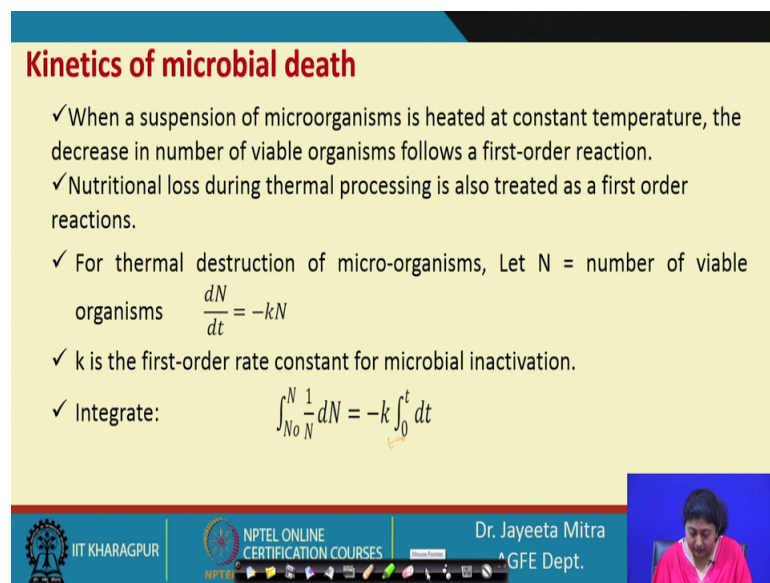


Fundamentals of Food Process Engineering
Prof. Jayeeta Mitra
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Lecture - 14
Thermal Processing and Kinetics of Microbial Death (Contd.)

Hello everyone, welcome to NPTEL online certification course on Fundamentals of Food Process Engineering. Today we will continue our 14th lecture that is the continuation of our third chapter that is Thermal Processing and Kinetics of Microbial Death. So, in the last class we have discuss about the various thermal processing that is being done for preservation of food such as blanching, pasteurization and sterilization. Today we will focus on the microbial death kinetics during thermal processing.

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Kinetics of microbial death

- ✓ When a suspension of microorganisms is heated at constant temperature, the decrease in number of viable organisms follows a first-order reaction.
- ✓ Nutritional loss during thermal processing is also treated as a first order reactions.
- ✓ For thermal destruction of micro-organisms, Let N = number of viable organisms $\frac{dN}{dt} = -kN$
- ✓ k is the first-order rate constant for microbial inactivation.
- ✓ Integrate: $\int_{N_0}^N \frac{1}{N} dN = -k \int_0^t dt$

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So, kinetics of microbial death; we know that normally any reaction whether it is physical, chemical or microbiological reaction it is very convenient to identify the pattern of change of concentration with time or temperature. Basically, this condition of microbial count with time at various temperature is termed as kinetics of microbial death and we have seen that the kinetics of microbial death follows a definite pattern like, we have seen that the chemical reaction generally categorized into zero order reaction or first order reaction and so on. So, although the zero order reaction is not much common

in food processing phenomena, very less cases we are getting based on the zero order kinetics.

However, the first order kinetics is very common so many nutrient degradation follows this first order kinetics and so, is in case of the microbial destruction. Now when a suspension of microorganism is heated at constant temperature the decrease in number of viable organism follows first order reaction. That means, the nutritional loss during thermal processing, which is also treated as first order reaction has the nature like this. That rate of degradation or rate of number of viable microorganism with respect to time will be proportional to the number of viable counts.

So, if we elaborate the case for thermal destruction of microorganism, let N is the number of viable organism, k is the first order rate constant for microbial inactivation, then we can represent dN by dt that is equal to minus kN . So, dN by dt that is with time the number of viable microbial count will be equal to minus k , that is the first order rate constant into number of viable microbial count at that time.

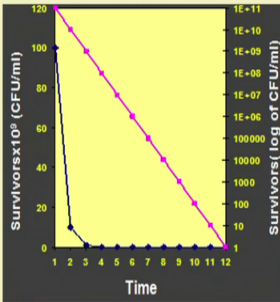
The minus sign showing that number of microorganism will be decrease with time. Now if we integrate this from number of micro organism N_0 at time t equal to 0 to N which is at any time t then we can get that we can get that expression that is.

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✓ $\text{Log}_e (N/N_0) = -kt$ or $\text{Log}_e (N_0/N) = kt$
 $kt = 2.303 \text{Log}_{10} (N_0/N)$

✓ There is a logarithmic relationship between the number of survivors N and time t at any given temperature. This is known as a **survivor curve** (ln N against t).

✓ The gradient of the survivor curve increases markedly with temperature



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Log of N by N_0 to the base e that is equal to minus k into t or \log of N_0 by N if you want to remove that minus we can write in this way N_0 by N to the base e that is equal to k into t . So, if we want to express in \log of N_0 by N to the base 10, we can write it as $k t$ equal to $2.303 \log N_0$ by N to the base 10.

Now if we plot these survivors in y axis and time in the x axis. So, we can get an exponentially decay kind of curve. And if you plot microbial viable microbial count in the \log scale with respect to time, then we can get a straight line. And the slope of this straight line will give us the value of k that is the first order reaction rate kinetics constant. So, this curve is known as the survivor curve that is \log of viable micro organism count with respect to time.

Now, if you want to see the effect of this, the gradient of survivor curve increases markedly with temperature; that means, if we increase the temperature the microbial count will decrease. So, the slope will be have more higher. So, that is why we can get the survivor curve increased markedly with temperature.

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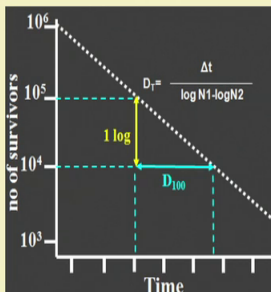
Kinetics of microbial death

- ✓ **Decimal reduction time (D value):**
- ✓ Time required to reduce the no micro organisms by **1 log cycle or 90% or by factor 10** (or or 10 fold) at given temperature.
- ✓ Higher values of D imply, at a given temperature, greater resistance of micro-organisms to thermal death.

$$\log \frac{N_0}{N} = \frac{kt}{2.303}$$

$$\frac{1}{D} = \frac{k}{2.303}$$

By definition, $t = D$ when $N_0/N = 10$
Then, $D = 2.303/k$

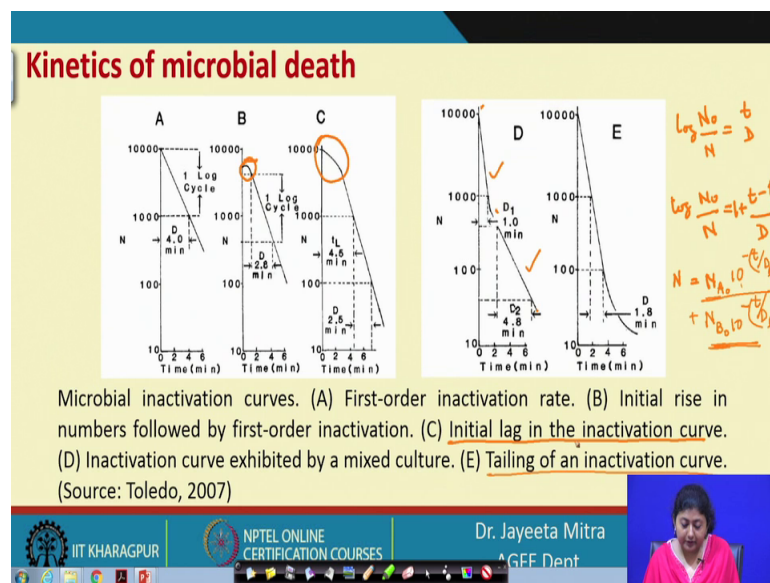


Now, we look into the important parameter that is called the decimal reduction time. In terms of microbial death kinetics D value has enormous important. It is defined as the time required to reduce the number of microorganism by 1 log cycle or by 90 percent or by a factor of 10 at a given temperature. So, D value will change if we change the temperature.

Higher values of D imply that at a given temperature the microorganism has higher resistance to thermal death. Now if we plot the number of microorganism number of viable microorganism in the log scale with respect to time. So, we can get that the time required to reduce the viable microorganism by 1 log cycle that is termed as a D value. So, we can write it as Δt that is divided by \log of N_1 that is at T_1 if we consider the viable microorganism minus \log of N_2 that we consider after time t_2 and this Δt will be then termed as t_1 minus t_2 .

So, by definition in the previous equation that we have developed where \log of N_0 we can write it here, \log of N_0 by N that is equal to $k t$. So, when t equal to D that is N_0 by N equal to 10. So, if we write this with respect to 10 then it is we can write it as $2.303 t$ by D where d equal to 2.303 by k ok. So, this is how we define the decimal reduction time.

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Now we will see certain interesting phenomena, when we have different pattern of microbial destruction curve if we plot the similar way like viable microorganism in the log scale in the y axis, and in the x axis the time in minute. So, let see; what are the different kind of curve we may get. First curve which is the simple first order inactivation curve, and it shows that the from the start of heat processing the viable microorganism start decreasing and we can easily calculate the D value that is the one log cycle destruction time, at a particular temperature

If we look into the curve B: if we look into the curve B here in this section we can find initial little increase or a little flat portion and then it start decreasing. So, this initial increase that we can observe here this is because there are certain heat resistant spore they may get activated during the start of or the onset of the thermal processing and as the as the severity of the heat treatment increases so, those again start decreasing.

So, therefore, after certain period of time they follow the first order destruction. Now look into the third plot that is initial lag in the inactivation curve. So, initial lag if it observed there will be this kind of a pattern that we may see in the microbial destruction curve and after that lag period it follows the first order destruction. So, this lag period is; obviously, lower than the decimal reduction time normally and almost 90 percent destruction may happen in this zone and then it start decreasing. So, this kind of pattern is visible when the initial lag in the inactivation curve will be observed.

The fourth one if we look into this pattern, this has a 2 distinct slope here and here. So, we can get the D value for first this to this section a different D value and from here to here, a different D value. So, these indicate that there are 2 microorganism, which have the different heat resistance to thermal death at the same temperature. So, the D value of which is lower will first show the destruction curve and then the D value for which it is higher will follow the next.

. So, in such case we can write the microbial inactivation requirement the time for both the 2 microorganism and then we can analyse that what will be the D value for those different combination. So, if we write the equation for this. So, for the normal destruction the curve will be simply \log of N_0 by N that is equal to t by D . And if we consider the case of initial lag in the inactivation curve, then we can write it as equation \log of N_0 by N this is equal to $1 + t - t_L$ by D . So, this t_L is the lag time t_L is the lag time; and obviously, the time t that we consider that should be greater than t_L .

After that if we consider the mix culture. So, then the total microbial count viable microbial count after processing time t will be will be N_{A0} into 10 to the power minus t by D_A which is the decimal reduction time for the first microorganism plus it will be N_{B0} into 10 to the power minus t by D_B . So, where N_{A0} and N_{B0} is the initial microbial count of microbe A and B respectively at the start of processing and then after time t the

viable number of microorganism for A will be $N_A 0$ into 10 to the power minus 10 to the power minus t by D A plus it will be $N_B 0$ 10 to the power minus t by D B.

So, when we consider that D B if since D B is higher, the thermal death time for the second microbes is higher D B or if we consider as D 2 here it is higher, than this second term does not have significance for the lower time period when t is small. So, then only the first term prevail that is showing by first part of the curve. And in the next section where the time is significantly higher than it shows that importance of the next curve will be shown, that is because of the second or more heat resistant microorganism.

Coming to the last plot that is tailing of an inactivation curve, this is because if the number of microorganism is very high. So, towards the end of the logarithmic cycle that it will follow will form a tail like structure with increasing time. So, it can be avoided if initial load of the microorganism can be reduced.

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✓ Example: The following data were obtained from a thermal resistance experiment conducted on a spore suspension at 112°C. Calculate the D value of micro-organism at given temperature.

Time (min)	Number of survivors
0	10^6
4	1.1×10^5
8	1.2×10^4
12	1.2×10^3

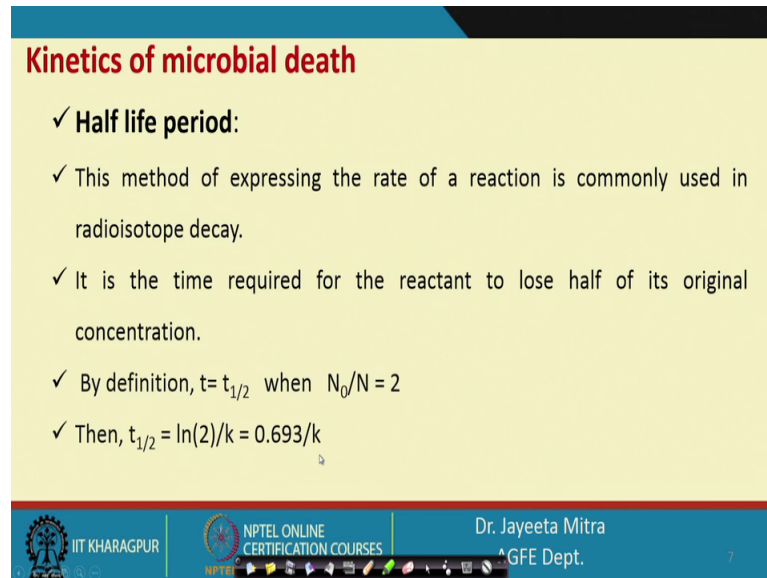
✓ Solution:
 ✓ plot $\ln(N)$ vs time

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So, let us take one numerical example, the following data were obtained from a thermal resistance experiment conducted on a spore suspension at 112 degree Celsius calculate the D value of microorganism at a given temperature. So, what is given simply? Time is given and number of survivors is given. What we can do is we can plot the number of survivors in log scale in the y axis and in the x axis we can plot the time and simply measure the time required to reduce the number of microorganism by 1 log cycle.

. So, what we can do is the first plot the log of N microbial population with respect to time and we can measure the D value here we are getting 4.1 minutes.

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Kinetics of microbial death

- ✓ **Half life period:**
- ✓ This method of expressing the rate of a reaction is commonly used in radioisotope decay.
- ✓ It is the time required for the reactant to lose half of its original concentration.
- ✓ By definition, $t = t_{1/2}$ when $N_0/N = 2$
- ✓ Then, $t_{1/2} = \ln(2)/k = 0.693/k$

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So, next is half-life period what is half-life period? So, this method of expressing the rate of a reaction is commonly used in radioisotope decay. So, for those case it is very common. It is the time required for the reactant to lose half of its original concentration, by definition t will be equal to half when N_0/N equal to 2 in this case. That means, we have made the number of viable microorganism half of the initial microbial population. So, then t half that is the time required to make the microbial population, half of its initial microbial population will be $\ln 2$ by k that is equal to 0.693 by k.

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Kinetics of microbial death

- ✓ **Thermal death time (F value):**
- ✓ Total time required to accomplish a stated reduction in a population of microorganisms at given temperature.
- ✓ This time can be expressed as a multiple of D values. For example, a 99.99% reduction in microbial population would be equivalent to four log cycle reductions or $F = 4 D$.
- ✓
$$F = D \log_{10} (N_0/N)$$

Handwritten notes on the slide:
 $\log_{10} \left(\frac{N_0}{N} \right) = \frac{t}{D}$
 $D \log_{10} \left(\frac{N_0}{N} \right) = t = F$
 $D \times S = F$

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Next is thermal death time that is F value. So, for we are talking about that total processing time and that depends on a particular temperature, because microbes have different resistant at resistance to thermal destruction at different temperature. So, total time required to accomplish a stated reduction in the population of microorganism at a given temperature is termed as F value. So, this time can be expressed as multiple of D value, because we know that one log cycle reduction takes a time which is represented by D value, but one log cycle reduction is not enough to preserve the food material. Normally there are fixed number of logarithmic cycle that is being stated for any food preservation.

For example commercial sterility is being done by 12 D that is 12 log cycle reductions. That means, if one log cycle reduction takes a time D. So, n log cycle or any log cycle reduction will be multiplied by that number with the D value. For example, 99.99 percent reduction in microbial population would be equivalent to 4 log cycle reduction that is F equal to 4 D. So that means, we can change this 99.99 percent to the probability value and we want to initially if it was one then. Now it will be 1 minus 0.9999 and that is eventually coming one by one in one divided by 1000. So, that is 10 to the power 4 so that means, F is equal to 4 into d.

So, that is the total process time is equal to F equal to D log 10 N 0 by N. If you remember our earlier equation was log of N 0 by N to the base 10 that is equal to t by D,

now we can write \log of N_0 by N that is equal to t , and this t is eventually F value for the total process time when we strictly define that how much log cycle reduction we want in a process ok. And this number of log cycle reduction is also called the sterilization value and sometime it is expressed as s . So, D into S that is F value or the total process time.

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✓ Example: The most probable spore load in a canned food is 100 and the D_0 of the spore is 1.5 minutes. Calculate a target F_0 for a thermal process such that the probability of spoilage is 1 in 100,000. If under the same conditions *C. botulinum* type B has a D_0 of 0.2 min, would the target F_0 value satisfy the minimum 12D process for *C. botulinum*? Assume an initial spore load of 1 per can for *C. botulinum*.

Solution: $N_0 = 100$, $N = 10^{-5}$ $S = \log_{10}(100/10^{-5}) = 7$
 $F_0 = D_0 \times S = 1.5 \times 7 = 10.5$ minutes
 For *C. botulinum* type B: $S = 12$ $F_0 = 0.2 \times 12 = 2.4$ minutes

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So, let us take one example the most probable spore load in a canned food is 100 and the D_0 value of the spore is 1.5 minute. Calculate a target F_0 for a thermal process such that the probability of spoilage is 1 in 1 lakh ok. So, if under the same condition clostridium botulinum type B has a D_0 value of 0.2 minute would the target F_0 value satisfy the minimum 12 D process for clostridium botulinum that is the question and assume an initial spore load of 1 per can of c botulinum. Now the case is that whenever we say that D_0 value or F_0 value, we want to mean that reference temperature. So, at a Celsius scale we mean the reference temperature as 121 degree Celsius and in the Fahrenheit we make it 250 degree Fahrenheit.

So, here we want to calculate that F_0 at 121; and D_0 at 121 is given as 1.5 minute. So, N_0 that is the spore load is 100 and the probability of spoilage that we want that is 10 to the power minus 5 ok. So, here it is that is the probability of spoilage. So, 1 divided by 1 and 100000. So, 10 to the power minus 5, N_0 is given now what is the sterilization

value? That is $\log_{10} N_0$ by N . So, that is coming 5 and 2.7. So, then we can calculate F_0 as D_0 into S that is 1.5 minute into 7 that is 10.5 minute.

Now, the second case it is mentioned that for the *C. botulinum* sterilization value is 12 and F_0 is 0.2 minute. So, 0.2 into 12 that is 2.4 minute. So, would the target F_0 value satisfy the minimum 12 D process of *C. botulinum* the answer will be yes because it will always consider that within this time.

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Kinetics of microbial death

- ✓ Temperature dependence of reaction rate
- ✓ Arrhenous eqn: $k = A_0 [e]^{-\frac{E_a}{RT}}$

where:
 A = a constant, Its units are the same as those of the rate constant k, which in turn depend on the order of the reaction.
 R = universal gas constant = $8.314 \text{ kJ.K}^{-1} . \text{kmol}^{-1}$
 T = absolute temperature, K
 E_a = activation energy, kJ.kmol^{-1}

$\frac{D_1}{D_2} = \frac{k_2}{k_1} = \frac{[e]^{-\frac{E_a}{RT_2}}}{[e]^{-\frac{E_a}{RT_1}}}$

$k_1 = A_0 [e]^{-\frac{E_a}{RT_1}}$ $k_2 = A_0 [e]^{-\frac{E_a}{RT_2}}$

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So, next is temperature dependence of reaction rate. Temperature dependence of reaction rate is expressed in terms of Arrhenous equation as the temperature dependence of any chemical reaction also expressed in terms of Arrhenous equation. So, this is k that is reaction rate constant that is equal to A_0 into e to the power minus E_a that is activation energy by R into T .

Now, generally it happens that with increasing temperature, the reaction become faster. So, that is activation energy become slower that is why minus sign has been incorporated. A is a constant here and its units are the same as those of the reaction rate constant k, which in turn depend on the order of the reaction. R is universal gas constant 8.314 kilo joule per kilo mole Kelvin. T is the absolute temperature in Kelvin E_a is the activation energy kilo joule per kilo mole. Now if we plot the $\ln k$ with respect to one by temperature absolute temperature. So, we are getting a slope which is a straight line

which is decreasing from the slope we can get the value of activation energy because we know the value of R.

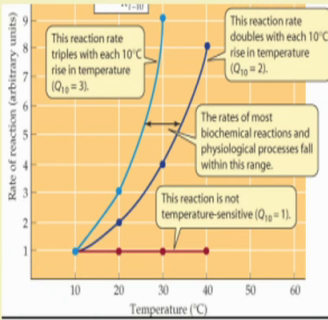
So, if the reaction has happened at 2 different temperature like T 1 and T 2. Since here we can see k equal to A 0. So, k is equal to A 0 e to the power minus E a by RT, now if it is at t 1 we can write k 1 that is equal to A 0 e to the power minus E a by RT 1 and k 2 that is equal to A 0 e to the power minus E a by RT 2 now k 2 by k 1 if we do. So, here it is minus E a by RT 2 and this will become I can write here k 2 by k 1;so e to the power minus E a by RT 2 plus E a by RT 1.

So, we can take E a by R out of this and it will become 1 by T1 minus 1 by T 2 and that is eventually T 2 minus T 1 by T 1 T 2. So, we are getting this expression k 2 by k 1 this is equal to e to the power E a by R T 2 minus T 1 by T 1, T 2. Now since, we know that k is inversely proportional with D which is the decimal reduction time we can here write that this will be D 1 by D 2. So, decimal reduction time at temperature T 1 by D 2 will be e to the power E a by R 1 by T 1 minus 1 by T 2.

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Kinetics of microbial death

- ✓ Temperature coefficient (Q_{10})
- ✓ Number of times a reaction rate changes with a 10^0 C change in temperature.
- ✓ Ex: If a reaction rate doubles with a 10^0 C change in temperature, then $Q_{10} = 2$
- ✓ By definition, $Q_{10} = \frac{10E}{RT_1(T_1 + 10)}$



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And temperature coefficient Q 10 it is nothing but the ratio of k 2 by k 1 number of times a reaction rate changes with the 10 degree change in temperature; that means, when in if you if you look into the previous equation when T 2 minus T 1 is 10 that time k 2 by k one can be represented as Q 10 ok. So, if the reaction rate doubles with a 10 degree, then the Q 10 will be 2. So, Q 10 by definition we can write 10 E that is where we have taken

previously this equation as k_2 by k_1 that is equal to e to the power E_a by R into T_2 minus T_1 by $T_1 T_2$.

So, now if we consider this as Q_{10} ; so, this will become Q_{10} we can get this as e to the power E_a by R into T_2 minus T_1 as 10 by $T_1 T_2$ that is if it is T_1 , then T_2 will become T_1 plus 10 we can take out that $\ln e$, and get the expression that is E_a by R that is into 10 by T_1 plus T_1 into T_1 plus 10 .

Now we can also see that if graphically we want to express the rate of reaction in the y axis and temperature in the x axis the reaction which does not change with temperature. That means, the rate will remain same if we increase the temperature that is represented by this red line, and where the Q_{10} or the reaction rate changes with a factor of 2 that is this deep blue line; and the light blue line showing the reaction rates change with the 10 degree change in the temperature by 3 times; so most of the biochemical reaction and physiological processes fall within this range. So, here we can write k_2 by k_1 that is Q_{10} that is equal to T_2 minus T_1 by 10 .

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Kinetics of microbial death

- ✓ **Z value(thermal resistance constant):**
- ✓ It is defined as the temperature change required to change the D value by a factor of 10 or 1 log cycle
- ✓ If D-value versus time is plotted on a logarithmic scale, the graph looks very similar to survivor curve. This one is called the **Thermal death time (TDT)** curve
- ✓ The straight line graph means that if you change the temperature by a certain amount, the D-value will change by a factor of 10.

The slide includes a graph showing a straight line on a semi-logarithmic scale. The vertical axis is labeled 'log D' and the horizontal axis is labeled 'T'. A red horizontal line is drawn at a certain level on the log D axis, and a light blue horizontal line is drawn above it. A vertical line connects these two horizontal lines to the straight line graph, illustrating the change in D-value with temperature.

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Next is Z value which is the thermal resistance constant, it is defined as the temperature change required to change the D value by a factor of 10 or 1 log cycle D value versus time if it is plotted in a logarithmic scale, the graph looks very similar to the survivor curve and this one is called the thermal death time plot. The straight line on the graph means that if you change the temperature by a certain amount, the D value will change

by a factor of 10. So, it is like if we plot this temperature here and D value in a in a log scale here.

So, we will get this kind of a plot from where at a particular temperature we can calculate the log d and at another temperature. And, we can get the value of z that is increase in temperature needed to cause one degree destruction one log cycle destruction in the microbial count.

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Kinetics of microbial death

- ✓ From fig: $\frac{D_1}{D_2} = \frac{k_2}{k_1} = [10]^{\frac{T_2 - T_1}{z}}$
- $z = \ln(10) \times \frac{T_1 T_2}{E_a / R}$
- ✓ In terms of Q_{10} $z = \frac{10 \ln(10)}{\ln(Q_{10})}$
- ✓ Example:
- ✓ For *Bacillus stearothermophilus*, Z value = 10°C, $D_{121} = 4$ minutes.
- ✓ Means for this organism heating for 40 minutes at 111°C, which would have the same effect as 400 minutes at 101°C.

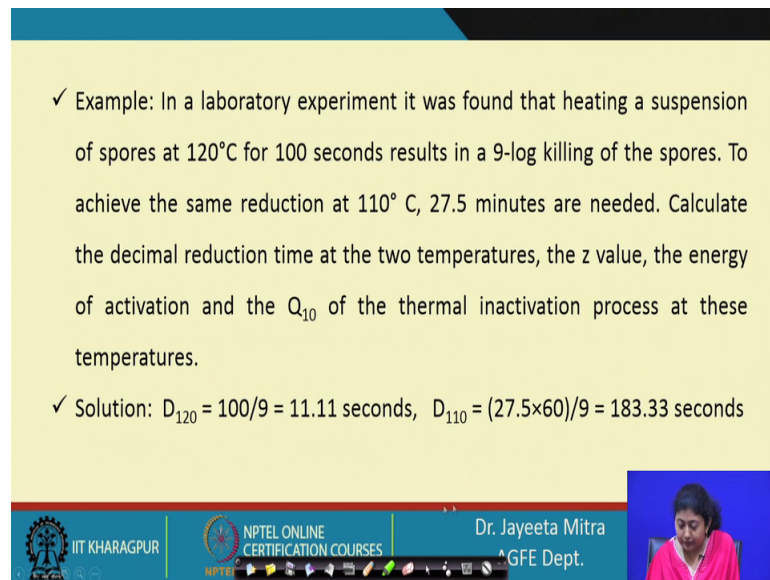
The graph shows D value (min) on a logarithmic y-axis (1, 10, 100) versus Temperature (°C) on a linear x-axis (100, 105, 110, 115, 120). A dashed line represents the relationship. A vertical line at 110°C intersects the line at D=10. A horizontal line from D=10 to the line and then a vertical line down to D=1 at 120°C shows a temperature change of 10°C for a 1 log reduction. The formula $z = \frac{\Delta T}{\log D_1 - \log D_2}$ is shown above the line.

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So, here it is this is the z value as i plotted there that the change in temperature needed in degree Celsius to cause one log cycle reduction. We can plot this as delta t temperature difference divided by log D 1 minus log D 2 that is D 1 initial decimal reduction time and minus the final one.

So, we can plot it as D 1 by D 2 that is equal to k 2 by k 1 that is equal to 10 to the power T 2 minus T 1 by z or we can express z in terms of activation energy that is l n 10 T 1 T 2 by E a by R. In terms of Q 10 we can write z as 10 l n 10 by l n Q 10. For bacillus stearothermophilus z value is 10 degree Celsius D 121 is 4 minute. That means, at 121 degree Celsius 4 minute if the processing time is the same microbial destruction if you want to cause at 11 111 degree Celsius. So, that time requirement will be 40 minutes and the same microbial destruction if you want to cause at 101 degree it will take 400 minutes.

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✓ Example: In a laboratory experiment it was found that heating a suspension of spores at 120°C for 100 seconds results in a 9-log killing of the spores. To achieve the same reduction at 110° C, 27.5 minutes are needed. Calculate the decimal reduction time at the two temperatures, the z value, the energy of activation and the Q_{10} of the thermal inactivation process at these temperatures.

✓ Solution: $D_{120} = 100/9 = 11.11$ seconds, $D_{110} = (27.5 \times 60)/9 = 183.33$ seconds

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So, there is an example in a laboratory experiment it was found that heating a suspension of spore at 120 degree Celsius for 100 second, results in a nine log cycle killing of the spores. To achieve the same reduction that is 9 log cycle at 110 degree Celsius, 27.5 minutes are needed calculate the decimal reduction time at the 2 temperature z value. And the activation energy and Q 10 value of the thermal inactivation process at this temperature also need to be calculated.

So, the 129.9 log cycle reduction is given. So, for D 129 there is one log cycle will be 11.11 and similarly at 1101 log cycle reduction is 183.33 second.

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✓ Z value is calculated using formula $\frac{D_1}{D_2} = \frac{k_2}{k_1} = [10]^{\frac{T_2 - T_1}{z}}$
 $Z = 10/1.2175 = 8.21^\circ\text{C}$

✓ The activation energy E_a is calculated from $z = \ln(10) \times \frac{T_1 T_2}{E_a / R}$
 $E = (2.3 \times 8.314 \times 393 \times 383) / 8.21$
 $E = 350.6 \times 10^3 \text{ kJ/kmol.K}$

✓ Q_{10} value is calculated from $(Q_{10}) = \frac{10E}{RT_1(T_1 + 10)}$
 $Q_{10} = (10 \times 350.6 \times 10^3) / (8.314 \times 393 \times 383) = 2.8$

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Z value we can calculate by the formula since we know the temperature difference and D_1 D_2 we can calculate the z. So, z is coming 8.21 degree Celsius, an activation energy we can calculate from this equation z equal to $\ln 10 T_1 T_2$ by E_a by R ok. So however, E is coming here 350.6 into 10 cube kilo joule per kilo mole kelvin. Finally, the Q_{10} value is calculated from this expression Q_{10} equal to $10 E$ by $R T_1$ into $T_1 + 10$. So, it is 2.8. So, for 10 degree increase in temperature the reaction rate will increase by 2.8 times.

So, we will stop here we will continue in the next class.

Thank you.