C_A = 1 \frac{\text{mol}}{\text{L}}$, $-r_A = 0.2 \frac{\text{mol}}{\text{L.s}}$

Therefore, $0.2 \frac{\text{mol}}{\text{L.s}} = k \times 1 \frac{\text{mol}}{\text{L}}$

Handwritten notes on the slide include a graph of concentration C_A versus time t showing an exponential decay curve, and the differential equation $-\frac{dC_A}{dt} = kC_A$.

Now today I am going to discuss the some numerical problems 4 numerical problems I am going to discuss in this lecture and first numerical problem deals with deals with that that you know that first order reaction it is a very simple reaction A to B and if you look at the rate this rate of reaction is given as 0.2 moles per liter per second, where when C A equal to 1 mole per liter what is the rate of reaction when C A equal to 10 mole per liter.

So, 1 condition is there suppose we have we know that if you if you look at the C A versus time if a actual profile is like this so in this problem that you know that maybe this we have at different concentration, you have to find out what is the rate of reaction. So, is this is we find at C A this is the rate of reaction is this and C B that when you when the concentration is C 10 that this this might be 10 and this might be 1. So, at different concentration what is, if you if you look at the equation it is $d C A$ by $d t$ equal to k into C A?

So, as your concentration increases your rate of reaction supposed to be increases. So, that that we shall have to find out and have to do this what we shall have to do that first to this is the rate equation that we have and we put the value this is r e is 0.2 and this is this is 1 mole per liter.

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Solution

Therefore,
The rate equation

$$k = 0.2 \text{ s}^{-1}$$
$$-r_A = 0.2 C_A \frac{\text{mol}}{\text{L.s}}$$

Now,

At $C_A = 10 \frac{\text{mol}}{\text{L}}$,

$$-r_A = 0.2 \times 10 \frac{\text{mol}}{\text{L.s}} = 2 \frac{\text{mol}}{\text{L.s}}$$

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So, here we can we can we can we can calculate the value of k this is the value of k we can easily calculated this is about 0.2 second inverse and then we put this value in the rate equation this is 0.2. So, our equation now changes to minus r A equal to 0.2 into C A now so we shall have to find out that when C A equal to 10 moles per liter what is the rate of reaction.

We proved that this is into 10 then 2 moles per the this is the rate you will get this reaction per liter, then 10 mole per liter then this will be equal to this 10 mole per liter then we will have to that that increases that higher substrate as I told you as the substrate concentration increases this value also will be increases.

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Problem

A human being (75 kg) consumes about 6000 kJ of food per day. Assume that the food is all glucose and that the overall reaction is

$$C_6H_{12}O_6 + 6 O_2 \rightarrow 6 CO_2 + 6 H_2O \quad -\Delta H_r = 2816 \frac{\text{kJ}}{\text{mol glucose}}$$

Find man's metabolic rate in terms of moles of oxygen used per m^3 of person per second

Handwritten calculations:
 $\frac{6000 \text{ kJ}}{2816} = 2.13 \text{ moles glucose}$
 $2.13 \text{ moles glucose} \times 6 = 12.78 \text{ moles } O_2$
Vol. air = 24 m^3

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Now, next problem that we have deals with 1 human system human being 75 kg consumes about the 6000 kg of food per day and assume that food is all glucose and that the overall reaction is based like this that is the same as when glucose, we burn it the same kind of reaction will take and if you take in our system we will get a similar type of results because that 6 moles of carbon dioxide and 6 moles of water.

Now, we have heat of reaction is 2800 and 16 kilo joules per mole (Refer Time: 07:06). So, what we shall have to find out that what is the metabolic rate in terms of moles of oxygen used per cubic meter volume per second. So, this is the this is the things we shall have to find out now how we can do that, because first we shall have to find out that how much energy is re energy we are consuming we are energy we are consuming about 6000 kilo joules; am I right. Now if you find out the heat of reaction of glucose is 2816-16 this is this we have. So, if you divide by that then we can find out for consuming this much of energy how much moles of glucose is required the moles of glucose that is required that we can calculate.

Now once you know that moles of glucose required for getting this much of energy and from this reaction from this reaction we can find out for 1 mole of glucose you required 6 moles of oxygen. So, once we calculate this if you multiply by 6 that we will get that how much moles of oxygen that is required in this process. Now if we divide this with

the volume of the man then then we can find out that what is the oxygen used per cubic meter person per second let us see how we can solve it.

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Solution

We want to find

$$(-r_{O_2}) = -\frac{1}{V_{person}} \frac{dN_{O_2}}{dt} = \frac{\text{mol } O_2 \text{ consumed}}{(\text{m}^3 \text{ of person})(s)}$$

$$V_{person} = \frac{\text{mass}}{\text{density of human body}} = \frac{75 \text{ kg}}{1000 \text{ kg/m}^3} = 0.075 \text{ m}^3$$

Assuming density of human body = 1000 kg/m³

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So, our question is this our equation what is the rate equation we have minus r_{O_2} means this is the dN_{O_2} this is the moles of oxygen consumed per cubic meter this is cubic meter volume of person per second. So, this we shall have to find out this is our destination.

Now first we shall have to calculate what is the volume of man whose weight is 75 kg? Now if you want to know the volume of the person or the man then we shall have to first we should know what is the density of the man? Now if you we know the human contains mostly the water though, if we assume the density of the human body is close to the water that is 1000 kg per cubic meter, then if we divide by that we will get the volume this is volume of the person we can easily calculate.


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Solution


Each mole of glucose consumed 6 mole of oxygen and release 2816 kJ of energy

$$-\frac{dN_{O_2}}{dt} = \left(\frac{6000 \text{ kJ/d}}{2816 \text{ kJ/mol glucose}} \right) \left(\frac{6 \text{ mol } O_2}{1 \text{ mol glucose}} \right) = 12.8 \frac{\text{mol } O_2}{d}$$



Therefore,

$$(-r_{O_2}) = \frac{1}{0.075 \text{ m}^3} \cdot \frac{12.8 \text{ mol } O_2 \text{ used}}{d} \cdot \frac{1 d}{24 \times 3600 s} = 0.002 \frac{\text{mol } O_2 \text{ used}}{\text{m}^3 \cdot s}$$


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Then If you come here then I told you that 6000 kg per day we are consuming the person is consuming energy and this is the heat content of glucose, then if we divide by that we can find out for getting this much of energy how much glucose is required.

Then if you multiplied by 6 moles of because 6 moles of oxygen is required for the consumption of 1 mole of glucose, if you multiply that we will get how much moles of oxygen is required per day. Now I want to tell you here that here what is the unit that you have moles of oxygen use per cubic meter per day am I right now question come how you can convert to per units per seconds.

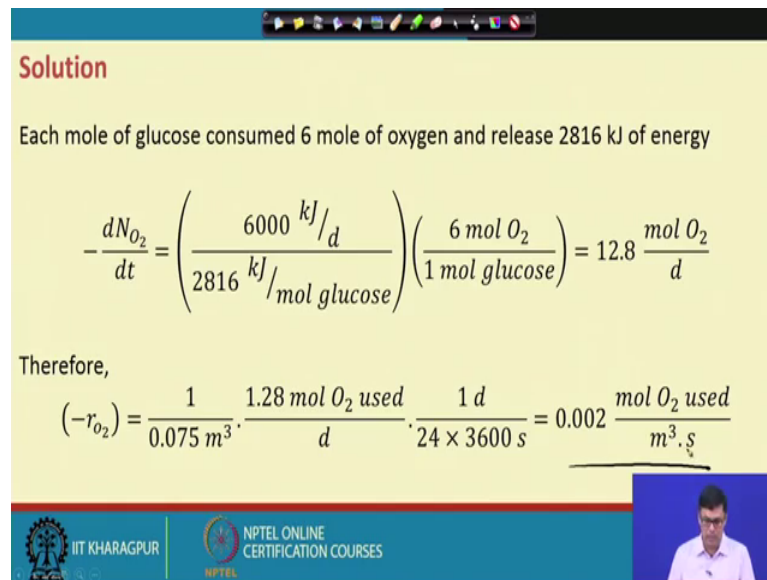
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$$\begin{aligned} \frac{\text{mol } O_2}{\text{m}^3 \cdot \text{d}} &\rightarrow \frac{\text{mol } O_2}{\text{m}^3 \cdot \text{s}} \\ \Rightarrow \frac{\text{mol } O_2}{\text{m}^3 \cdot \text{d}} \times \frac{1 \text{ d} \times 24 \text{ hr} \times 60 \text{ min}}{24 \times 60 \times 60} &= \frac{\text{mol } O_2}{\text{m}^3 \cdot \text{s}} \end{aligned}$$

So, this I can show it like this that suppose we have the data that moles of oxygen moles of oxygen per cubic meter per day how you can convert it mole oxygen per cubic meter per second, how you can convert we can convert very easily how we can convert this is mole of oxygen cubic meter .

Now, this is day am I right. So, I can write though here I can write 1 day; 1 day is equal to 24 hours, then we can write 1 hour is equal to how much 60 minutes and then we can write 1 minutes this is multiplied by 60 seconds. So, what you what basically we shall have to do we shall we shall have to multiply it by 1 by 24 into 60 into 60 to get the value in terms of cubic meter per second.

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Solution

Each mole of glucose consumed 6 mole of oxygen and release 2816 kJ of energy

$$-\frac{dN_{O_2}}{dt} = \left(\frac{6000 \text{ kJ/d}}{2816 \text{ kJ/mol glucose}} \right) \left(\frac{6 \text{ mol } O_2}{1 \text{ mol glucose}} \right) = 12.8 \frac{\text{mol } O_2}{d}$$

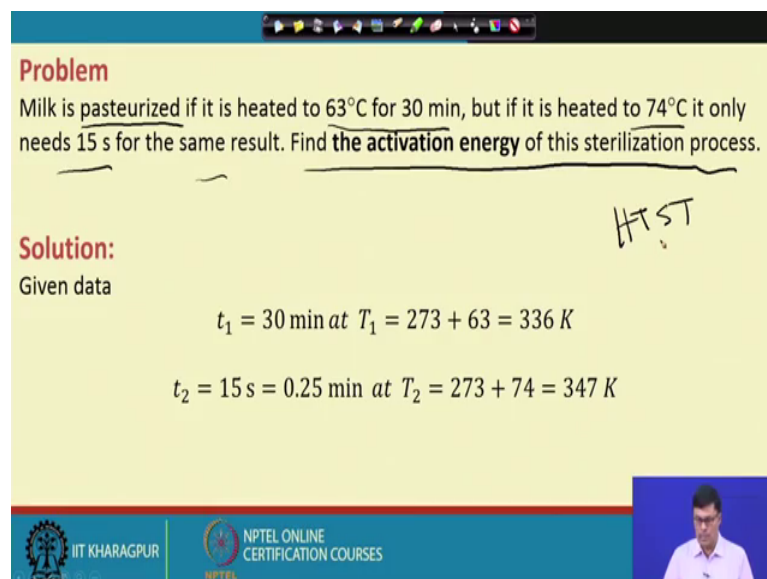
Therefore,

$$(-r_{O_2}) = \frac{1}{0.075 \text{ m}^3} \cdot \frac{12.8 \text{ mol } O_2 \text{ used}}{d} \cdot \frac{1 d}{24 \times 3600 \text{ s}} = 0.002 \frac{\text{mol } O_2 \text{ used}}{\text{m}^3 \cdot \text{s}}$$

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So, this is what we have done in this particular place that you can see that how we have calculated this has come about 0.002 moles of oxygen used per cubic meter per second next problem that we deals with the pasteurization process.

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Problem

Milk is pasteurized if it is heated to 63°C for 30 min, but if it is heated to 74°C it only needs 15 s for the same result. Find the activation energy of this sterilization process.

Solution:

Given data

$$t_1 = 30 \text{ min at } T_1 = 273 + 63 = 336 \text{ K}$$
$$t_2 = 15 \text{ s} = 0.25 \text{ min at } T_2 = 273 + 74 = 347 \text{ K}$$

H.T.S.T

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Now as I mentioned that pasteurization is the process through which we can we kill the germs. So, mostly the pathogenic organisms, but when you kill the pathogenic organism; obviously, some non-pathogenic organisms also killed, but main purpose of pasteurization kill the pathogens organism it has been observed that at low temperature

you required more time. So, at 63 degree centigrade it required pasteurization time required is 30 minutes, but if it heated to 74 degree centigrade only 15 seconds (Refer Time: 12:46) and for the same results find out the activation energy for the for the sterilization process.

Now here I want to tell you one interesting thing this technique this process we call it HT ST technique HT ST technique; HT ST means high temperature short time technique because we find that if we that you know that if you keep the material at the smaller time then your destruction of the nutrient particularly vitamin or amino acid will be (Refer Time: 13:24) low as compared to that of if you keep it for longer period of time. The reason is that the deactivation energy requirement for the vitamins and amino acid is much less as compared to that of microbial cells.

So, microbial cells require more activation energy as compared to that of the amino acid and the vitamin. So, at low temperature it is always detrimental what the quality of the medium with respect to vitamin and amino acids.

So, if you increase the high temperature since you are exposed it for lower period of time we can maintain the quality of the material in the better with that is why that that we follow in the industry. Now what are you want to discuss hear that how we can find out the activation energy what is the activation energy, the energy required to have this reaction what is the energy required. So, to solve this problem that what I want to tell that if you look at this rate of reaction this is dA/dt equal to $k \cdot C^A$; am I right.

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Problem
Milk is pasteurized if it is heated to 63°C for 30 min, but if it is heated to 74°C it only needs 15 s for the same result. Find the **activation energy** of this sterilization process.

Solution:
Given data

$$t_1 = 30 \text{ min at } T_1 = 273 + 63 = 336 \text{ K}$$

$$t_2 = 15 \text{ s} = 0.25 \text{ min at } T_2 = 273 + 74 = 347 \text{ K}$$

Handwritten notes: $-dC = kt$ and a diagram showing $k \propto \frac{1}{t}$

So, if you look at the C A C A that is cancels. So, your rate constant k basically it is inversely proportional with time this is inversely proportional with time.

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Solution



From the Arrhenius law

$$\ln\left(\frac{t_1}{t_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{30}{0.25}\right) = \frac{E_a}{8.314} \left(\frac{1}{336} - \frac{1}{347}\right)$$

Handwritten notes: $k_1 = A e^{-E_a/RT_1}$ and $k_2 = A e^{-E_a/RT_2}$

From which the activation energy

$$E_a = 422000 \frac{\text{J}}{\text{mol}}$$



So, now here this is the problem that is given now we know the Arrhenius what is the Arrhenius equation that we have Arrhenius equation we have the k equal to A to the power e to the power minus a by R T. Now at different temperatures we have different Arrhe; that k 1 suppose this k 1 this is T 1 and you can write k 2 we have A E to the

power E_a by $R T^2$ am I right. Now this is equal to I told you this is inversely proportional to this T_1 and this is 1 by T_2 .

So, if we write this then we can if you solve this we can get this equation that $\ln T_1$ by t_2 equal to E_a by R 1 by T_a so in this equation if we put the value of T_a , in terms of minutes then and we can easily calculate the value of e_a that is the activation energy required for this for this process you can easily find it out.

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Problem
Liquid A decomposes by first-order kinetics, and in a batch reactor 50% of A is converted in a 5-minute run. How much longer would it take to reach 75% conversion?

Solution:
Given data,
 $X_{A1} = 0.50, t_1 = 5 \text{ min}$
 $X_{A2} = 0.75, t_2 = ?$

For 1st order reaction
$$-r_A = -\frac{dC_A}{dt} = kC_A$$

Where, $k \rightarrow$ reaction rate constant

Handwritten notes:
 $X_A = \frac{C_{A0} - C_A}{C_{A0}}$
 $X_{A1} = 0.50$
 $X_{A2} = 0.75$

Next problem that we have that is a liquid a decompose by the first order kinetics this is a first order kinetics and in a batch reaction reactor 50 percent of a is converted in 5 minutes run, how much longer it will take for 75 percent conversion. So, this is we know the fraction the X_A is what X_A equal to C_{A0} minus C_A by C_{A0} this is called fraction. So, if you say this is 50 percent conversion then X_A will be what 0.50.

And what if you say 75 percent conversion this what we can write this is equal to 0.75. So, this is exactly what he has written there at 5 minutes this is 0.5 and X_2 is 0.75 and what is the rate expression that we have that minus r_A equal to minus dC_A by dt into k into C_A this is because this is the follow the first order kinetics.


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Solution


Integrating,

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^t k dt$$
$$-\ln\left(\frac{C_A}{C_{A0}}\right) = kt$$
$$-\ln\left(\frac{C_{A0}(1-X_A)}{C_{A0}}\right) = kt$$
$$-\ln\left(\frac{1-X_A}{1}\right) = kt$$


$C_A = C_{A0}(1-X_A)$




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Now this is this is the equation that we have this is from this if you solve it we can get this equation ln. So, your ultimate equation is $\ln \frac{C_A}{C_{A0}} = -kt$ now what is the $\frac{C_A}{C_{A0}}$ equal to $\frac{C_{A0}(1-X_A)}{C_{A0}}$ am I right. So, if you put this here then what you will get $\ln \frac{C_{A0}(1-X_A)}{C_{A0}} = -kt$

So, this this will cancel. So, what you will get $-\ln(1-X_A) = kt$


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Solution


It is known that

$$C_A = C_{A0}(1 - X_A)$$


Now,


$$-\ln\left(\frac{C_{A0}(1 - X_A)}{C_{A0}}\right) = kt$$
$$-\ln\left(\frac{(1 - X_A)}{1}\right) = kt$$


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Now this is what exactly we this this I told you this is exactly what you get this you understand this.

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Solution

It can be written

$$\frac{\ln(1 - X_{A2})}{\ln(1 - X_{A1})} = \frac{t_2}{t_1}$$

$$t_2 = t_1 \times \frac{\ln(1 - X_{A2})}{\ln(1 - X_{A1})}$$

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Now at different so since our expression is like this. So, at so this what we have minus we can have minus ln 1 minus X A k into t.

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Solution

It is known that

$$C_A = C_{A0}(1 - X_A)$$

Now,

$$-\ln\left(\frac{C_{A0}(1 - X_A)}{C_{A0}}\right) = kt$$

$$-\ln\left(\frac{(1 - X_A)}{1}\right) = kt$$

Handwritten notes on the right side of the slide:

$$-\ln(1 - X_{A1}) = kt_1$$

$$-\ln(1 - X_{A2}) = kt_2$$

$$\frac{t_2}{t_1} = \frac{-\ln(1 - X_{A2})}{-\ln(1 - X_{A1})}$$

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Now, if you use the t 1 then this will be X 1 t X 1 and if t 2 1 minus X A 2 equal to k into t 2.

Now, if you take the ratio t_2 by t_1 how you can write $\ln(1 - X_{A2})$ by $\ln(1 - X_{A1})$ sorry now this is exactly what we get here.

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Solution

It can be written

$$\frac{\ln(1 - X_{A2})}{\ln(1 - X_{A1})} = \frac{t_2}{t_1}$$
$$t_2 = t_1 \times \frac{\ln(1 - X_{A2})}{\ln(1 - X_{A1})}$$

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And then we have the expression for t_2 what is the expression for t_2 t_2 is this like this t_2 equal to t_1 into $\ln(1 - X_{A2})$ and this is the this is another expression that we have. So, $\ln(1 - X_{A1})$. So, now, we know at t_1 what is the X_{A1} value and we want to know 75 percent conversion what is the time is required just we can put the value we can get the results.

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Solution

Putting all the known values

$$t_2 = 5 \times \frac{\ln(1 - 0.75)}{\ln(1 - 0.50)}$$
$$t_2 = 5 \times 2$$
$$t_2 = 10 \text{ min}$$

Therefore, 75% conversion will be achieved in 10 minutes

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So, we find out the time as 10 minutes. So, 75 percent conversion we required 10 minutes time this is how we can solve it very easily. So, in this particular lecture what I try to cover I tried to cover that a couple of numerical problem. The first problems I deal with this irreversible reaction that for simple first order reaction, that if you know the rate constant at a particular substrate concentration then we can find out the rate constant at the different concentration that we can find out. Now second problem that we try to find out that if a in the human system we know that how much energy we are consuming per day.

And if you consider that glucose as a source of energy from that we can easily calculate. What is the molecular oxygen consumption that take place by the human beings and third problem that I deal with the pasteurization process pasteurization process basically I told you it is deals with the killing of pathogenic organism. Now it has been observed that HT ST Technique is the more useful for the pasteurization process because effective, why it is effective because you are exposing the food material for smaller time. The since we know the deactivation energy required for the amino acid and vitamins are very less as compared to that of the microorganism killing of microorganisms.

So, naturally at low temperature it is more detrimental the quality of the material rather than the killing of organism. So, that is why the high temperature always be required low smaller time for giving the pathogenic organism. So, this problem deals with that and we try to find out what should be the activation energy required for this particular process and second and last problem that, we also try to find out at a particular time suppose in a problem that is giving that at 5 minutes time that 50 percent conversion is there, when we want to find out that how much conversion is required if you have 75 percent conversion required for 75 conversion of substrate.

Now, this is very important as per chemical and biochemical reaction is concerned because when you when you carry out any kind of chemical and biochemical reactions we always try to we want to know how much is required first because as you know that as per industries concern that we always look forward high conversion efficiency. Because why we look for high conversion efficiency, because if you have high conversion efficiency then amount of that you know substrate remain in the effluent will be computably less and if the amount of organic matter present in the effluent is less it gives the less load to the effluent treatment process, but if you look at this that you know

that other processes that the now question comes that if you go for the higher conversion or higher percentage of conversion which whether it is really economic to the process.

So, all these consequences I think at the end we will discuss in all of my lecture this course I shall discuss those issue, that if you increase the conversion efficiency of the process whether it will really help us for the economics of the process because this is very important, because we will find that 1 way we are reducing the load to the wastewater treatment process that is true, but whether it is going to affect the economy of the process. So, when you that those are the different things we will that at the later part of my presentation.

Thank you very much.