Polymer Process Engineering

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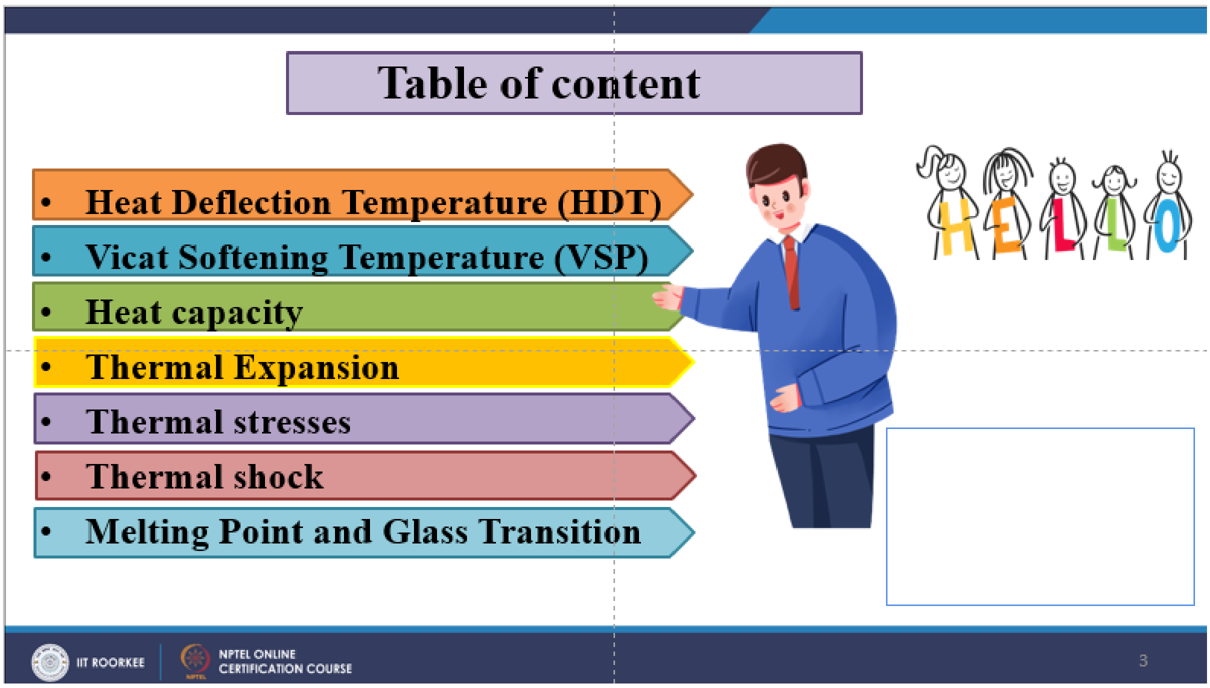
Lecture – 17

Heat Transfer Phenomenon in polymer systems: Thermal properties

Hello friends, welcome to the Heat Transfer Phenomena in Polymer Systems. Here we are going to discuss the thermal properties of the various polymeric systems. Now, before we go into the details of this particular aspect, let us have a brief outlook on what we discussed in the previous lecture. In the previous lecture, we discussed the fundamental aspect of heat transfer, what are the different modes of heat transfer, and how these heat transfer processes are carried out in different modes. Apart from this, we discussed heat capacity and modes of different heat transfer in which conduction, convection, and radiation, are all these things we covered. In this particular segment, we are going to discuss about the heat deflection temperature.



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- Vicat Softening Temperature (VSP)
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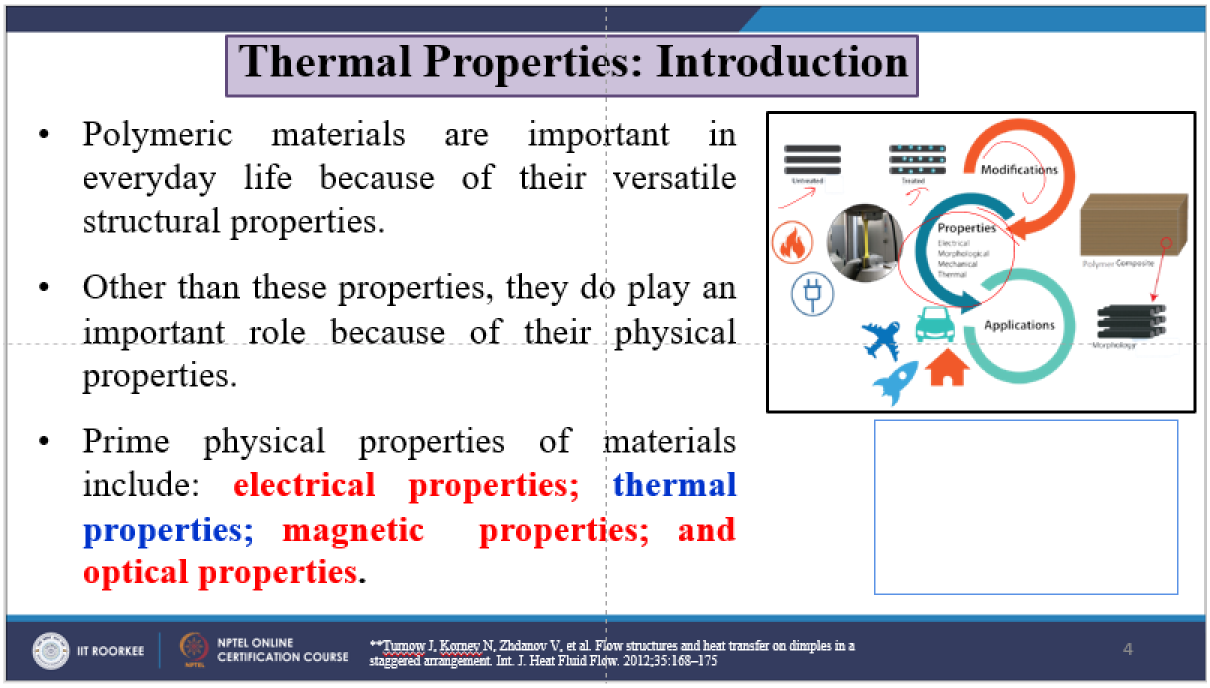
We will discuss the Vicat softening temperature, sometimes referred to as VSP. We will deliberately discuss about the heat capacity, thermal expansion, thermal stresses, thermal shock, melting point, and glass transition. All these segments are extremely important when we discuss different aspects of the polymeric system, especially from the polymerization to the processing to develop the final product. Now, let us discuss the thermal properties.



Thermal Properties: Introduction

- Polymeric materials are important in everyday life because of their versatile structural properties.
- Other than these properties, they do play an important role because of their physical properties.
- Prime physical properties of materials include: **electrical properties; thermal properties; magnetic properties; and optical properties.**

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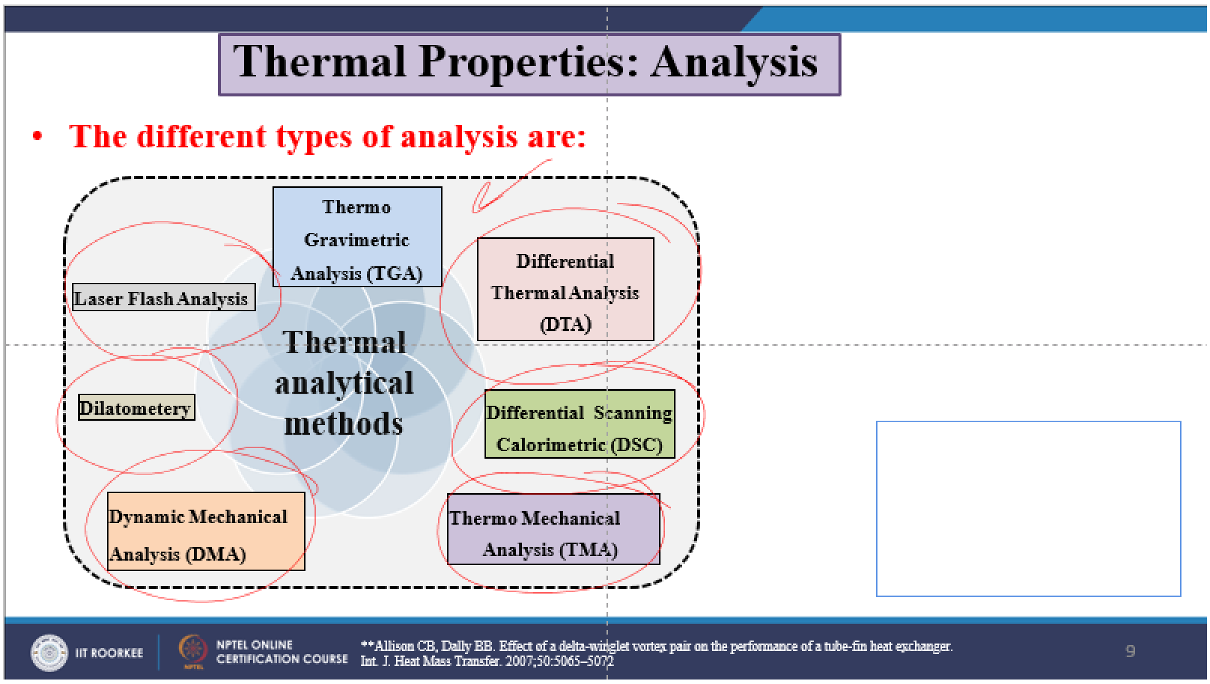
**Turnow J, Korney N, Zhdanov V, et al. Flow structures and heat transfer on dimples in a staggered arrangement. Int. J. Heat Fluid Flow. 2012;35:168–175

A brief outline I am going to present over here. These polymeric materials are important in everyday life because they have versatile structural properties. I discussed in the very first chapter that polymers are an integral part of our day-to-day affairs, right from toothbrushes to linen to medicine to all kinds of community aspects. Polymers have become embedded in every aspect of our segments. So, they are because they possess versatile structural properties, and now other than these properties they do play an important role because of their physical properties.

Now, prime physical properties all these materials possess like electrical properties, thermal properties, magnetic properties, and optical properties. So, all these things you can see and by various kinds of treatment we can impart the other properties. Now, here you see that these are untreated polymers and when we treat them with several modifications, we can impart the various properties as per the requirement, as per the need. Now, the thermal properties of the polymeric materials are very diverse in nature. So, they use in different applications like electrical, morphological and all these things you can modify all these polymeric structure with the help of the thermal properties.



Thermal Properties: Analysis

- **The different types of analysis are:**

Thermal analytical methods

Thermo Gravimetric Analysis (TGA)

Differential Thermal Analysis (DTA)

Differential Scanning Calorimetric (DSC)

Thermo Mechanical Analysis (TMA)

Dynamic Mechanical Analysis (DMA)

Dilatometery

Laser Flash Analysis

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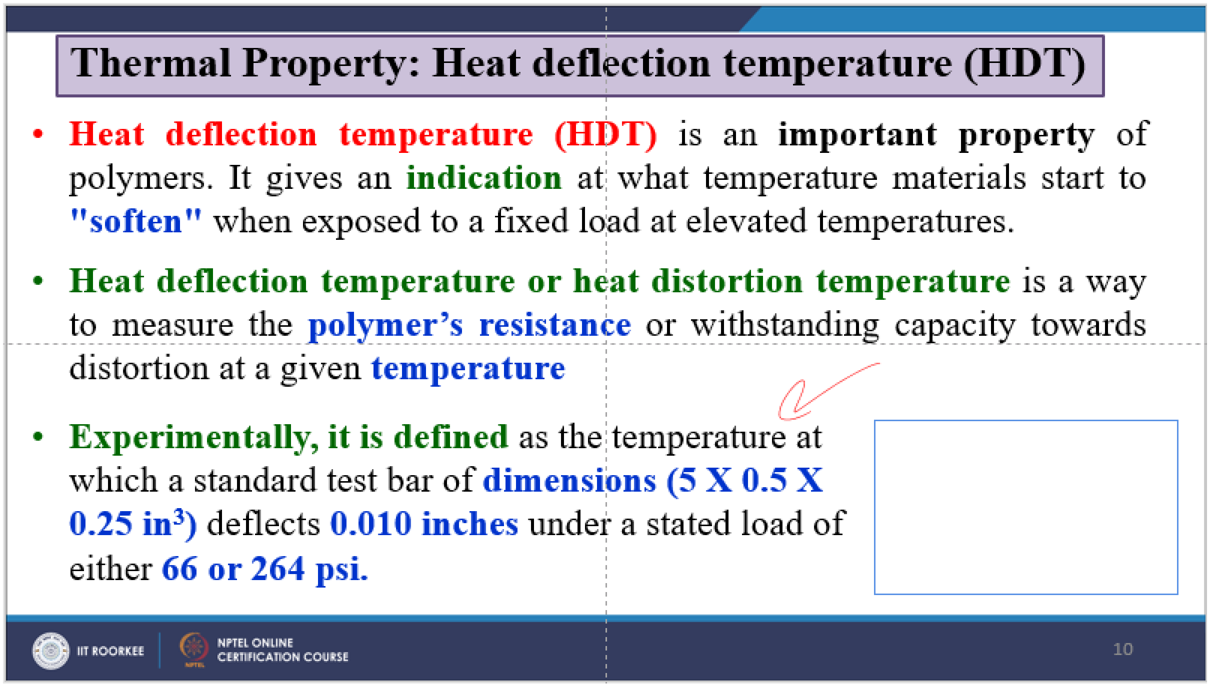
**Allison CB, Dally BB. Effect of a delta-winglet vortex pair on the performance of a tube-fin heat exchanger. Int. J. Heat Mass Transfer. 2007;50:5065–5072

Now, these properties in polymeric systems mean their response towards the temperature change and how they react when applied to heat. Now, as a solid material absorbs heat its temperature rises with a slight increase in the dimension. Now, if you recall the first lecture when we told that these polymers are composed of various kinds of chains, and these chains are also composed of monomers and these chains are entangled in nature. So, once we supply the heat to these chains then they try to unentangle and that is why these thermal properties are of prime importance, and awareness about these properties to develop the new product to develop the product of desired properties is quite essential. So, that is why these thermal properties usually play a very vital role in evaluating the product performance processability characteristics in the polymers because every day right from the polymerization to the processability everywhere you cannot overlook the importance of these thermal properties.

Now, the thermal analytical methods monitor differences in some sample property as a temperature increases or decreases between a sample as a function of added heat and these methods are usually applied in solid to characterize the materials. So, characterization, analysis all these are very important aspect of this polymer repossessing the thermal properties. Now, thermal analysis usually when we talk about the thermal analysis this is a branch of material science by which the physical, chemical and mechanical properties of the material are evaluated as a function of temperature. Now, this usual measurement provides the information of the physical phenomena such as phase transition, absorption, adsorption and desorption as well as the chemical phenomena including the thermal decomposition and solid gas reactions. Now, here you see the different type of analysis which are quite essential for the evaluation of any polymer.



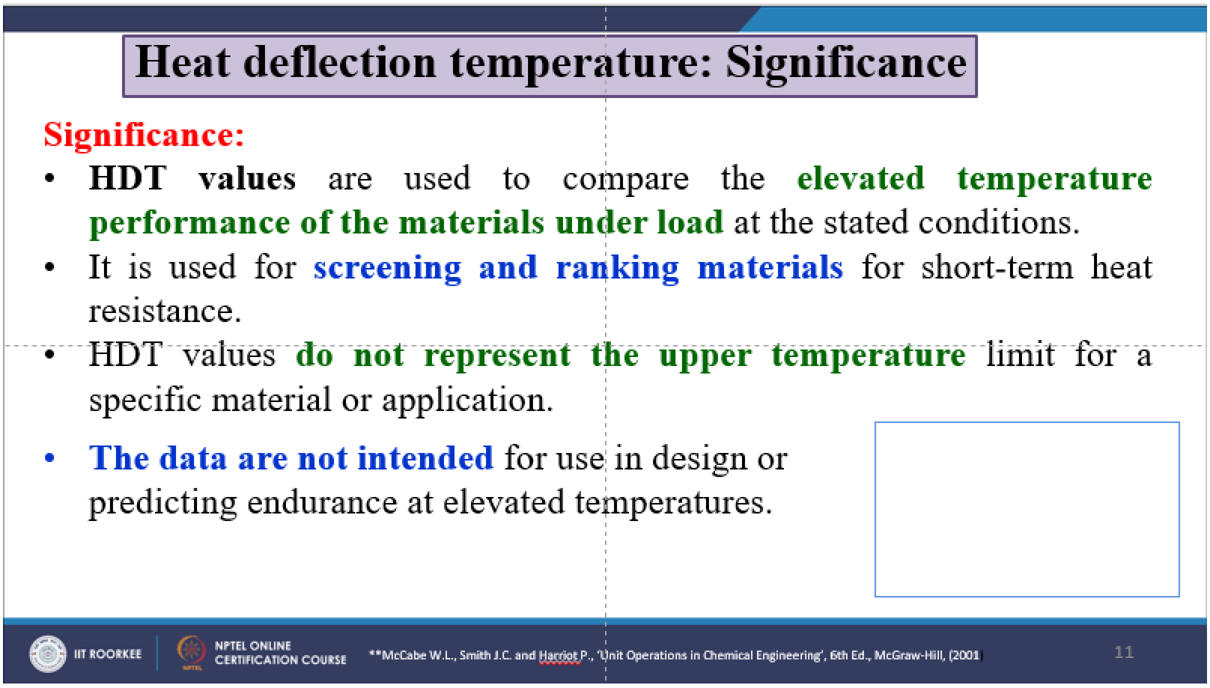
Thermal Property: Heat deflection temperature (HDT)

- **Heat deflection temperature (HDT)** is an **important property** of polymers. It gives an **indication** at what temperature materials start to **"soften"** when exposed to a fixed load at elevated temperatures.
- **Heat deflection temperature or heat distortion temperature** is a way to measure the **polymer's resistance** or withstanding capacity towards distortion at a given **temperature**
- **Experimentally, it is defined** as the temperature at which a standard test bar of **dimensions (5 X 0.5 X 0.25 in^3)** deflects **0.010 inches** under a stated load of either **66 or 264 psi.**

One is the thermal gravimetric analysis and laser flash analysis, dilatometry, dynamic mechanical analysis, thermo mechanical analysis, DSC or differential scanning calorimeter test then differential thermal analysis DTA. So, all these are the thermal analytical methods. Now, let us talk about the heat deflection temperature HDT. This is an important property of the polymer and gives an indication at what temperature material start to soften when exposed to the fixed load of elevated temperature. Now, HDT or sometimes it is referred as the heat distortion temperature.

This is a way to measure the polymers resistance or with the standing capacity towards the distortion at a given temperature. Now, experimentally it is defined as the temperature at which the standard test bar of dimension 5 into 0.5 into 0.25 cubic inch deflects 0.010 inch under a stated load of either 66 or 264 PSI.

So, this is the standard definition. Now, what is the significance and somebody may ask that what is the significance of this HDT. These values are used to compare the elevated temperature, but especially when we evaluate the performance of the material under load. Now, it is used as a screening and a ranking of material for short-term heat resistance. Now, these HDT values do not represent the upper-temperature limit for a specific material application and the data are not intended for the use in design or predicting endurance at elevated temperature.



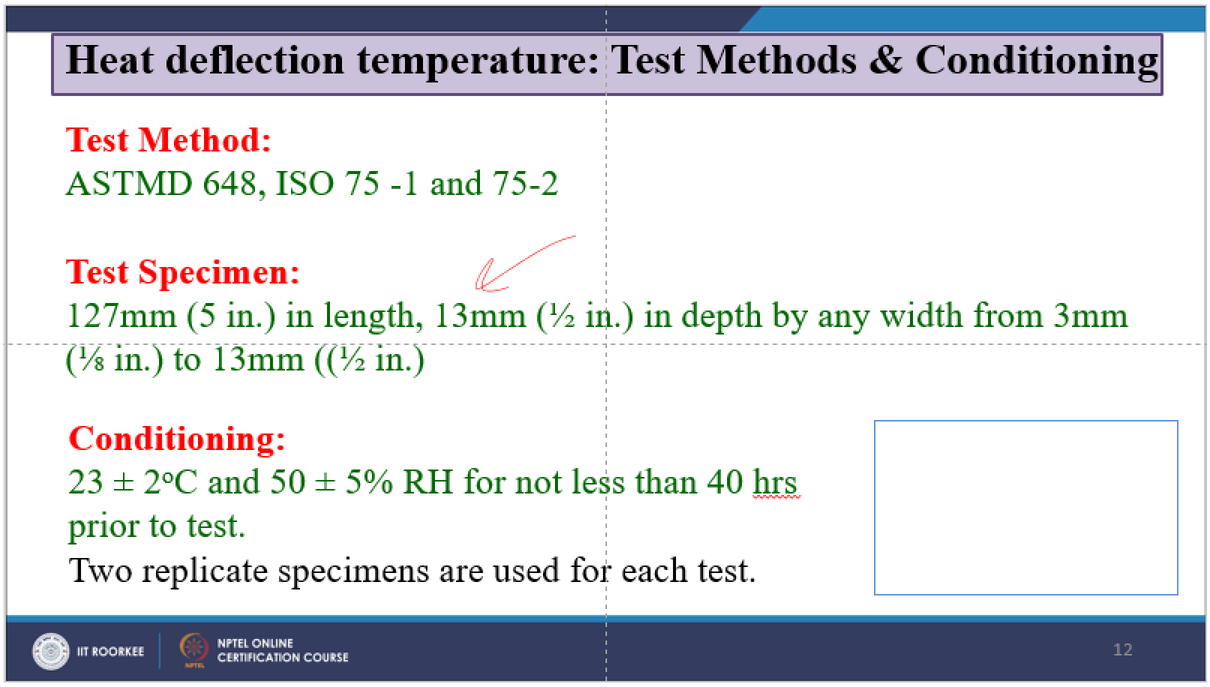
Heat deflection temperature: Significance

Significance:

- **HDT values** are used to compare the **elevated temperature performance of the materials under load** at the stated conditions.
- It is used for **screening and ranking materials** for short-term heat resistance.
- HDT values **do not represent the upper temperature** limit for a specific material or application.
- **The data are not intended** for use in design or predicting endurance at elevated temperatures.

IIT ROORKEE | NPTEL ONLINE CERTIFICATION COURSE **McCabe W.L., Smith J.C. and Harriot P., 'Unit Operations in Chemical Engineering', 6th Ed., McGraw-Hill, (2001

Now, there are various test methods standard test methods applicable like American Society for testing materials they give so many standards for this HDT. Now, one of the test methods is ASTM D648 ISO 75 1 and 75 2. Now, here you require some test specification or test specimen, it must be it must possess the specified length diameter on all these things. So, usually the specimen carries 127 millimeters that is usually 5 inch in length, 13 mm or half inch in depth by any width from 3 mm to 13 mm. Now, you prepare the test specimen then it requires the conditioning.



Heat deflection temperature: Test Methods & Conditioning

Test Method:
ASTMD 648, ISO 75 -1 and 75-2

Test Specimen:
127mm (5 in.) in length, 13mm (½ in.) in depth by any width from 3mm (⅛ in.) to 13mm ((½ in.)

Conditioning:
23 ± 2°C and 50 ± 5% RH for not less than 40 hrs prior to test.
Two replicate specimens are used for each test.

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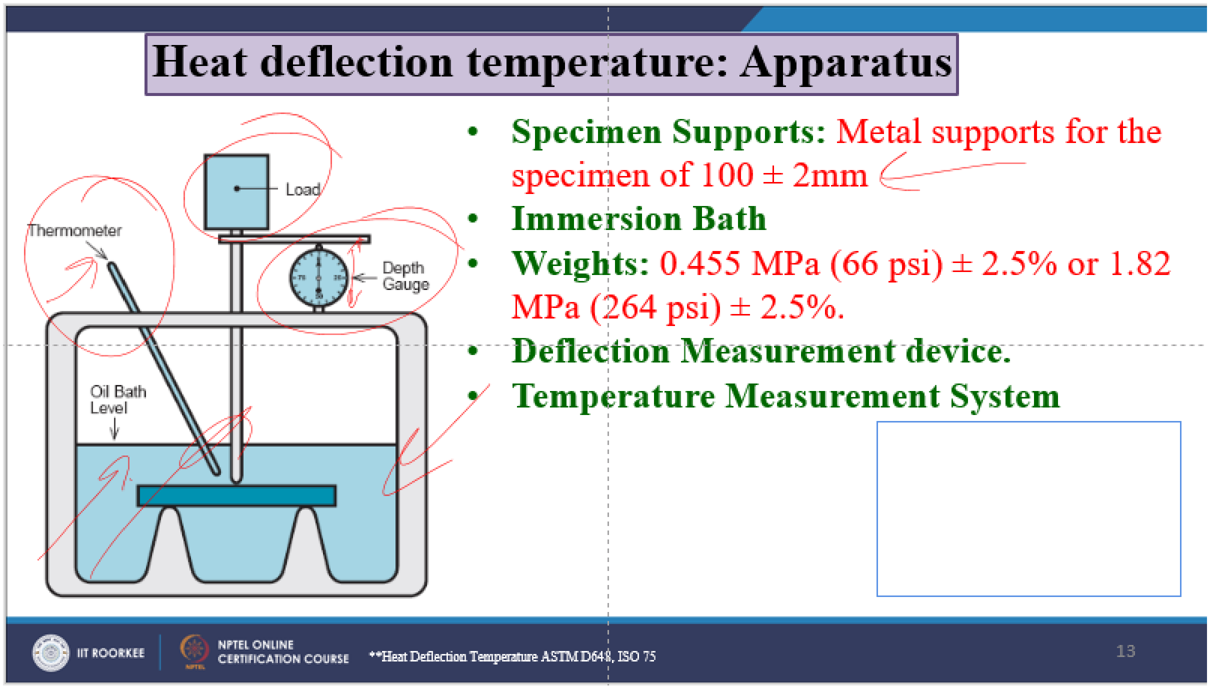
So, the condition requires a specified temperature and relative humidity. So, this is 23 plus minus 2 degrees Celsius and 50 plus minus 5 percent of relative humidity not less than 40 hours prior to the test. Now, two replicate specimens are used for each test so that the efficacy of the experiment can be evaluated. Now, this is the apparatus where you can have you can determine the HDT. Now usually this carries the oil bath usually the depth gauge with a specified applied load and this is the thermometer.

Usually, the specimen support carries the metal support for the specimen of say 100 plus minus 2 mm then there is an immersion bath which is maintained at 0.455 mega Pascal plus usually 2.5 percent plus minus or 1.82 mega Pascal 264 PSI that is plus minus 2.5 percent and deflection measurement device and temperature measurement system.

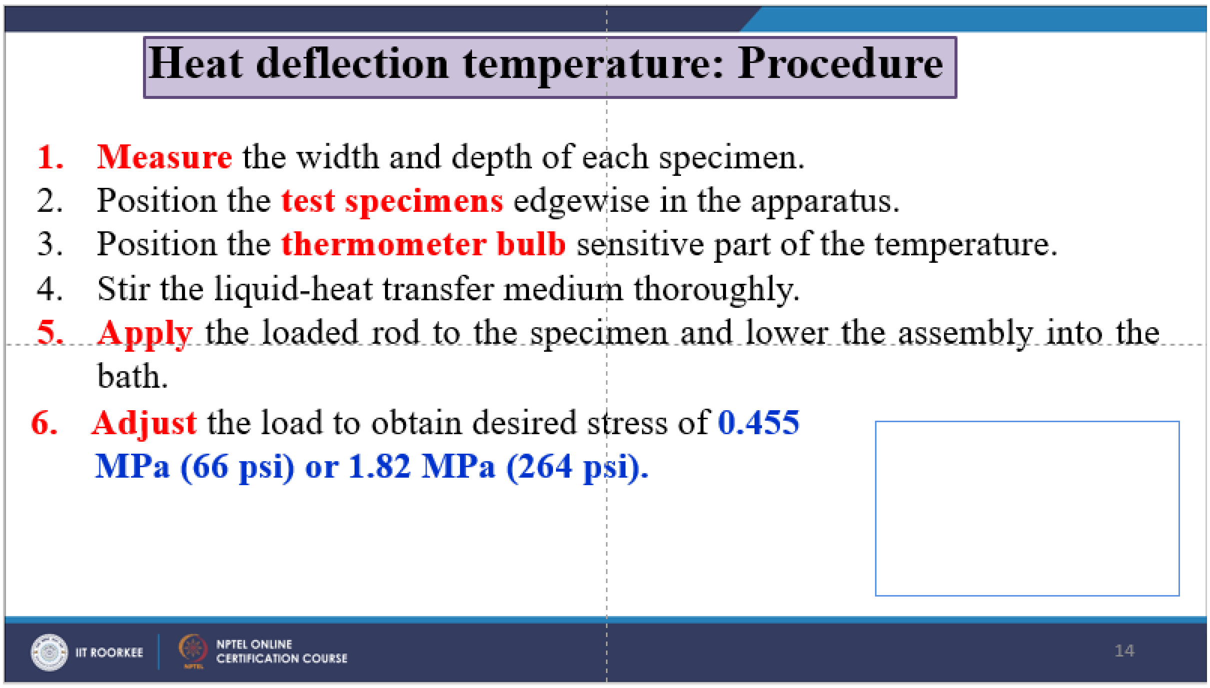


Heat deflection temperature: Apparatus

- **Specimen Supports:** Metal supports for the specimen of 100 ± 2mm
- **Immersion Bath**
- **Weights:** 0.455 MPa (66 psi) ± 2.5% or 1.82 MPa (264 psi) ± 2.5%.
- **Deflection Measurement device.**
- **Temperature Measurement System**

**Heat Deflection Temperature ASTM D648, ISO 75

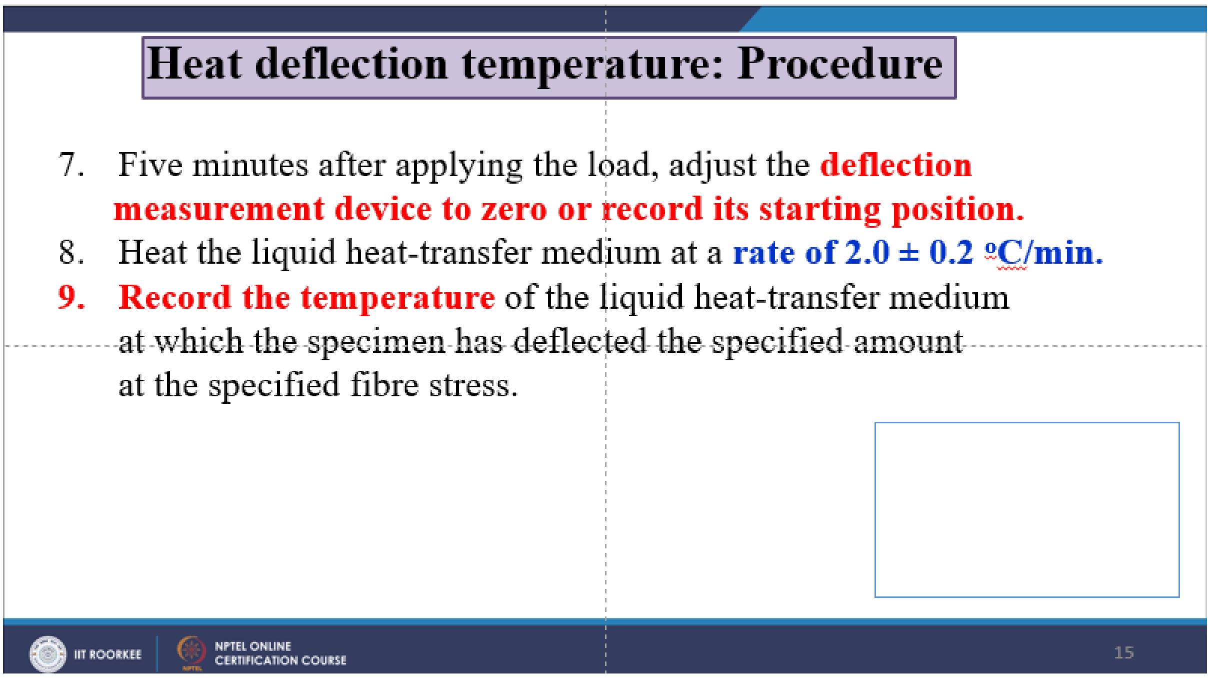
So, here is that the temperature measurement system. Now, let us talk about the procedure. This measures the width and depth of each specimen and then positions of the test specimen edge-wise in this particular apparatus. Then the thermometric bulb you need to position and which is a very sensitive part to the temperature and you need to stir the liquid heat transfer medium thoroughly. So, this is the heat transfer media and apply the load loaded rod to the specimen and lower the assembly into the bath.



Heat deflection temperature: Procedure

1. **Measure** the width and depth of each specimen.
2. Position the **test specimens** edgewise in the apparatus.
3. Position the **thermometer bulb** sensitive part of the temperature.
4. Stir the liquid-heat transfer medium thoroughly.
5. **Apply** the loaded rod to the specimen and lower the assembly into the bath.
6. **Adjust** the load to obtain desired stress of **0.455 MPa (66 psi) or 1.82 MPa (264 psi).**

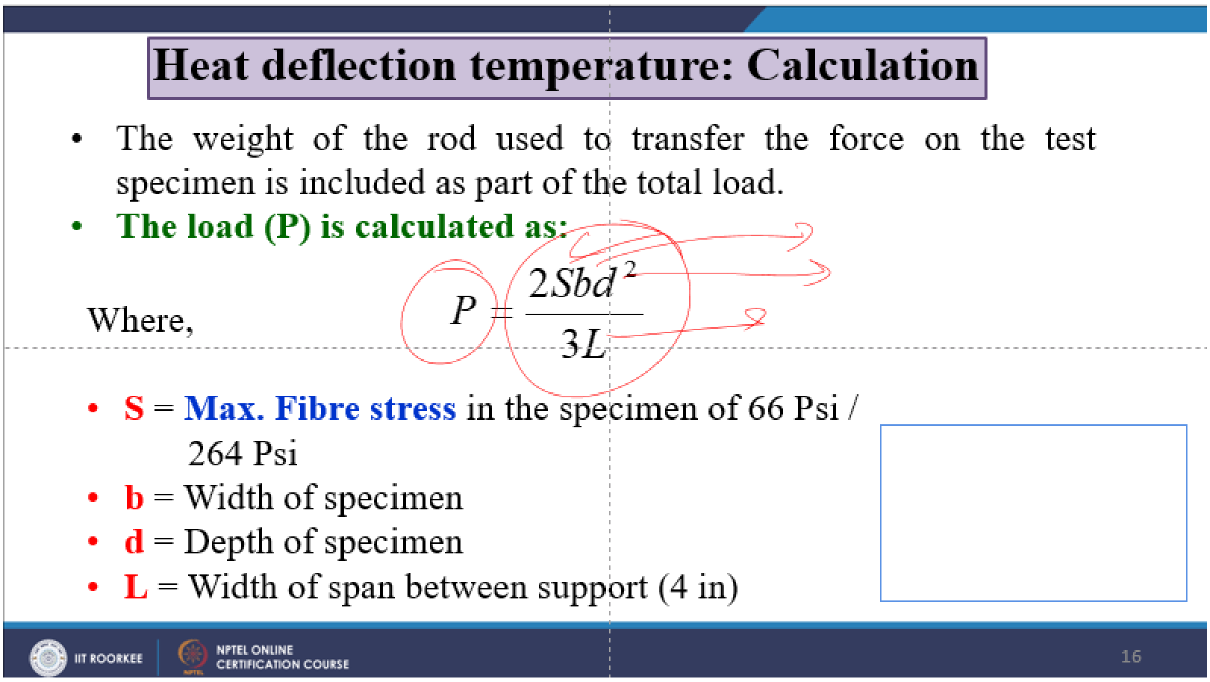
For this you need to calculate the depth gauge. Now adjust the load to obtain the desired stress of say 0.455 mega Pascal or 1.82 mega Pascal. So, you need to wait for 5 minutes after applying the load and then deflection the measurement device to 0 or record its starting position.



Heat deflection temperature: Procedure

7. Five minutes after applying the load, adjust the **deflection measurement device to zero or record its starting position.**
8. Heat the liquid heat-transfer medium at a **rate of 2.0 ± 0.2 ºC/min.**
9. **Record the temperature** of the liquid heat-transfer medium at which the specimen has deflected the specified amount at the specified fibre stress.

Now, heat the liquid heat transfer medium at a rate of say 2.0 plus minus 0.2 degrees Celsius per minute. You need to record the temperature for the liquid heat transfer medium at which the specimen is deflected by a specified amount at the specified fiber stress. Now, how can we calculate it? The weight of the rod used to transfer the force on the test specimen is included as a part of the total load.



Heat deflection temperature: Calculation

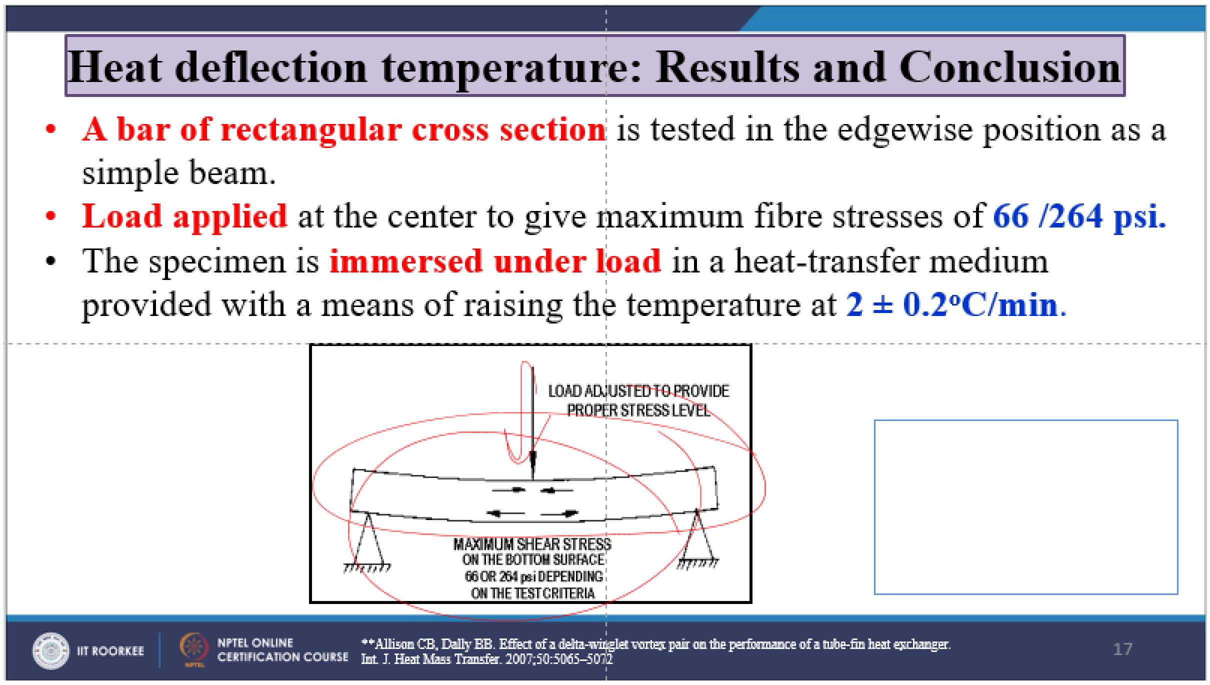
- The weight of the rod used to transfer the force on the test specimen is included as part of the total load.
- **The load (P) is calculated as:**

$$P = \frac{2Sbd^2}{3L}$$

Where,

- **S** = **Max. Fibre stress** in the specimen of 66 Psi / 264 Psi
- **b** = Width of specimen
- **d** = Depth of specimen
- **L** = Width of span between support (4 in)

Therefore, the total load P can be calculated as equal to P is equal to 2 SBD square over 3 L where S is the maximum fiber stress in the specimen of 66 PSI or 264 PSI, which is specified. This B is the width of the specimen, D is the depth of the specimen and L is the width of the span between the support usually 4 inches. Now, when we talk about the results the bar of rectangular now here you see this is a bar. The bar of the rectangular cross-section is tested in the edgewise position as a simple beam. Now, the load applied at the center here gives the maximum stress of 66 or 264 PSI, and the specimen is immersed under load in a heat transfer media.



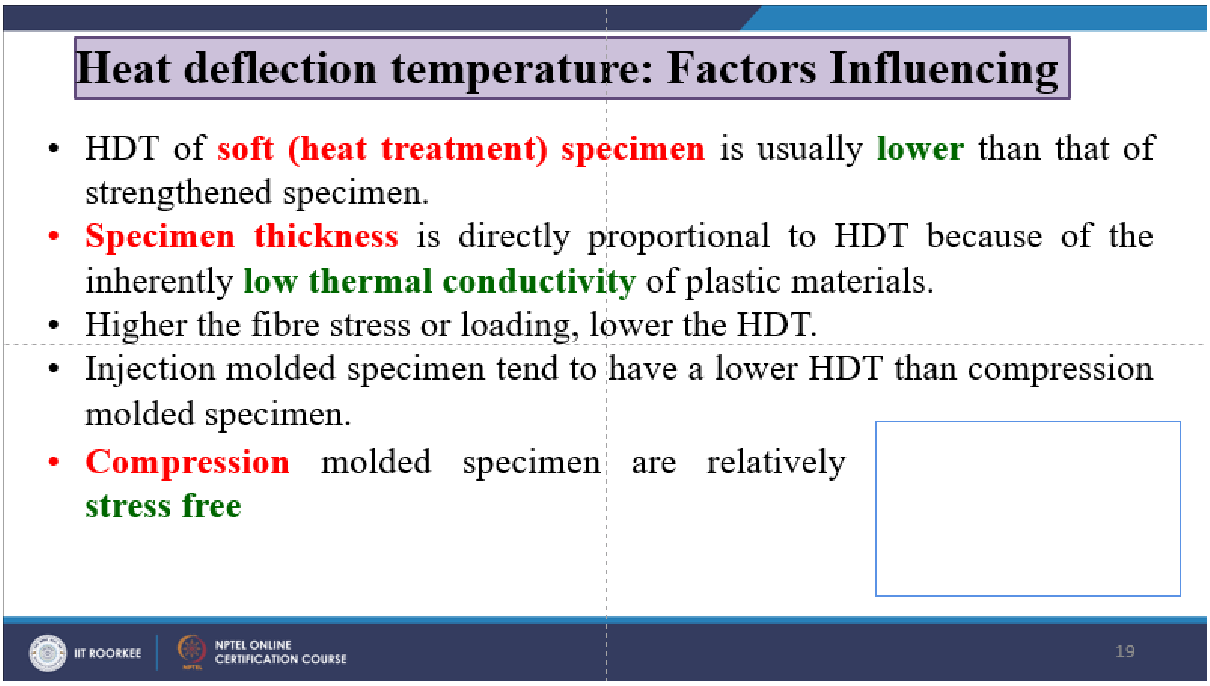
Heat deflection temperature: Results and Conclusion

- **A bar of rectangular cross section** is tested in the edgewise position as a simple beam.
- **Load applied** at the center to give maximum fibre stresses of **66 /264 psi.**
- The specimen is **immersed under load** in a heat-transfer medium provided with a means of raising the temperature at **2 ± 0.2°C/min**.

**Allison CB, Dally BB. Effect of a delta-winglet vortex pair on the performance of a tube-fin heat exchanger. Int. J. Heat Mass Transfer. 2007;50:5065–5072

This provided a means of raising the temperature in a graduation of 2.2 or 1.9 heat graduation degrees Celsius per minute. Now, the temperature of the medium is usually measured when the test bar has a deflection of 0.

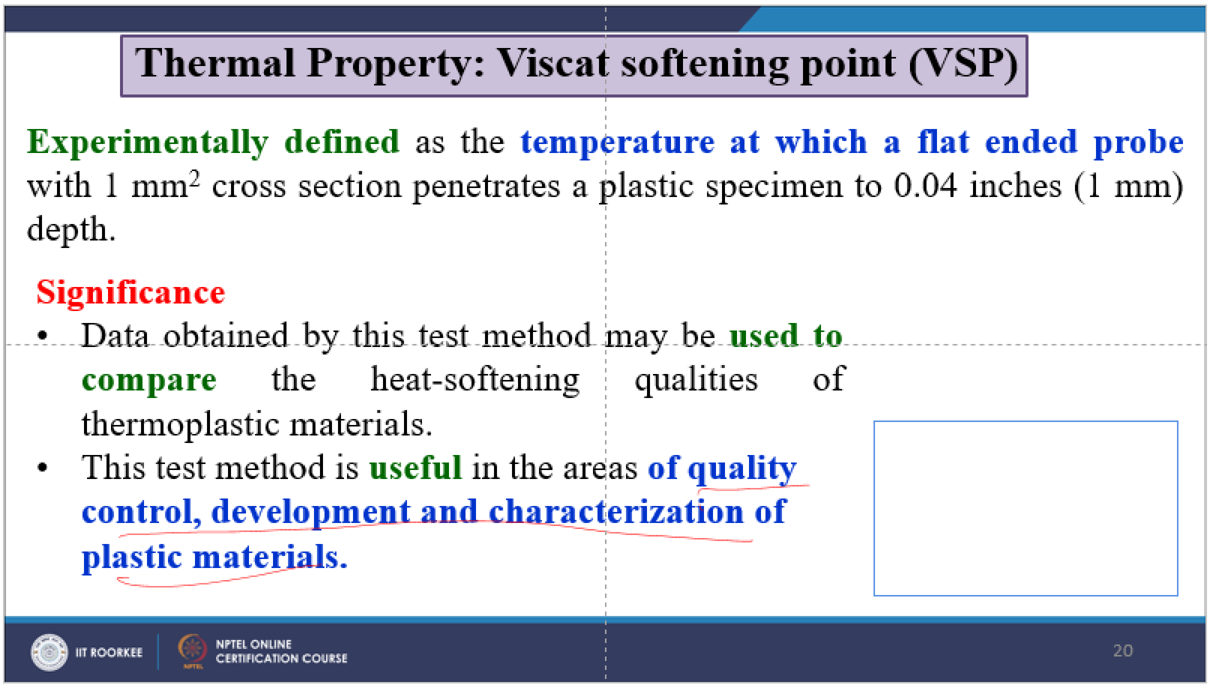
25 mm. Now, this temperature is recorded as the deflection temperature under the flexural load of the test specimen. So, there are various factors influencing this aspect now edge over HDT. The HDT of soft or heat treatment specimens is usually lower than that of the strength and specimen. Specimen thickness it is again very important is directly proportional to the HDT because of the inherently low thermal conductivity of the plastic material. Higher fiber stress or loading lowers the HDT.



Heat deflection temperature: Factors Influencing

- HDT of **soft (heat treatment) specimen** is usually **lower** than that of strengthened specimen.
- **Specimen thickness** is directly proportional to HDT because of the inherently **low thermal conductivity** of plastic materials.
- Higher the fibre stress or loading, lower the HDT.
- Injection molded specimen tend to have a lower HDT than compression molded specimen.
- **Compression** molded specimen are relatively **stress free**

Another is the injection molded specimen tend to have a lower HDT than compression molded specimens and usually it is said that compression molded specimen are relatively stress-free. Let us talk about the EVSP, viscat softening point. Now usually it is experimentally defined as a temperature at which a flat-ended probe with 1 square millimeter cross section penetrates a plastic specimen of 0.04 inches. Now, what is the significance? So, once we calculate the data obtained by this test method, this can be used to compare the heat-softening qualities of thermoplastic material.



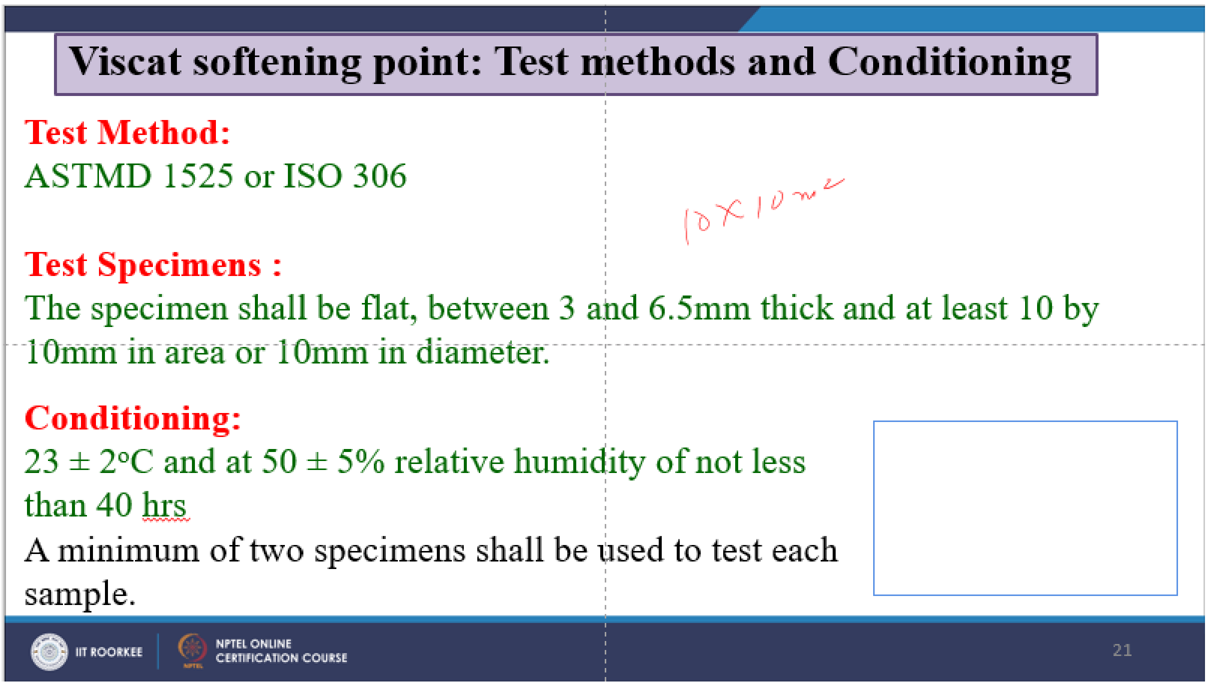
Thermal Property: Viscat softening point (VSP)

Experimentally defined as the **temperature at which a flat ended probe** with 1 mm^2 cross section penetrates a plastic specimen to 0.04 inches (1 mm) depth.

Significance

- Data obtained by this test method may be **used to compare** the heat-softening qualities of thermoplastic materials.
- This test method is **useful** in the areas **of quality control, development and characterization of plastic materials.**

Now this test method is very useful in the area of quality control, development, and characterization of various plastic materials. Again, question arises what are the test methods and how do we condition the specimen for the same? Now the test method is the ASTM D1525 or ISO 306 and again for the test you need to prepare the specimen. So, the specimen shall be flat between the 3 and 6.5 mm thick and at least 10 by 10 by 10 mm area or 10 mm in diameter.



Viscat softening point: Test methods and Conditioning

Test Method:

ASTMD 1525 or ISO 306

10×10 mm^2

Test Specimens :

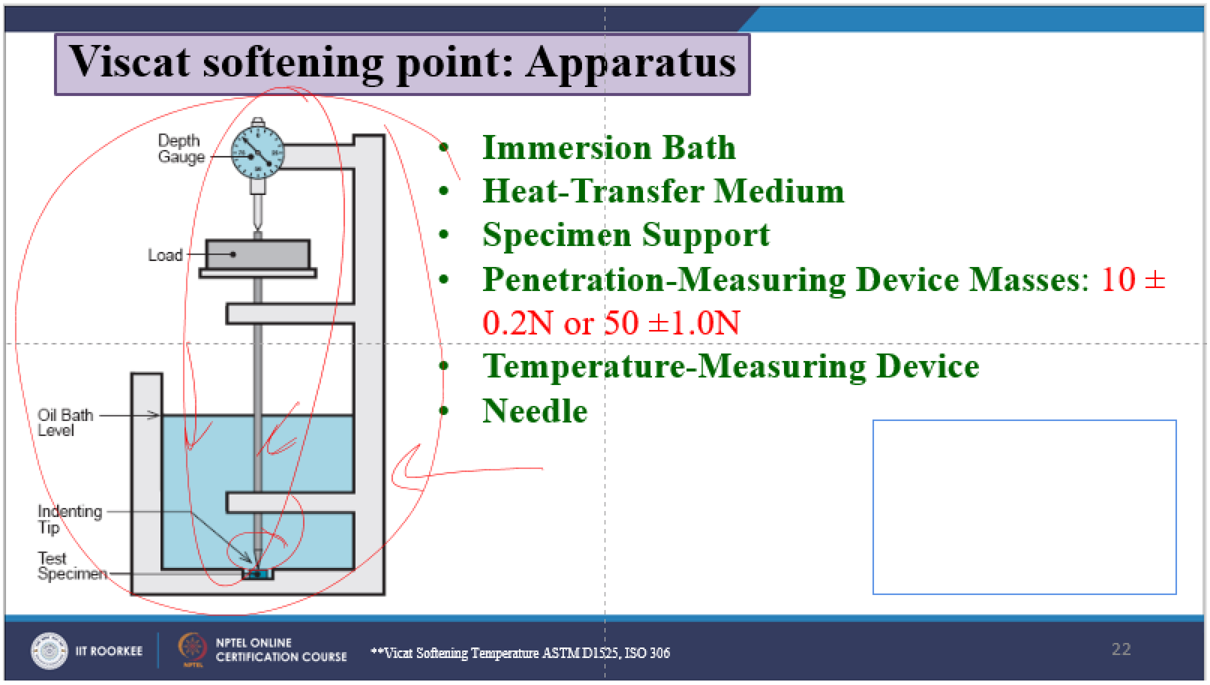
The specimen shall be flat, between 3 and 6.5mm thick and at least 10 by 10mm in area or 10mm in diameter.

Conditioning:

23 ± 2°C and at 50 ± 5% relative humidity of not less than 40 hrs

A minimum of two specimens shall be used to test each sample.

So, if you are taking the bar, then it may be 10 mm in bar. Then the question arises: how do we condition it? So usually 23 plus minus 2-degree Celsius temperature is maintained with the relative humidity of 55, 45 to 55 percent, and which is not less than for 40 hours. A minimum of 2 specimens usually shall be used to test each sample.

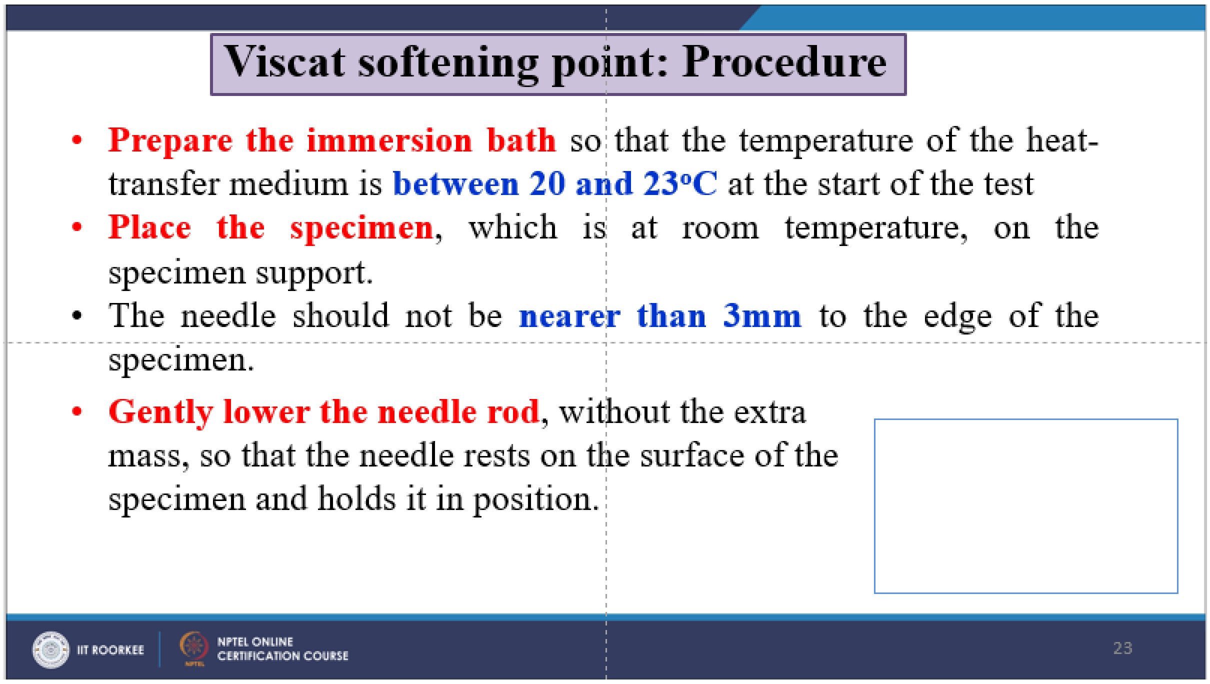


Viscat softening point: Apparatus

- **Immersion Bath**
- **Heat-Transfer Medium**
- **Specimen Support**
- **Penetration-Measuring Device Masses:** 10 ± 0.2N or 50 ±1.0N
- **Temperature-Measuring Device**
- **Needle**

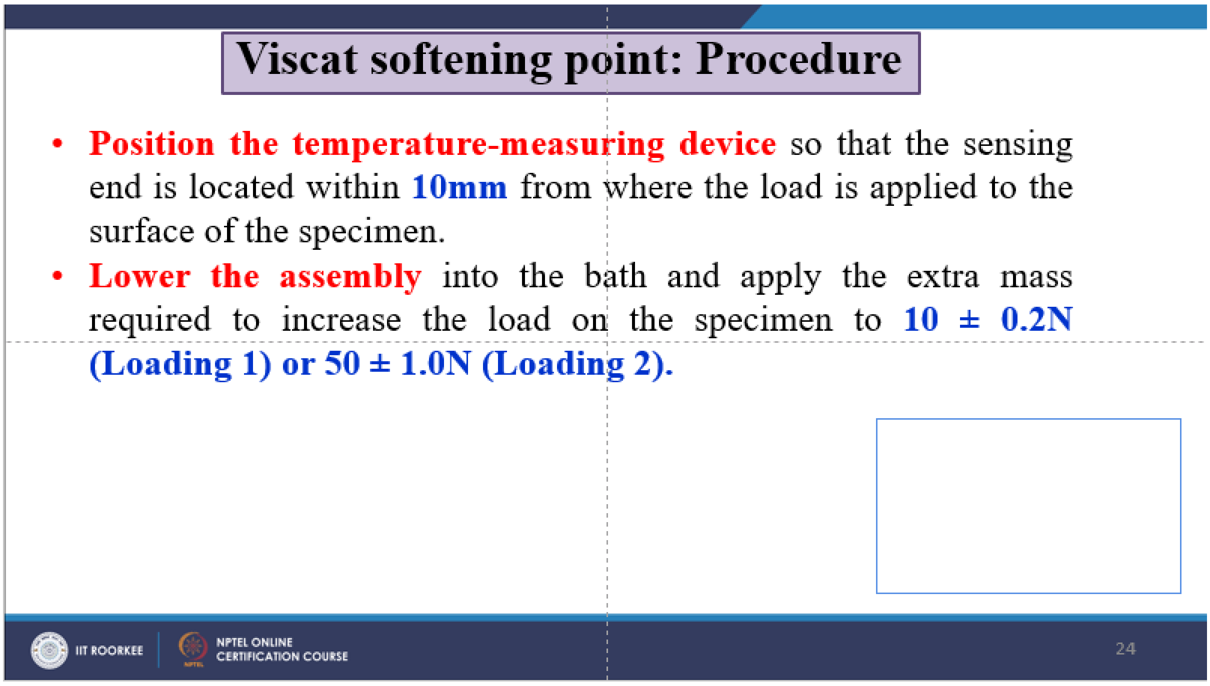
**Vicat Softening Temperature ASTM D1525, ISO 306

Now this is the softening point apparatus. Here you see that there is an immersion bath and usually when we have the heat transfer media then the specimen support and penetration measuring device masses and the temperature measuring device and there are needles.



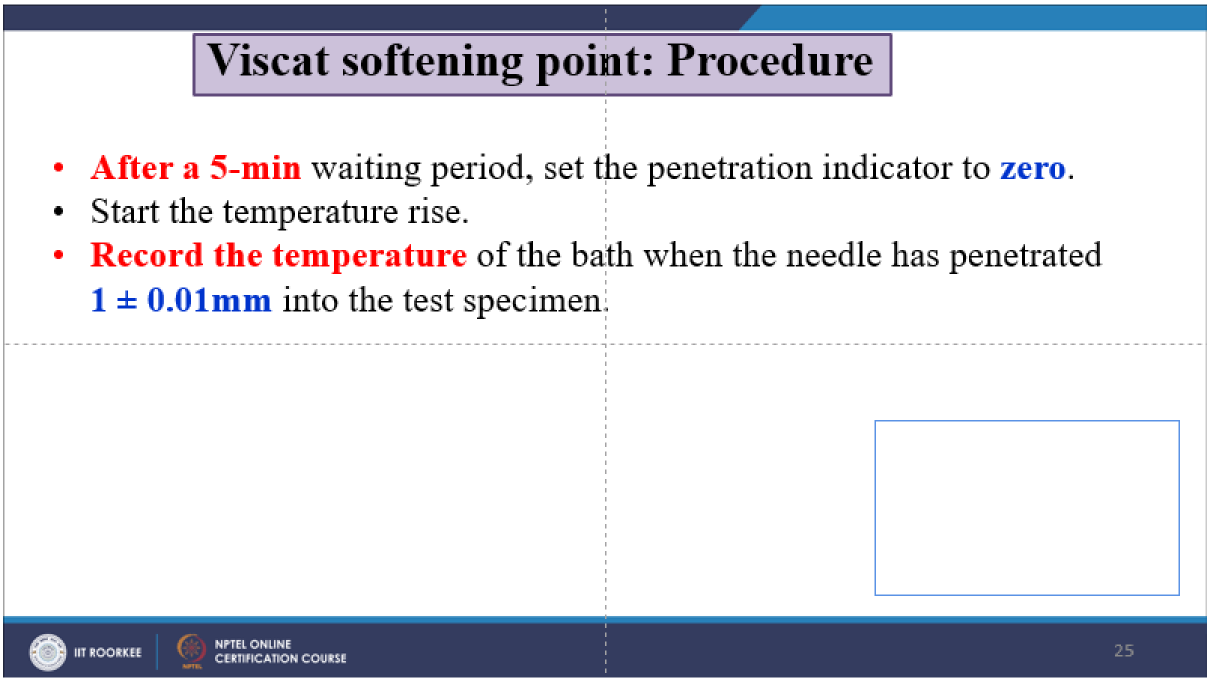
Viscat softening point: Procedure

- **Prepare the immersion bath** so that the temperature of the heat-transfer medium is **between 20 and 23°C** at the start of the test
- **Place the specimen**, which is at room temperature, on the specimen support.
- The needle should not be **nearer than 3mm** to the edge of the specimen.
- **Gently lower the needle rod**, without the extra mass, so that the needle rests on the surface of the specimen and holds it in position.



Viscat softening point: Procedure

- **Position the temperature-measuring device** so that the sensing end is located within **10mm** from where the load is applied to the surface of the specimen.
- **Lower the assembly** into the bath and apply the extra mass required to increase the load on the specimen to **10 ± 0.2N (Loading 1) or 50 ± 1.0N (Loading 2).**

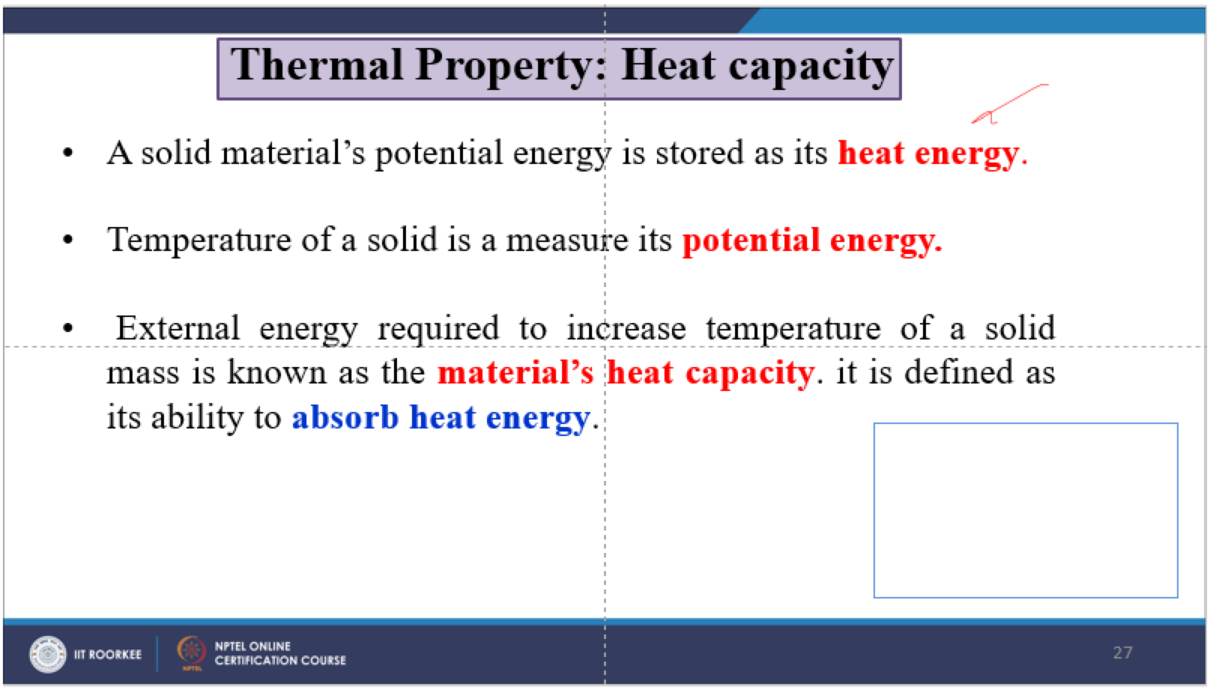


Viscat softening point: Procedure

- **After a 5-min** waiting period, set the penetration indicator to **zero**.
- Start the temperature rise.
- **Record the temperature** of the bath when the needle has penetrated **1 ± 0.01mm** into the test specimen.

So, what is the procedure? The procedure is first to prepare the immersion bath so that the temperature of the heat transfer media should be maintained between 20 and 23 degrees Celsius at the start of the test. Then the thing arises with respect to the place of the specimen which is at room temperature on the specimen support and needle should not be nearer than 3 mm to the edge of the specimen and you need to gently lower the needle rod here. This is a needle rod without the extra mass so that the needle rests on the surface of the specimen and holds it in position. Now position of the temperature measuring device usually needs to maintain a proper positioning so that the sensing end is located within 10 mm from where the load is applied to the surface of the specimen. Then lower the assembly into the bath, and apply the extra mass required to increase the load on the specimen.

So, to say 10 plus minus 0.2 Newton or 50 plus minus 1 Newton if we are performing the second loading. After 5 minutes waiting period set the penetration indicator to 0 and then start the temperature rise. Then gradually you need to record the temperature of the bath when the needle has penetrated 1 mm into the test specimen. So, this Vicut softening temperature is expressed as the arithmetic mean of the temperature of the penetration of all specimen tested. Now if the range of penetration temperature for the individual test exceeds 2 degrees Celsius record the individual result and repeat the test using at least 2 new specimens.



Thermal Property: Heat capacity

- A solid material's potential energy is stored as its **heat energy**.
- Temperature of a solid is a measure its **potential energy.**
- External energy required to increase temperature of a solid mass is known as the **material's heat capacity**. it is defined as its ability to **absorb heat energy**.

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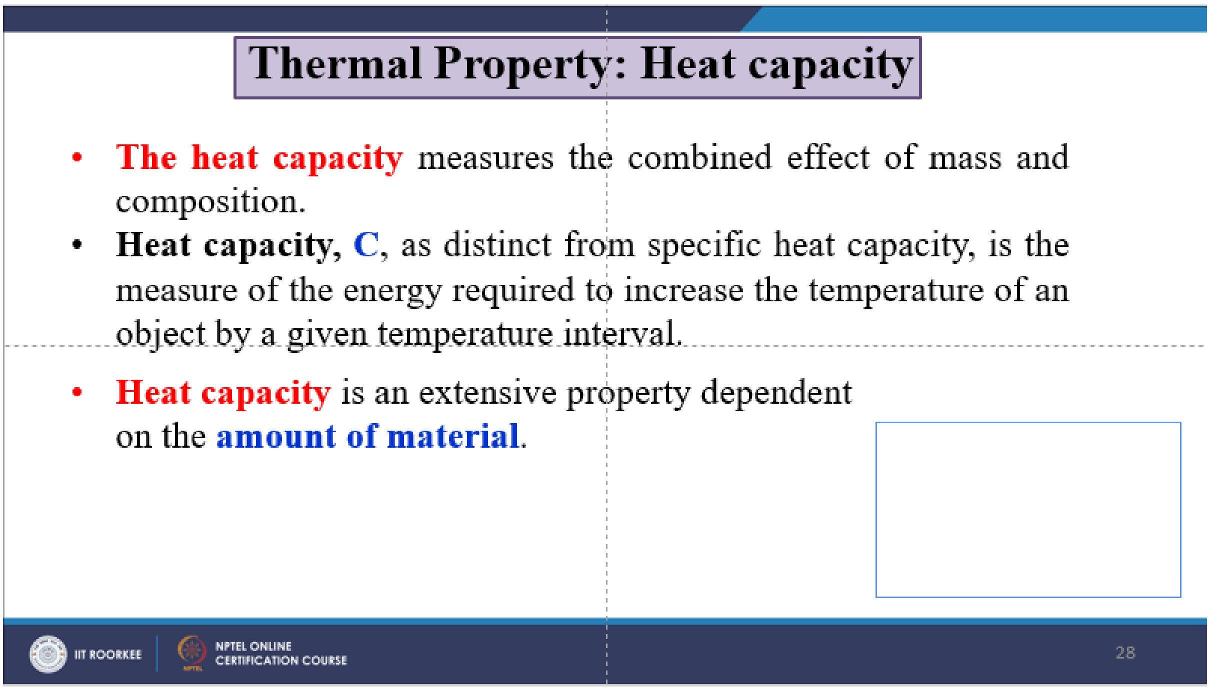
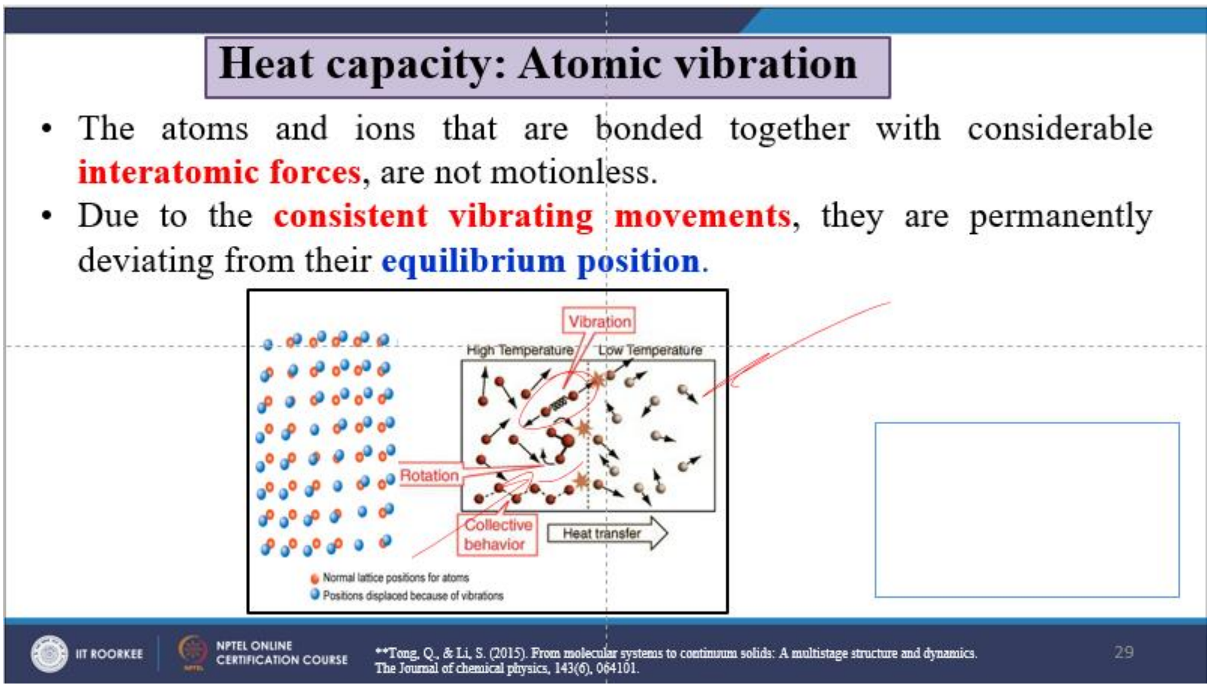
So, this particular thing is extremely important. Now let us talk about the heat capacity. Solid material's potential energy is stored in heat energy and the temperature of the solid is measured as its potential energy. So, the external energy required to increase the temperature of the solid mass is known as the material heat capacity and it is defined as its ability to absorb heat energy. So, the heat capacity measures the combined effect of mass and composition and usually it is denoted as C.



Thermal Property: Heat capacity

- **The heat capacity** measures the combined effect of mass and composition.
- **Heat capacity, C**, as distinct from specific heat capacity, is the measure of the energy required to increase the temperature of an object by a given temperature interval.
- **Heat capacity** is an extensive property dependent on the **amount of material**.

This is distinct from the specific heat capacity. This is measured by the energy required to increase the temperature of an object by a given temperature interval. Now, heat capacity is an extensive property depending on the amount of material. Now, let us talk about the atomic vibration. The atoms and ions that are bonded together with considerable inter-atomic forces are not motionless. Due to the consistent vibration movement they are permanently deviating from their equilibrium position.

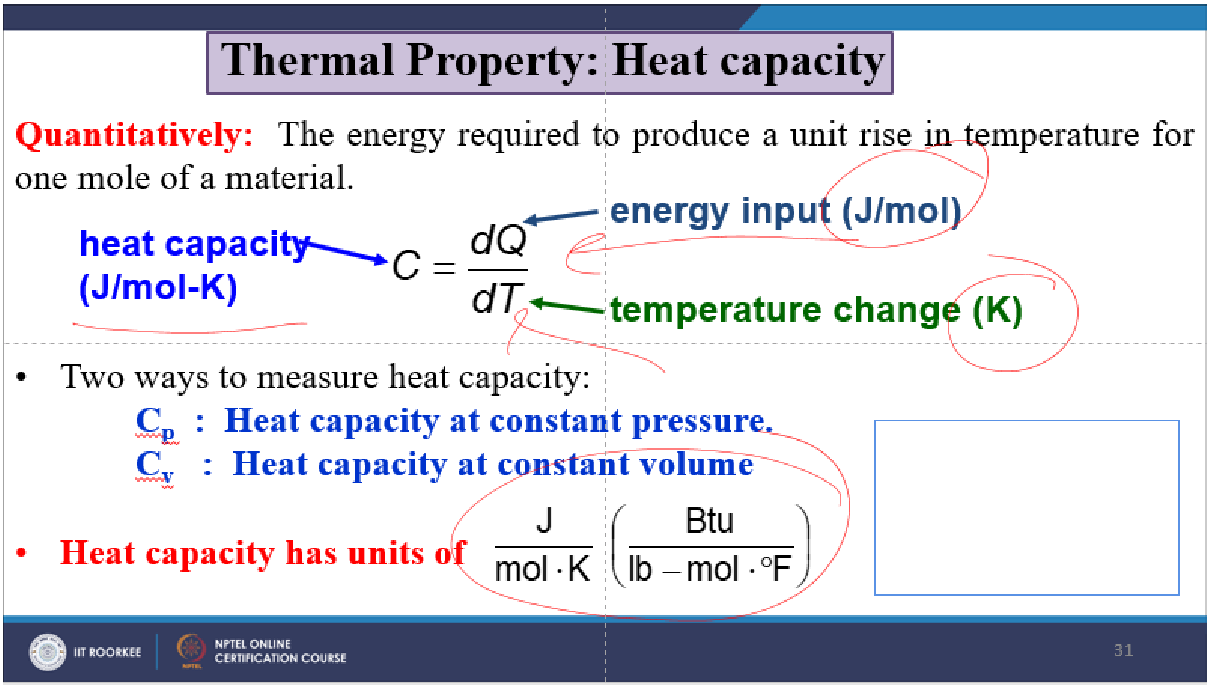


Heat capacity: Atomic vibration

- The atoms and ions that are bonded together with considerable **interatomic forces**, are not motionless.
- Due to the **consistent vibrating movements**, they are permanently deviating from their **equilibrium position**.

**Tong, Q., & Li, S. (2015). From molecular systems to continuum solids: A multistage structure and dynamics. The Journal of chemical physics, 143(6), 064101.

Now, here you see that these are the molecules in some of the rotations and collective behaviors. Now, atomic vibrations are in the form of lattice waves or phonons. Now, faster molecules shrink slower ones, the boundary in the elastic collision will increase the velocity of the slower ones and decrease the velocity of the faster ones. Transfer sometimes they need to transfer the energy from the higher temperature to the lower temperature region.



Thermal Property: Heat capacity

Quantitatively: The energy required to produce a unit rise in temperature for one mole of a material.

heat capacity (J/mol-K) → $C = \frac{dQ}{dT}$ ← **energy input (J/mol)**, **temperature change (K)**

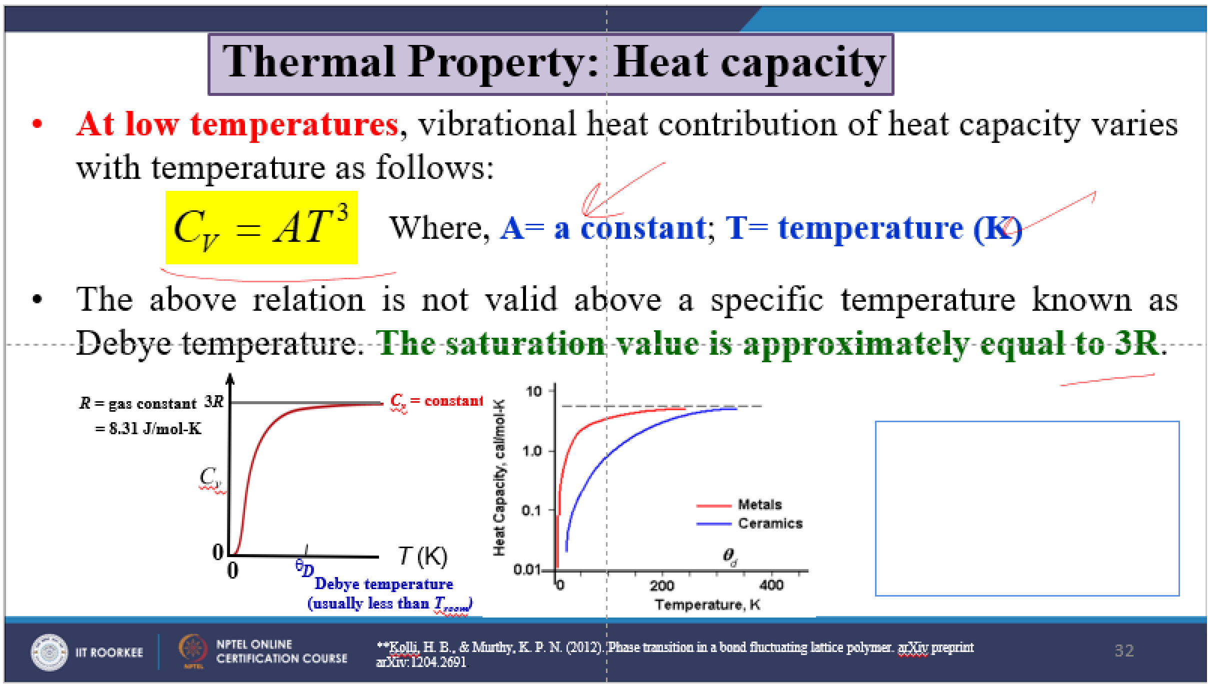
- Two ways to measure heat capacity:
  - **C_p : Heat capacity at constant pressure.**
  - **C_v : Heat capacity at constant volume**
- **Heat capacity has units of** $\frac{J}{mol \cdot K}$ $\left(\frac{Btu}{lb-mol \cdot °F}\right)$

$$C = \frac{dQ}{dT}$$

- **Heat capacity has units of**

$$\frac{J}{\mathrm{mol} \cdot K} \quad \left(\frac{\mathrm{Btu}}{\mathrm{lb} - \mathrm{mol} \cdot {}^{\circ}F}\right)$$

So, by this way the vibrations take place. Now if we talk about the things in quantitatively aspect the energy required to produce a unit rise in temperature for 1 mole of material. Now here you see that it is referred as or the units of this heat capacity is generally referred as joule per mole Kelvin. Now C is equal to dQ over dt where dQ is the energy input and T is the temperature change and usually they are denoted in Kelvin and joule per mole respectively. There are two ways to measure the heat capacity one is the heat capacity at constant pressure another one is that heat capacity at constant volume. So usually, this heat capacity is having the units of joule per mole Kelvin, BTU over ponce mole Fahrenheit.



Thermal Property: Heat capacity

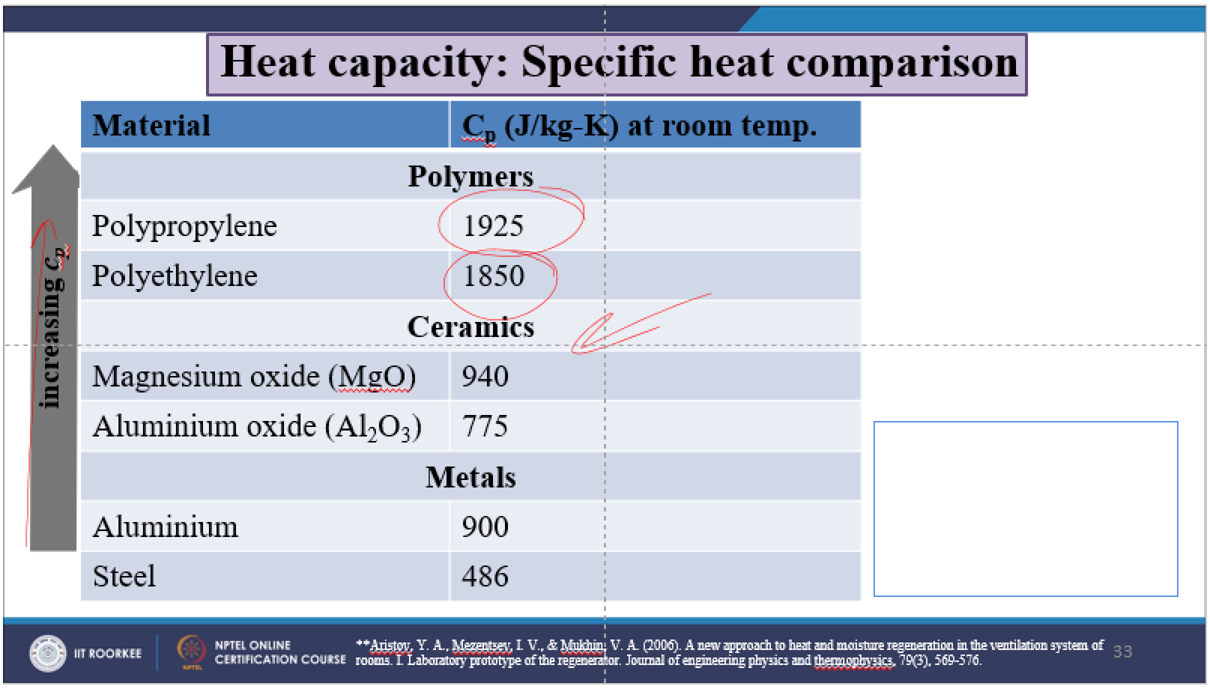
- **At low temperatures**, vibrational heat contribution of heat capacity varies with temperature as follows:

$$C_V = AT^3$$ Where, **A= a constant**; **T= temperature (K)**

- The above relation is not valid above a specific temperature known as Debye temperature. **The saturation value is approximately equal to 3R.**

**Kolli, H. B., & Murthy, K. P. N. (2012). Phase transition in a bond fluctuating lattice polymer. arXiv preprint arXiv:1204.2691

Now at low temperature the vibrational heat contribution of heat capacity varies with the temperature and usually it follows the CV is equal to AT cube where A is a constant and T is temperature which is denoted in Kelvin. So, this relation is not valid above a specified temperature known as Debye temperature and the saturation value is approximately equal to 3R. Now here you see that different materials having the specific heat capacities. So, this is a comparative chart where the material like polypropylene they are having the heat capacity at constant pressure that is 1925 joule per kilogram Kelvin at room temperature and polyethylene 1850. Now if we talk about the ceramic's magnesium oxide 940 and aluminium oxide 775 similarly the metal aluminium they are having 900 and steel 486.

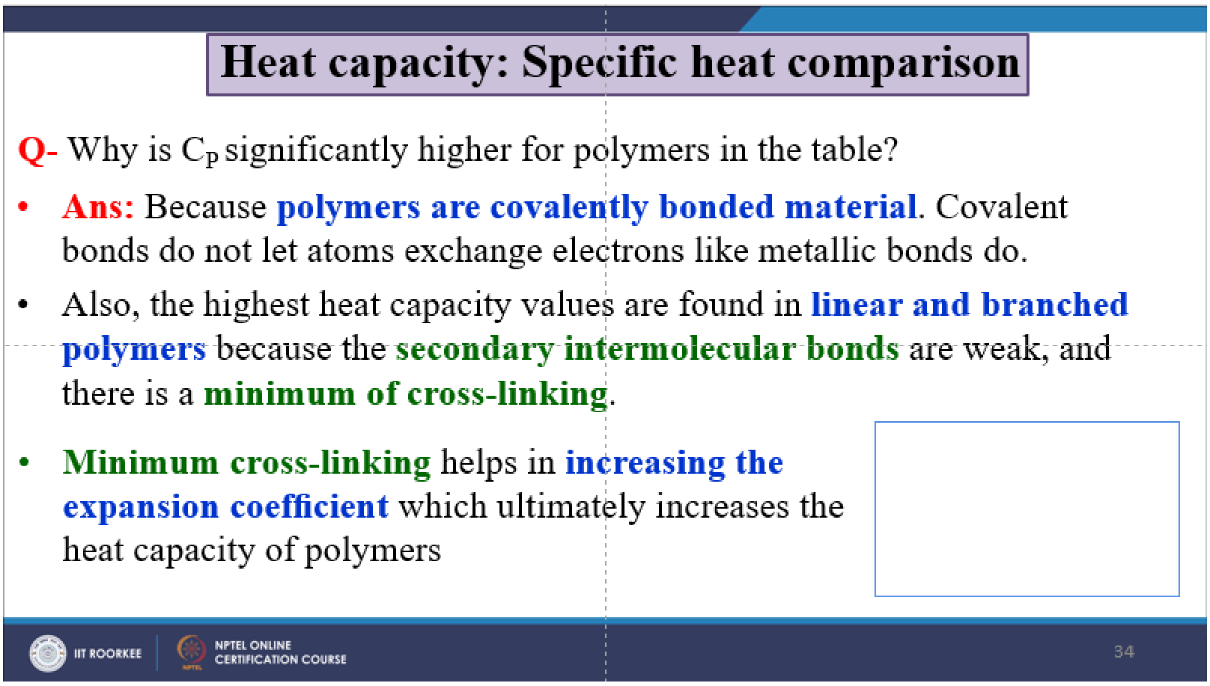


Heat capacity: Specific heat comparison

Material	C_p (J/kg-K) at room temp.
Polymers	
Polypropylene	1925
Polyethylene	1850
Ceramics	
Magnesium oxide (MgO)	940
Aluminium oxide (Al_2O_3)	775
Metals	
Aluminium	900
Steel	486

**Aristov, Y. A., Mezentsev, I. V., & Mukhin, V. A. (2006). A new approach to heat and moisture regeneration in the ventilation system of rooms. I. Laboratory prototype of the regenerator. Journal of engineering physics and thermophysics, 79(3), 569-576.

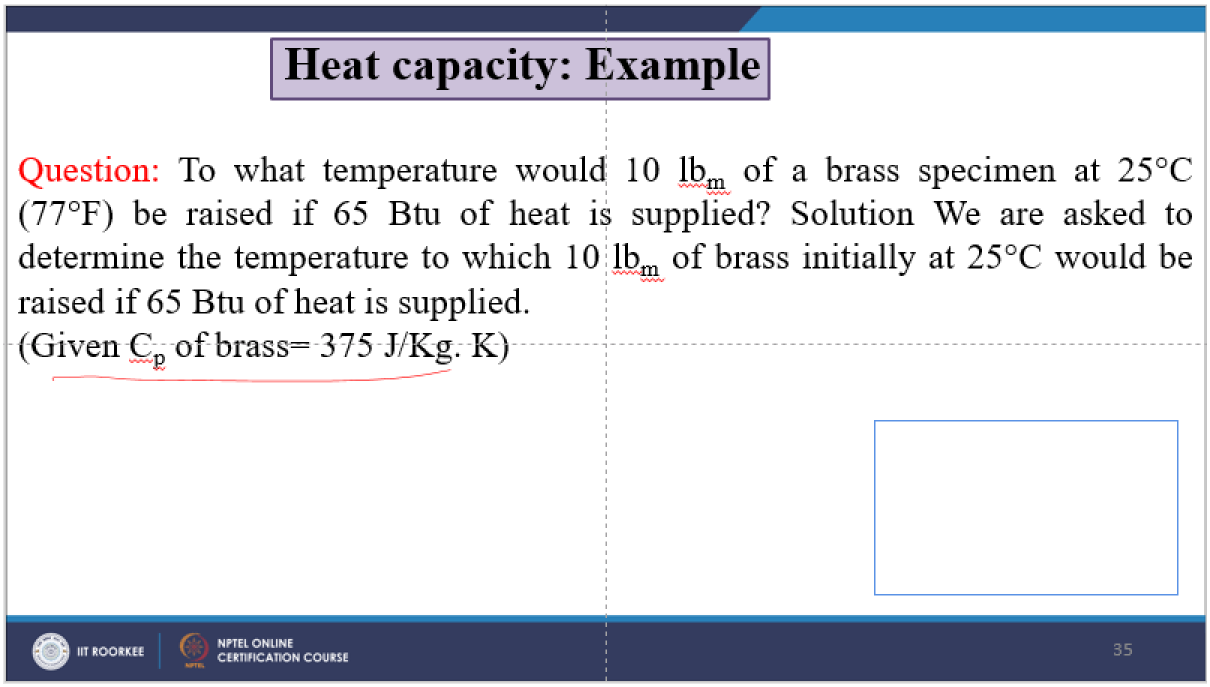
So, this is a respective heat capacity or C_P, and this is in the form of an increasing one. Now there may be certain questions may arise in your mind as to why this C_P is significantly higher for polymer in that particular table. The reason is that polymers are covalently bonded materials and covalent bonds do not let atoms exchange electrons like metallic bonds do. There are also the highest heat capacity values are found in linear and branched polymers because the secondary intermolecular bonds are weak and there is a minimum of crosslinking and minimum crosslink this minimum crosslinking helps in increasing the expansion coefficient which ultimately increases the heat capacity of polymers. Another question may arise, and let us take one numerical examination.



Heat capacity: Specific heat comparison

Q- Why is C_P significantly higher for polymers in the table?

- **Ans:** Because **polymers are covalently bonded material**. Covalent bonds do not let atoms exchange electrons like metallic bonds do.
- Also, the highest heat capacity values are found in **linear and branched polymers** because the **secondary intermolecular bonds** are weak, and there is a **minimum of cross-linking**.
- **Minimum cross-linking** helps in **increasing the expansion coefficient** which ultimately increases the heat capacity of polymers

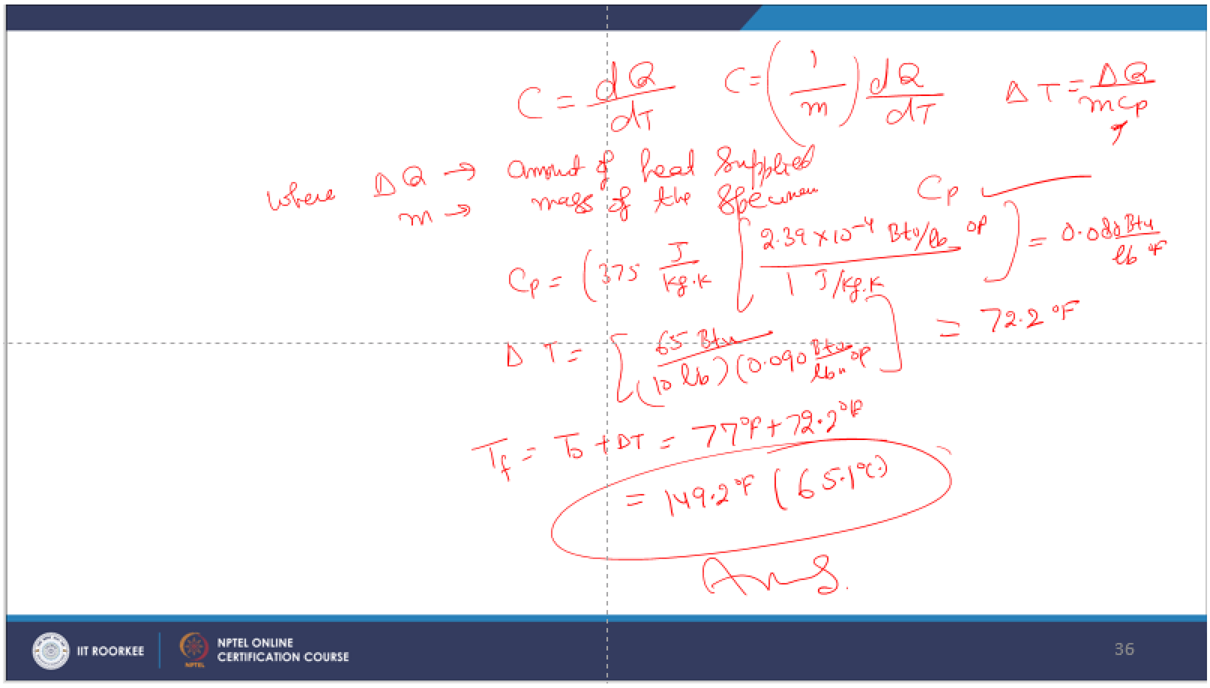


Heat capacity: Example

Question: To what temperature would 10 lb_m of a brass specimen at 25°C (77°F) be raised if 65 Btu of heat is supplied? Solution We are asked to determine the temperature to which 10 lb_m of brass initially at 25°C would be raised if 65 Btu of heat is supplied.
(Given C_p of brass= 375 J/Kg. K)

Now let us take a numerical question that to what temperature would 10 pound of a brass specimen at 25 degree Celsius be raised if 65 BTU, BTU stands for British thermal unit of heat is supplied. We asked to determine the temperature at which the 10 pound of brass initially at 25 degree Celsius would be raised to 65 BTU if heat supplied. Now this is given because ultimately you require the CP of the brass and which is given that 375 joule per kilogram Kelvin. So let us solve this particular problem.

Now this C is equal to dQ over dt where C is equal to 1 upon m dQ over dt and delta t is equal to delta Q over m CP.



$C = \frac{dQ}{dT}$ $C = \left(\frac{1}{m}\right)\frac{dQ}{dT}$ $\Delta T = \frac{\Delta Q}{m C_p}$

where $\Delta Q \rightarrow$ amount of heat supplied

$m \rightarrow$ mass of the specimen

$C_p = \left(375 \frac{J}{kg \cdot K}\right)\left[\frac{2.39 \times 10^{-4}\ Btu/lb\ ^\circ F}{1\ J/kg \cdot K}\right] = 0.088 \frac{Btu}{lb\ ^\circ F}$

$\Delta T = \left[\frac{65\ Btu}{(10\ lb)(0.090\ \frac{Btu}{lb\ ^\circ F})}\right] = 72.2\ ^\circ F$

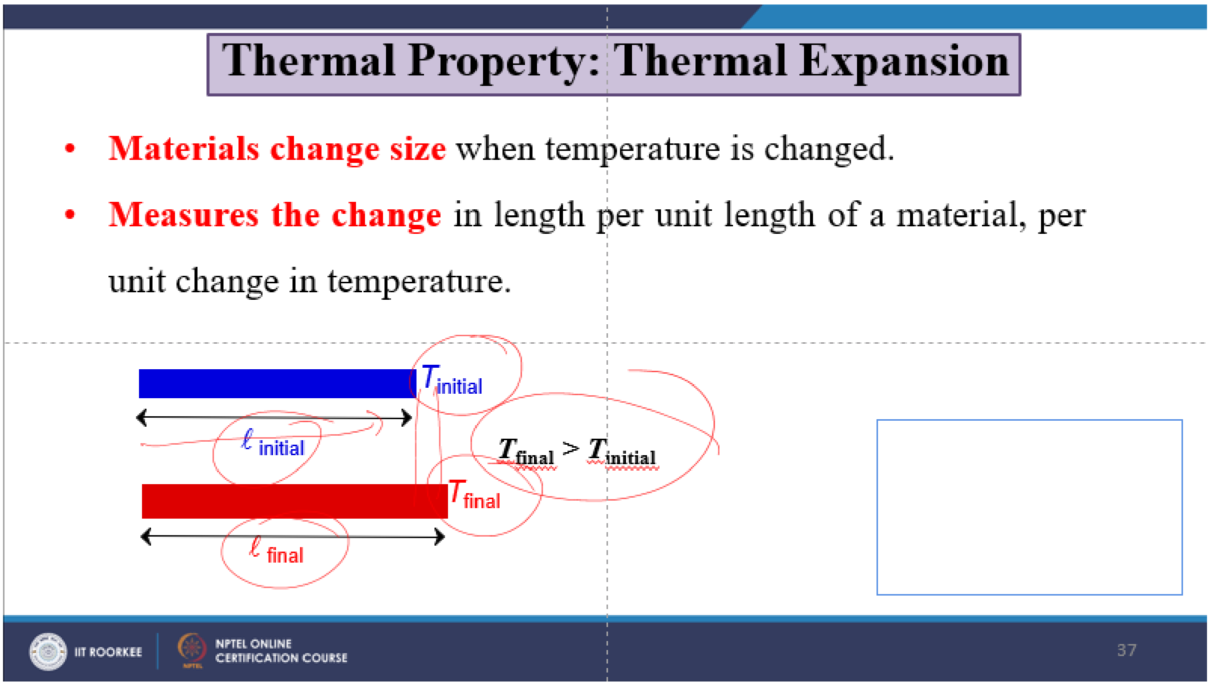
$T_f = T_0 + \Delta T = 77^\circ F + 72.2^\circ F$

$\boxed{= 149.2^\circ F\ (65.1^\circ C)}$

Ans.

Now this CP is given to you. Now this where delta Q is the amount of heat supplied and m is the mass of the specimen and CP is always given to you. So CP is equal to 375 joule per kilogram Kelvin 2.39 into 10 to the power minus 4 BTU upon and this comes out to be 0.080 BTU. Now delta t is equal to 65 BTU which is given in the problem and 10 pound into 0.

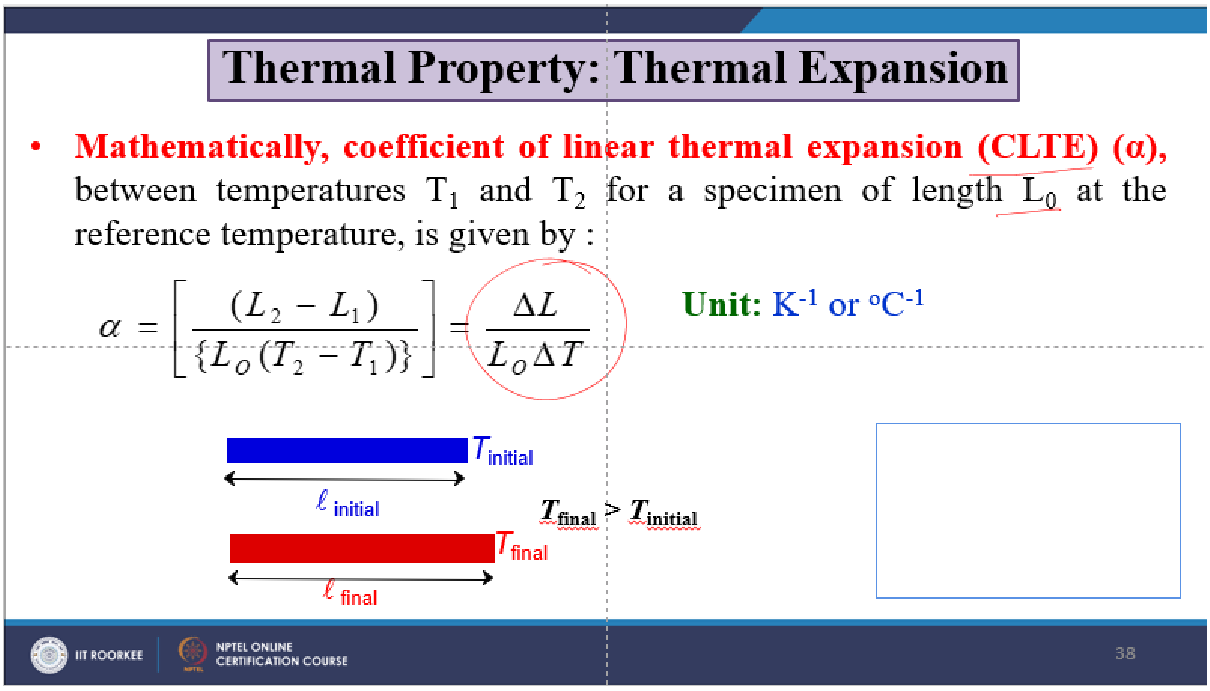
090 BTU which is 72.2 degree Fahrenheit. So t f is equal to initial plus delta t which is initially it is given that 77 degree Fahrenheit plus what we have calculated that is 72.2 degree Fahrenheit and which comes out to be 149.2 degree Fahrenheit and which is 65.1 degree Celsius and that is your desired answer. So, this is one of the example that how you can calculate the things.



Thermal Property: Thermal Expansion

- **Materials change size** when temperature is changed.
- **Measures the change** in length per unit length of a material, per unit change in temperature.

Now let us talk about the thermal expansion. Now usually material change in size when the temperature is changed and the measures the change in length per unit length of a material per unit change in the temperature. Now if you see that initially we are having a things at say specified temperature which is Ti. Now this is the initial length. Now if you raise the temperature to say T final then you may experience there is a change in the size. So this is the final length and this is initial length and obviously that the final temperature is greater than the initial temperature.



Thermal Property: Thermal Expansion

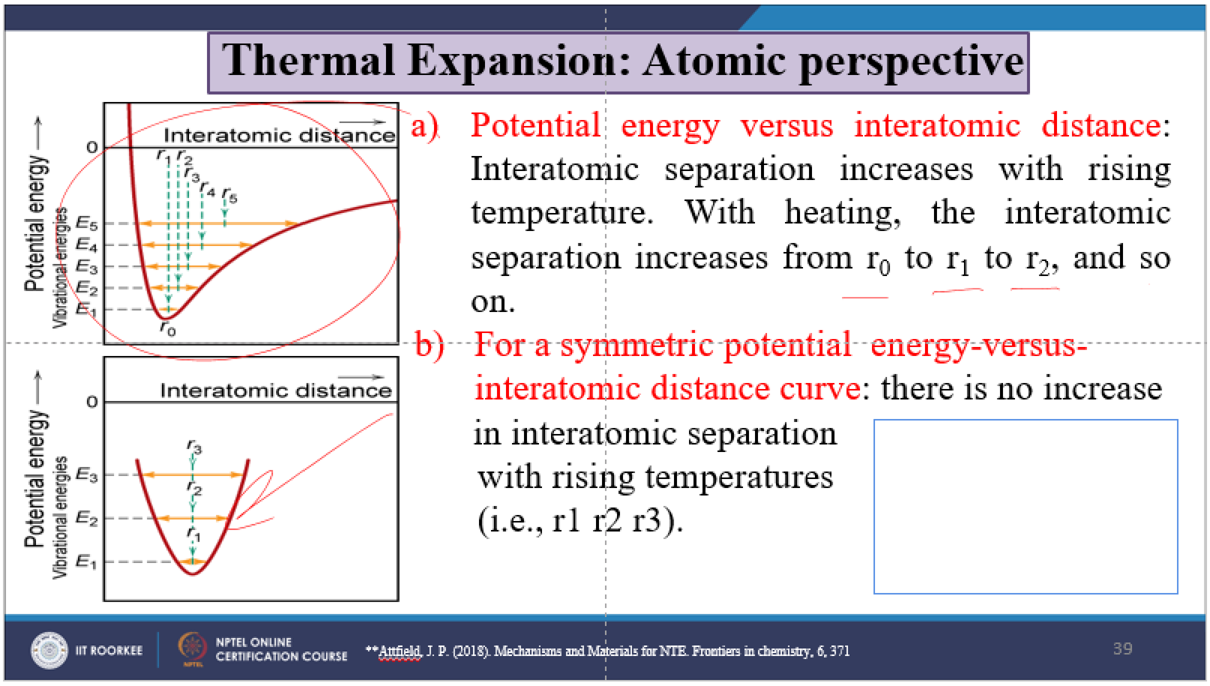
- **Mathematically, coefficient of linear thermal expansion (CLTE) (α),** between temperatures T_1 and T_2 for a specimen of length L_0 at the reference temperature, is given by :

$$\alpha = \left[\frac{(L_2 - L_1)}{\{L_O(T_2 - T_1)\}}\right] = \frac{\Delta L}{L_O \Delta T}$$

Unit: K^{-1} or $^oC^{-1}$

$$\alpha = \left[\frac{(L_2 - L_1)}{\{L_O(T_2 - T_1)\}}\right] = \frac{\Delta L}{L_O \Delta T}$$

So mathematically if we talk about the things then the coefficient of a linear thermal expansion and this is referred as C l t e alpha this is between the temperature initial temperature and the final temperature for a specimen of length say L naught at the reference temperature. Usually it is given by alpha is equal to L 2 this is the final length minus initial length upon original length into T 2 minus T 1. So, delta L over L naught into delta T, and usually, it is represented as the Kelvin inverse or degree Celsius inverse. So, what is the atomic perspective of this thermal expansion? So, the potential energy versus inter-atomic distances. So, the inter-atomic separation increases with the rise in the temperature while heating the inter-atomic separation increases from R naught to R 1 and R 2 so on.



Thermal Expansion: Atomic perspective

a) Potential energy versus interatomic distance: Interatomic separation increases with rising temperature. With heating, the interatomic separation increases from r_0 to r_1 to r_2, and so on.

b) For a symmetric potential energy-versus-interatomic distance curve: there is no increase in interatomic separation with rising temperatures (i.e., r1 r2 r3).

**Attfield, J. P. (2018). Mechanisms and Materials for NTE. Frontiers in chemistry, 6, 371

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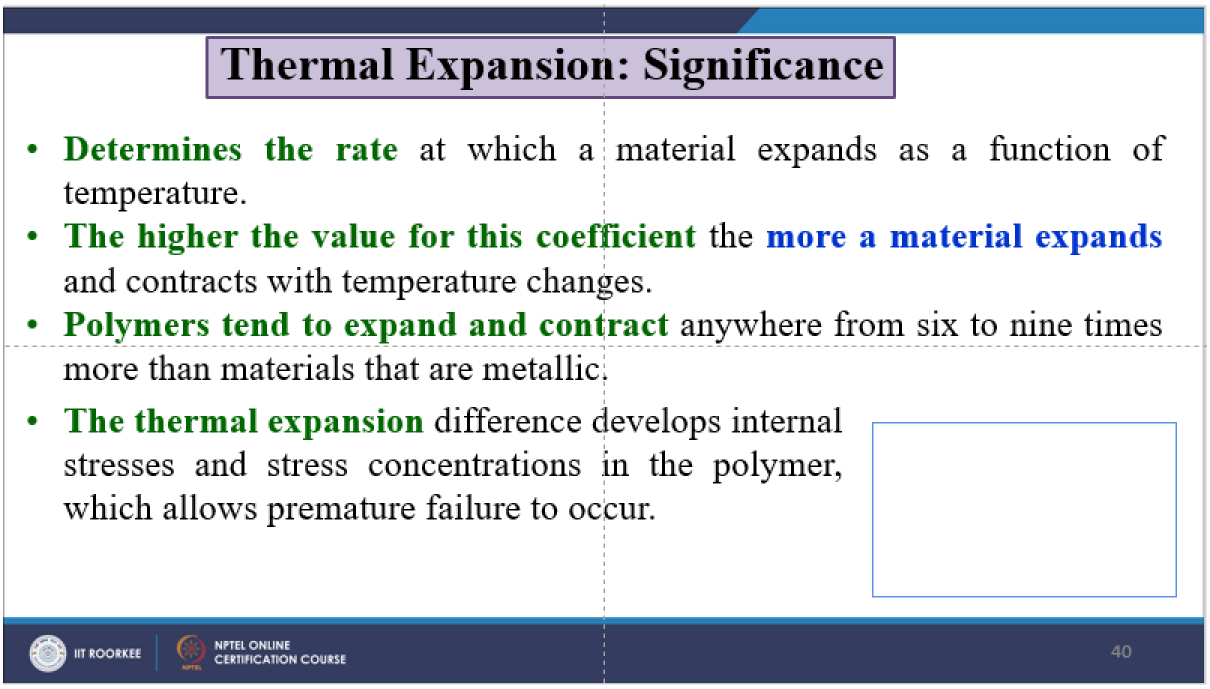
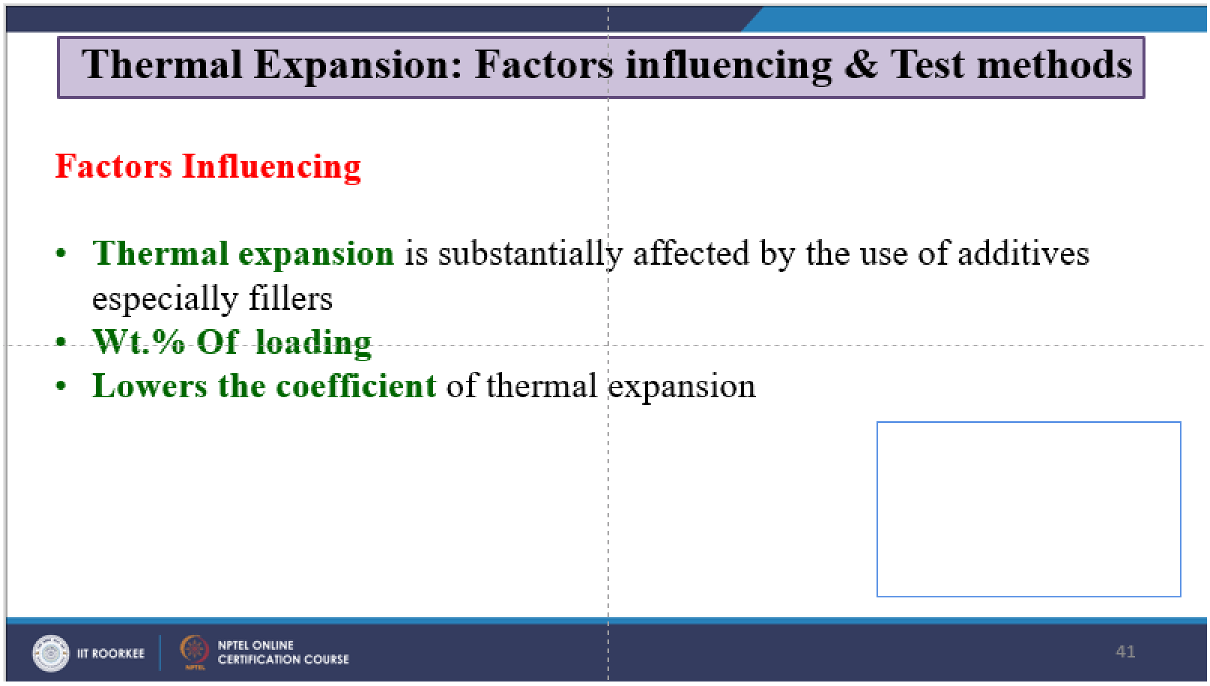
So here this is you can see with respect to the potential energy. Now for the symmetric potential energy versus inter atomic distance cover there is no increase you see that there is no increase in the inter atomic separation with rising the temperature. Now what is the significance of this thermal expansion? This determines the rate at which the material expands as a function of a temperature and higher the value of this coefficient the more the material expands and contracts with the temperature change. So, this is extremely important because during the polymer processing the polymer experiences a lot of thermal stress because sometimes at a room temperature to the higher temperature of say 100 degree Celsius and then cooling down. So, all these things and that is why this thermal expansion properties evaluation of this thermal expansion properties is extremely important.



Thermal Expansion: Significance

- **Determines the rate** at which a material expands as a function of temperature.
- **The higher the value for this coefficient** the **more a material expands** and contracts with temperature changes.
- **Polymers tend to expand and contract** anywhere from six to nine times more than materials that are metallic.
- **The thermal expansion** difference develops internal stresses and stress concentrations in the polymer, which allows premature failure to occur.

Now this polymer tends to expand and contract anywhere from the 6 to 9 times more than the material that are metallic. Now if you talk about the commodity plastic then if you experience there are some reason in India where the temperature varies from 2 degree Celsius to 47 degree Celsius in that case you need to evaluate and you need to prefix all these aspect before carry out any kind of the processing of two utility product. Now, the thermal expansion differences develop internal stresses and stress concentration in the polymer, which allows the premature failure to occur. Now there are various factors influencing and we will discuss about various test methods.



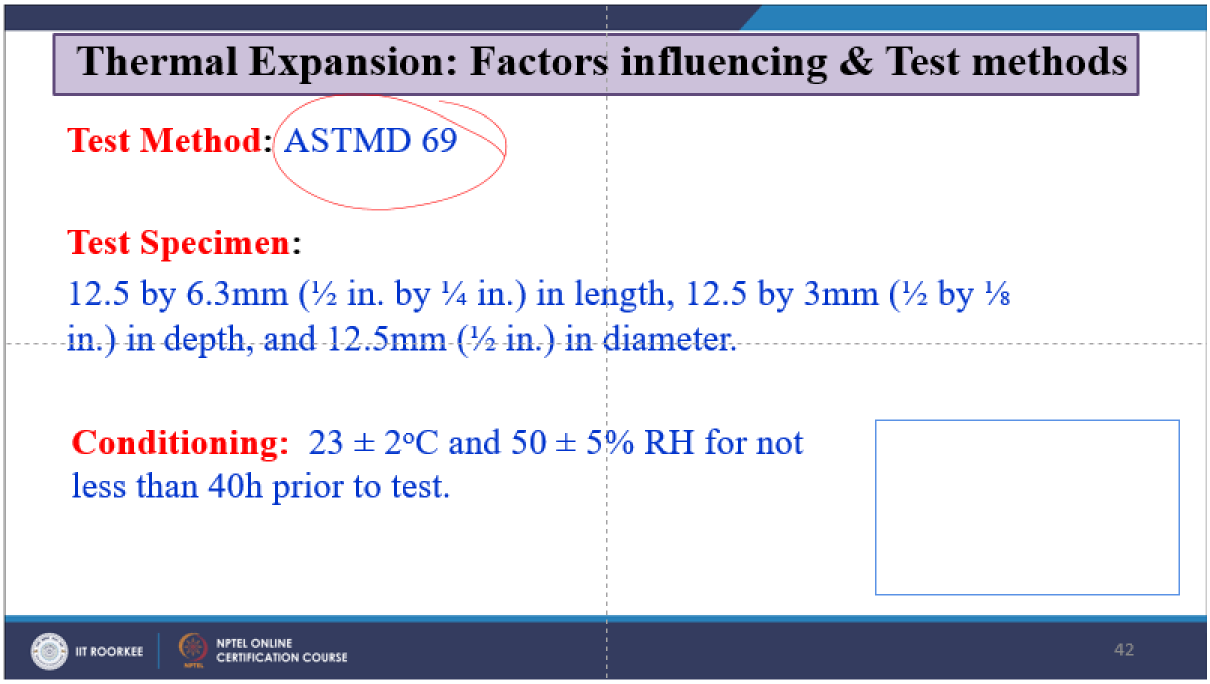
Thermal Expansion: Factors influencing & Test methods

Factors Influencing

- **Thermal expansion** is substantially affected by the use of additives especially fillers
- **Wt.% Of loading**
- **Lowers the coefficient** of thermal expansion

The factor influencing the thermal expansion is substantially affected by the use of additives especially fillers because during the processing of the polymeric product you need to add certain additives, fillers, dyes, chemicals all these things and these play a very vital role.

The weight percent of the loading is again very crucial for evaluating this thermal expansion and lowers the coefficient of thermal expansion which is attributed to the weight percent of the loading. Usually the test method applied is ASTM the 69 and test specimen is usually 12.



Thermal Expansion: Factors influencing & Test methods

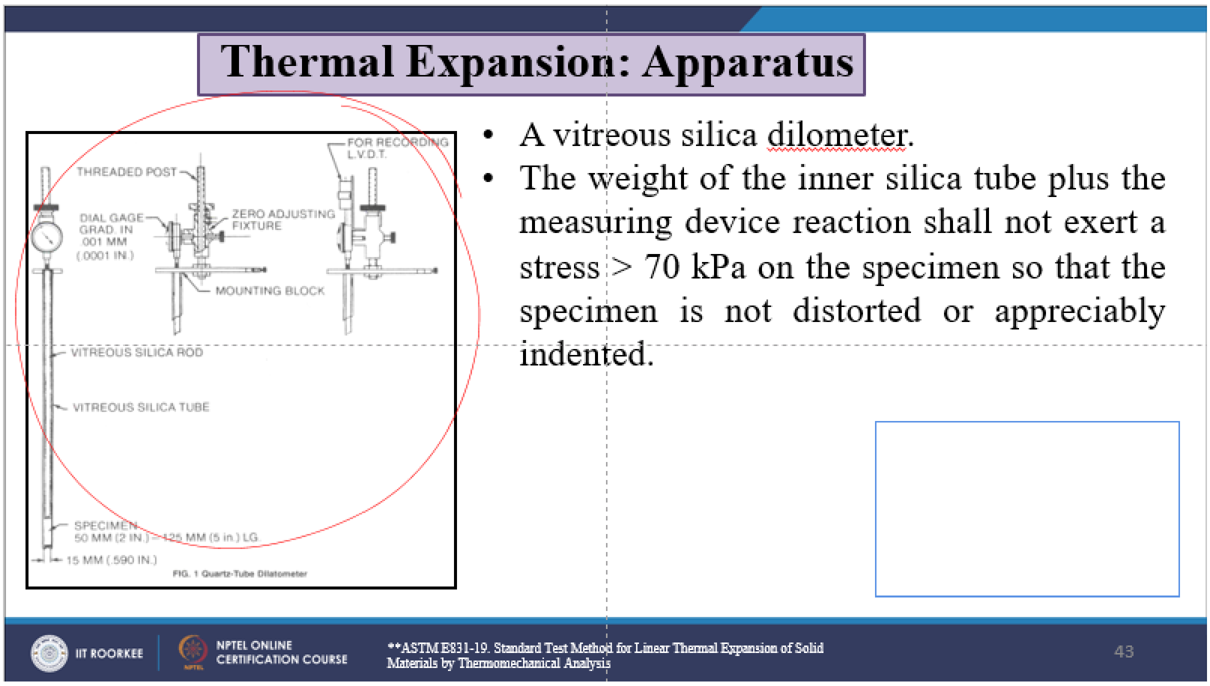
Test Method: ASTMD 69

Test Specimen:

12.5 by 6.3mm (½ in. by ¼ in.) in length, 12.5 by 3mm (½ by ⅛ in.) in depth, and 12.5mm (½ in.) in diameter.

Conditioning: 23 ± 2°C and 50 ± 5% RH for not less than 40h prior to test.

5 into 6.3 mm in length and 12.5 into 3 mm in depth and 12.5 mm in diameter. You need to carry out the conditioning which is around carried out at around 23 degree Celsius with the relative humidity of 50 percent and usually it should not be less than 40 hour prior to the test. Now this is the apparatus being used for evaluation of the thermal expansion. It is a vitreous silica dilometer. The weight of the inner silica tube plus the measuring device reaction it should not exert more than 70 kilo Pascal on the specimen so that the specimen is not distorted or appreciably intended.



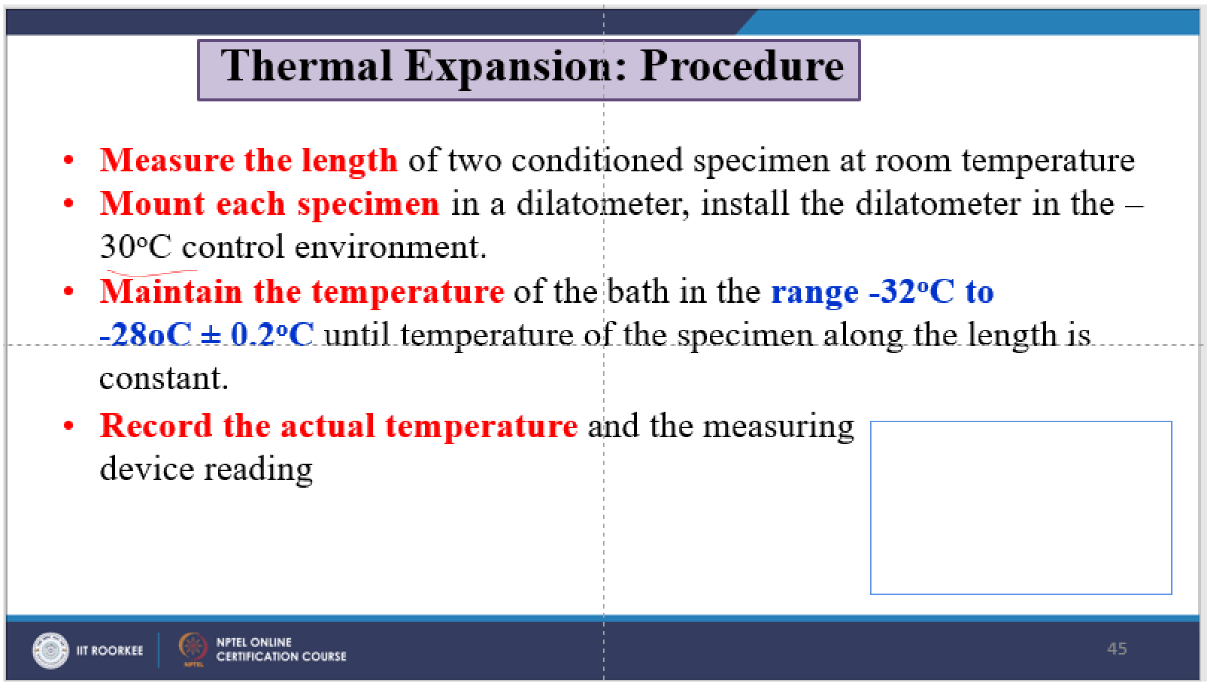
Thermal Expansion: Apparatus

FIG. 1 Quartz-Tube Dilatometer

- A vitreous silica dilometer.
- The weight of the inner silica tube plus the measuring device reaction shall not exert a stress > 70 kPa on the specimen so that the specimen is not distorted or appreciably indented.

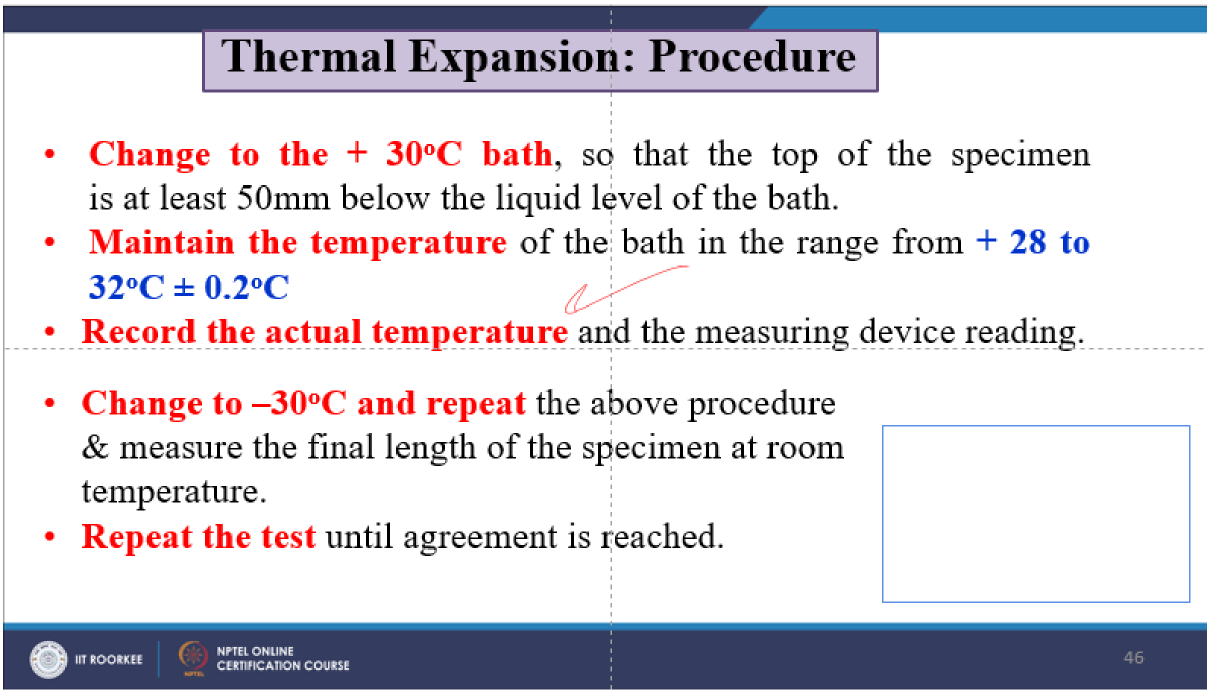
**ASTM E831-19. Standard Test Method for Linear Thermal Expansion of Solid Materials by Thermomechanical Analysis

Now the control you must possess the control temperature environment and scale or caliper must be there and dial gauge here you see that this is the dial gauge and this means shall provide the stirring of the bath and thermometer or thermocouple. Now what is the procedure? The procedure is that the first you measure the length of a two-condition specimen at room temperature, mount each specimen in a dilatometer, install the dilatometer in the 30-degree Celsius controlled environment and you must maintain the temperature in the bath in the range of minus 32 degree Celsius to 28 degree Celsius until the temperature of the specimen along the length is constant. Then you need to record the actual temperature and the measuring device reading. Now change to the plus 30 degree Celsius so that the top of the specimen is at least 50 mm below the liquid level of the bath. Then you need to maintain the temperature of the bath in the range of 28 to 32 degree Celsius and then you need to record the actual temperature.



Thermal Expansion: Procedure

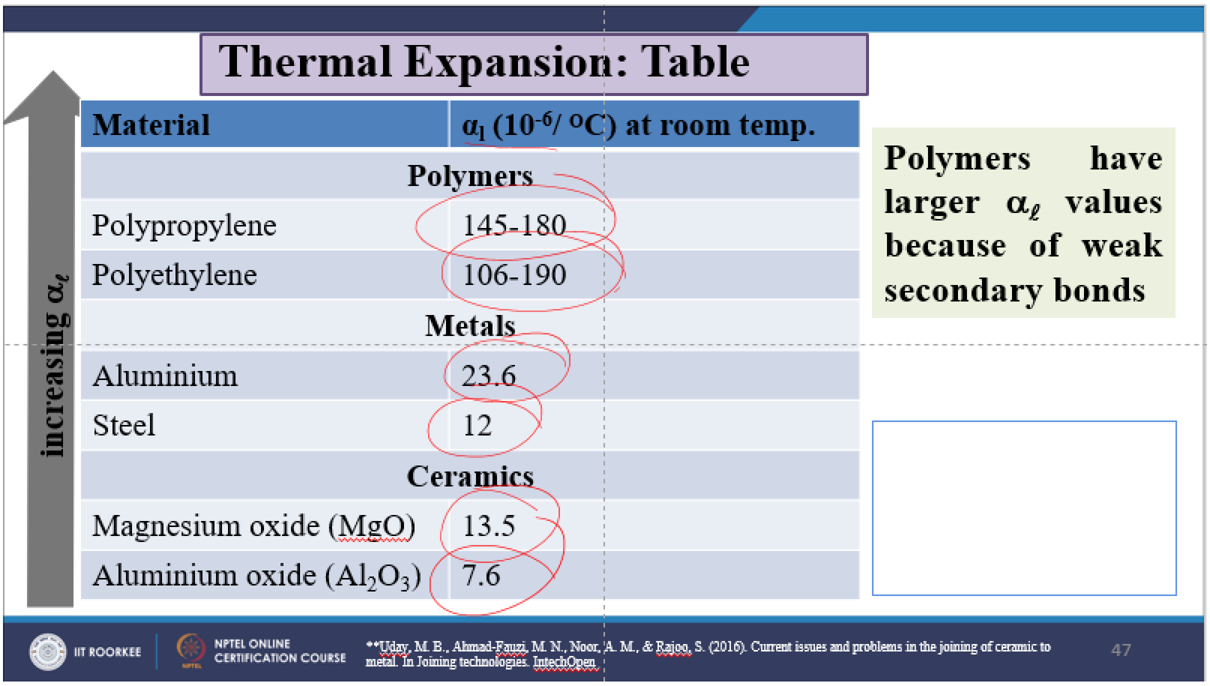
- **Measure the length** of two conditioned specimen at room temperature
- **Mount each specimen** in a dilatometer, install the dilatometer in the – 30°C control environment.
- **Maintain the temperature** of the bath in the **range -32°C to -28oC ± 0.2°C** until temperature of the specimen along the length is constant.
- **Record the actual temperature** and the measuring device reading



Thermal Expansion: Procedure

- **Change to the + 30°C bath**, so that the top of the specimen is at least 50mm below the liquid level of the bath.
- **Maintain the temperature** of the bath in the range from **+ 28 to 32°C ± 0.2°C**
- **Record the actual temperature** and the measuring device reading.
- **Change to –30°C and repeat** the above procedure & measure the final length of the specimen at room temperature.
- **Repeat the test** until agreement is reached.

So the change to minus 30 degree Celsius and repeat this above procedure because you see that from minus 32 you are carrying out the term to minus 32 to plus 32 degree Celsius. So by this there is a lot of variation in the temperature. Then you need to repeat the test until usually the two values are close to each other. Now here you see that the thermal expansion of the various materials in question usually represented by alpha. Now this polypropylene this is having 145 to 180 into 10 to the power minus 6 Celsius inverse then polyethylene 106 to 190, aluminum 23.



Thermal Expansion: Table

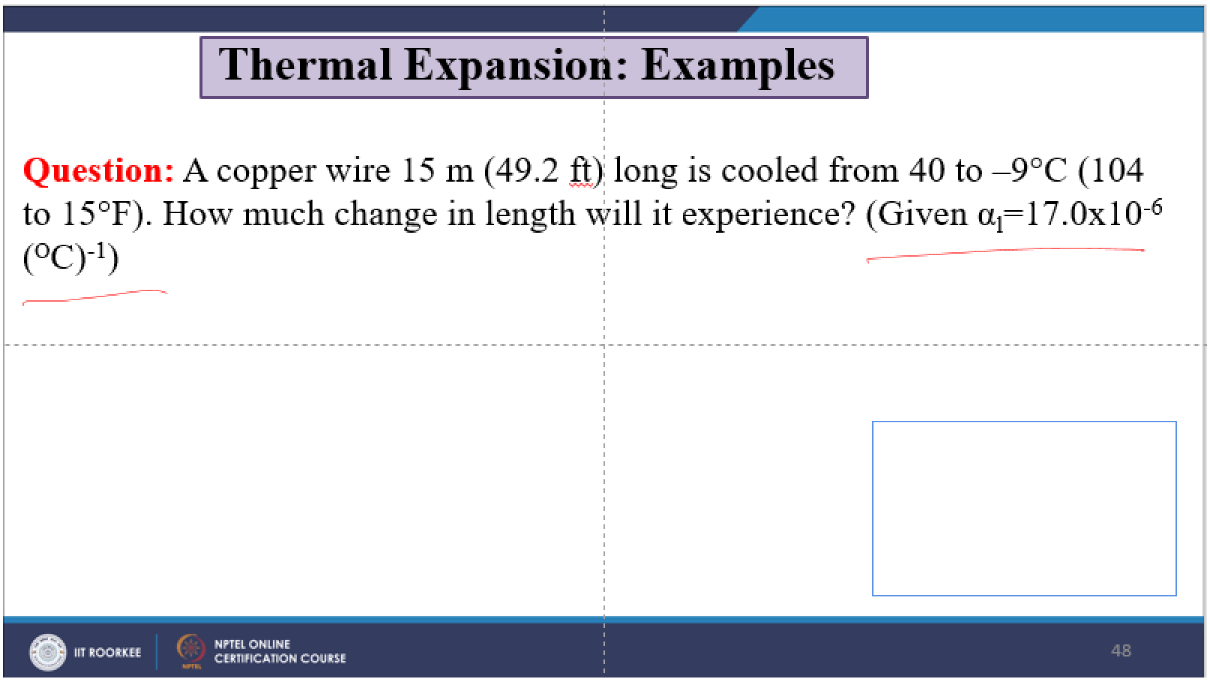
increasing α_ℓ

Material	α_l (10^{-6}/ °C) at room temp.
Polymers	
Polypropylene	145-180
Polyethylene	106-190
Metals	
Aluminium	23.6
Steel	12
Ceramics	
Magnesium oxide (MgO)	13.5
Aluminium oxide (Al_2O_3)	7.6

Polymers have larger α_ℓ values because of weak secondary bonds

**Uday, M. B., Ahmad-Fauzi, M. N., Noor, A. M., & Rajoo, S. (2016). Current issues and problems in the joining of ceramic to metal. In Joining technologies. IntechOpen.

6. So you see that the polymer possesses the higher degree of thermal expansion. Then steel 12 and magnesium oxide 13.5 and aluminum oxide 7.6. Now the polymer have a larger this thermal expansion values because of the weak secondary bonds.



Thermal Expansion: Examples

Question: A copper wire 15 m (49.2 ft) long is cooled from 40 to –9°C (104 to 15°F). How much change in length will it experience? (Given $\alpha_l = 17.0 \times 10^{-6}$ $(^{o}C)^{-1}$)

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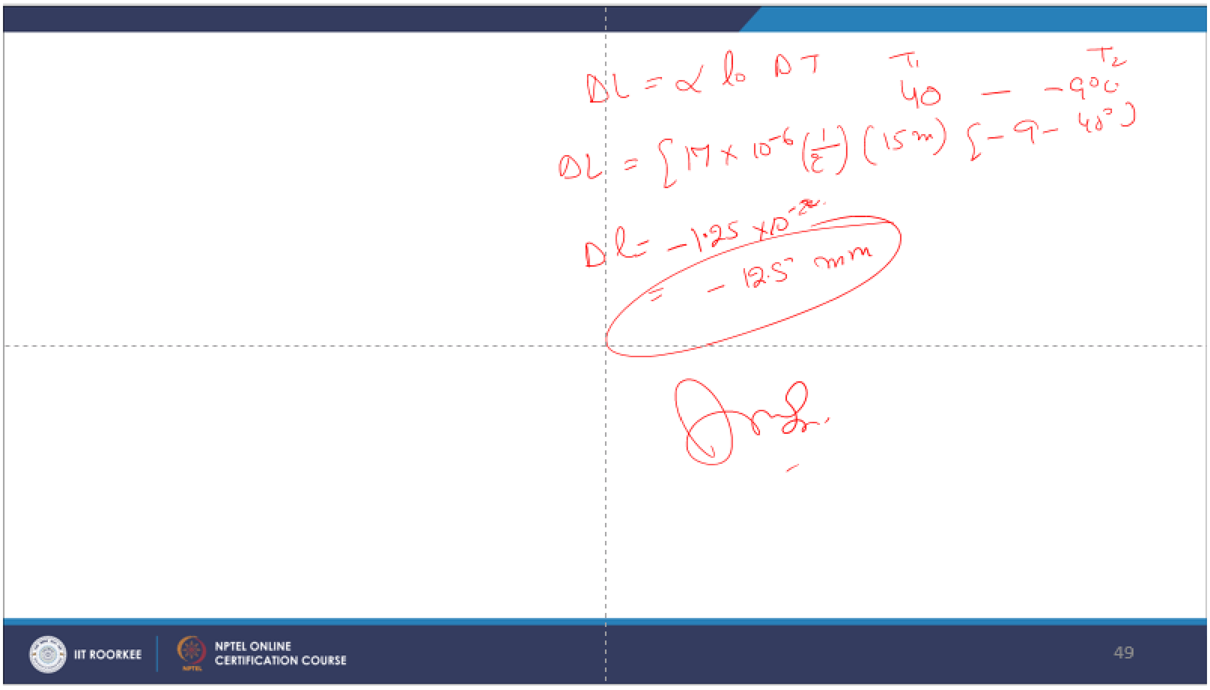
Now let us take up another example and this example is that a copper wire of 15 meter long is cooled from say 40 to minus 9 degree Celsius and how much change in the length will experience. Obviously, you require the thermal expansion coefficient which is given that 17 into 10 to the power minus 6 degree Celsius inverse. Let us use the formula delta L is equal to alpha L naught, L naught is the initial length of the copper wire which is 15 meter and delta T. Now here you see that we are changing the temperature from 40 to minus 9 degree Celsius. So delta L is equal to 17 into 10 to the power minus 6 this is the alpha and length is initial length is 15 meter and temperature change in this is T 2 and this is T 1.



$\Delta L = \alpha\, l_0\, \Delta T$ $\quad \overset{T_1}{40} \; — \; \overset{T_2}{-9°C}$

$\Delta L = \{17 \times 10^{-6} (\frac{1}{°C})\} (15\,m) \{-9 - 40°\}$

$\Delta l = -1.25 \times 10^{-2}$

$\boxed{= -12.5 \text{ mm}}$

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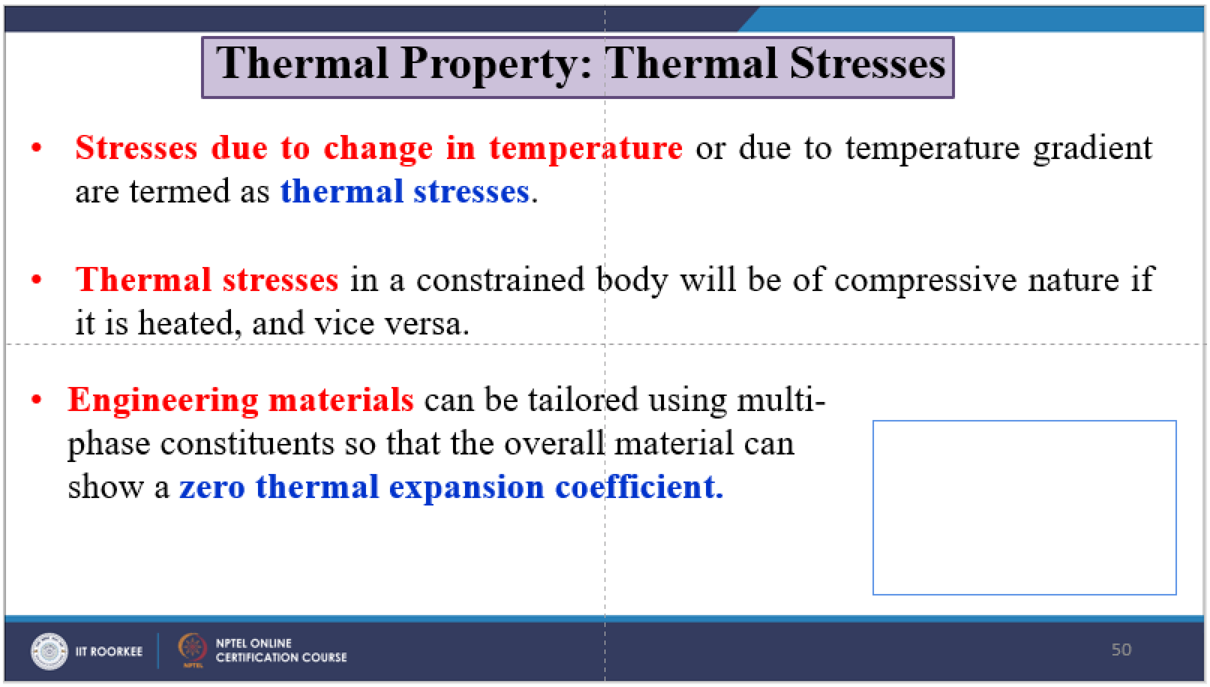
So minus 9 to 40 degree Celsius. So delta L comes out to be minus 1.25 into 10 to the power then it is comes out to be minus 12.5 mm this is the answer. Let us talk about the thermal stress. This stress due to the change in temperature or due to temperature gradient this is termed as a thermal stress.

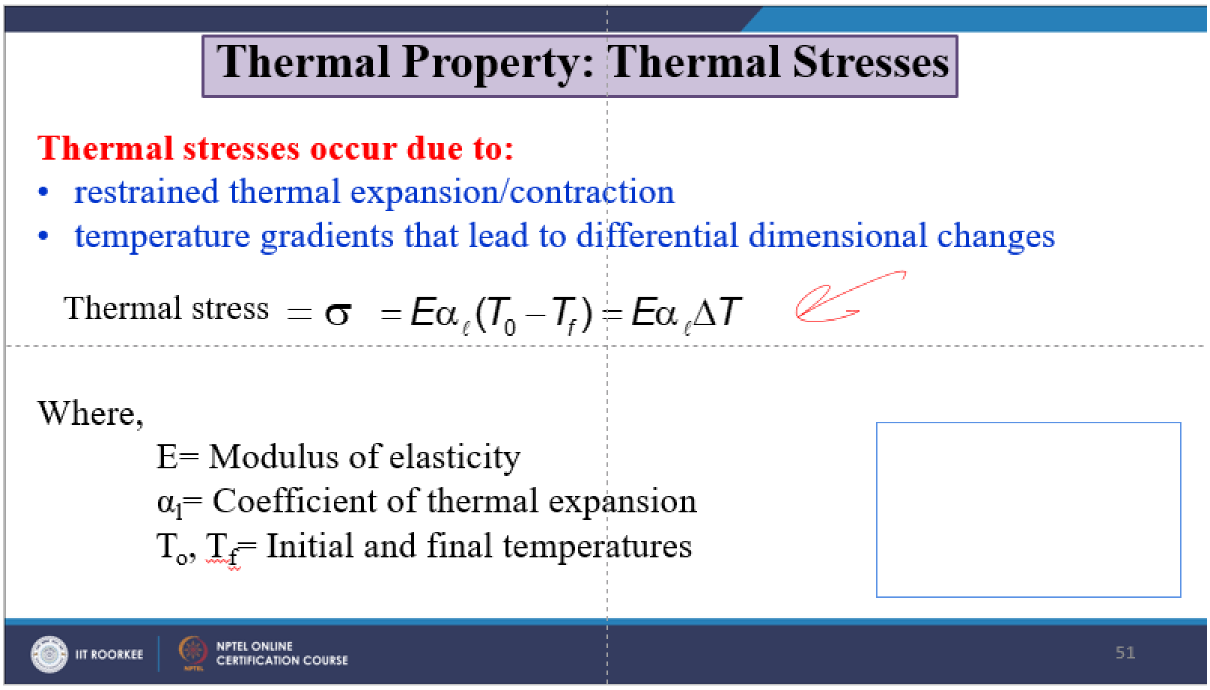
Now thermal stress is constrained body, and this will be a compressive nature if it is heated or it is in vice versa.



Thermal Property: Thermal Stresses

- **Stresses due to change in temperature** or due to temperature gradient are termed as **thermal stresses**.
- **Thermal stresses** in a constrained body will be of compressive nature if it is heated, and vice versa.
- **Engineering materials** can be tailored using multi-phase constituents so that the overall material can show a **zero thermal expansion coefficient.**

Engineering materials we talked about various engineering materials in different lectures. The engineering materials can be tailored using the multi-phase constituents so that the overall material can show a zero thermal expansion effect. Now this thermal stress is attributed to the restrained thermal expansion or contraction. The temperature gradient that lead to differential dimensional changes and this thermal stress is represented this particular by this particular mathematical relation where E is the modulus of elasticity alpha is the coefficient of thermal expansion we talked about in previous slides and T naught and T is the initial and final temperature.



Thermal Property: Thermal Stresses

Thermal stresses occur due to:

- restrained thermal expansion/contraction
- temperature gradients that lead to differential dimensional changes

Thermal stress $= \sigma = E\alpha_\ell (T_0 - T_f) = E\alpha_\ell \Delta T$

Where,

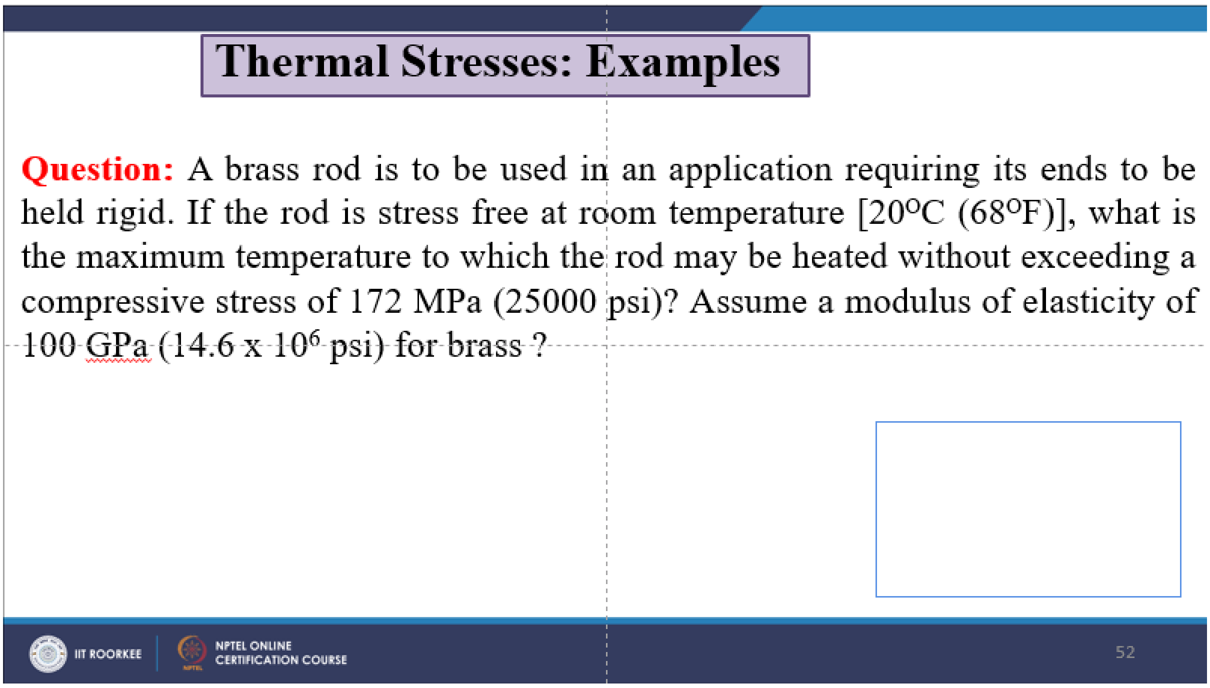
E= Modulus of elasticity

α_l= Coefficient of thermal expansion

T_o, T_f= Initial and final temperatures

$$= E\alpha_\ell (T_0 - T_f) = E\alpha_\ell \Delta T$$

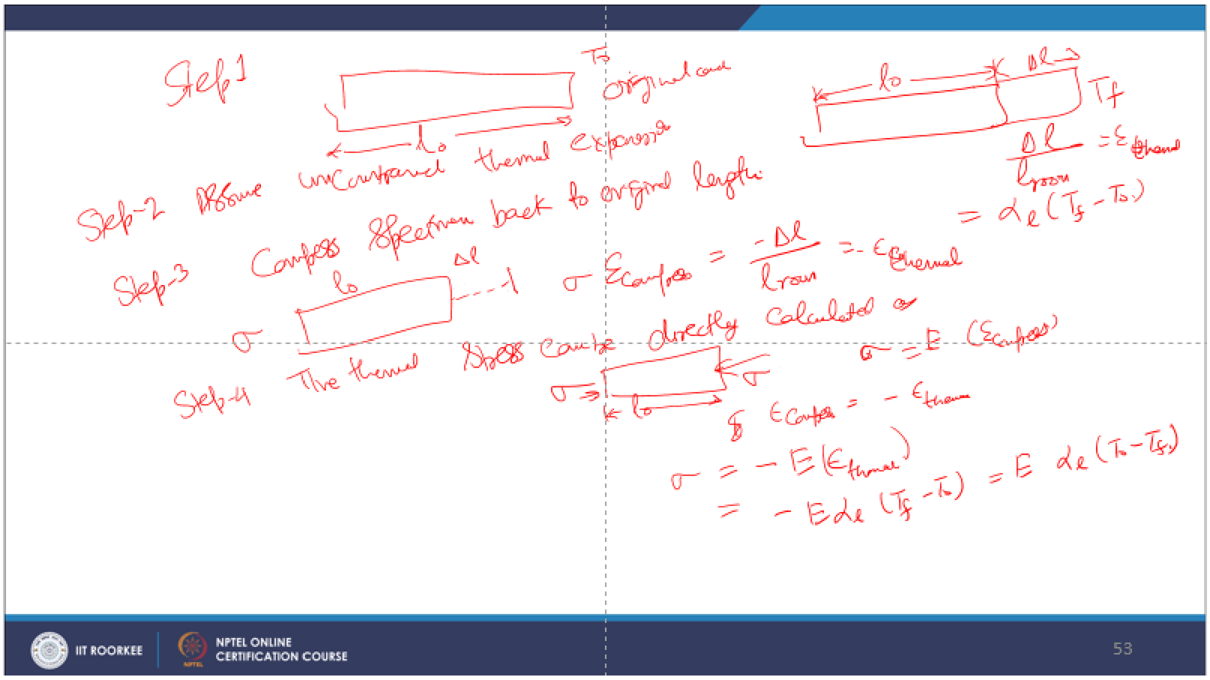
So, delta T you can easily calculate. Now let us take another example a brass rod is to be used in an application requiring and to be held rigid. Now if the rod is stress free at room temperature which is maintained at say 20 degree Celsius what is the maximum temperature to which the rod may be heated without exceeding a compressive stress of 172 mega Pascal. Now you need to assume certain things and you need to assume the modulus of elasticity is 100 GPa for brass. Now let us take up this example. Let us step 1 now this is your original condition where this is at maintenance T naught and initial length is L naught.



Thermal Stresses: Examples

Question: A brass rod is to be used in an application requiring its ends to be held rigid. If the rod is stress free at room temperature [20°C (68°F)], what is the maximum temperature to which the rod may be heated without exceeding a compressive stress of 172 MPa (25000 psi)? Assume a modulus of elasticity of 100 GPa (14.6 x 10^6 psi) for brass ?

Then another is assuming unconstrained thermal expansion where this having a delta L length change this is original L naught from here to here and this is delta L. Now here delta L over L at room is equal to and which is represented as alpha L T f minus T naught final temperature minus T naught this is at the final temperature. Now another step the compress specimen back to original length. So, small sigma which is L naught and you see that this is the delta L which need to be compressed.



Step 1 T_0 original cond.

l_0

l_0 Δl T_f

$\frac{\Delta l}{l_{room}} = \varepsilon_{thermal}$

$= \alpha_\ell (T_f - T_0)$

Step-2 Assume unconstrained thermal expansion

Step-3 Compress specimen back to original length

l_0 Δl σ $\varepsilon_{compress} = \frac{-\Delta l}{l_{room}} = -\varepsilon_{thermal}$

Step-4 The thermal stress can be directly calculated as $\sigma = E\,(\varepsilon_{compress})$

σ l_0 σ & $\varepsilon_{compress} = -\varepsilon_{thermal}$

$\sigma = -E(\varepsilon_{thermal}) = E\,\alpha_\ell (T_0 - T_f)$

$= -E\,\alpha_\ell (T_f - T_0)$

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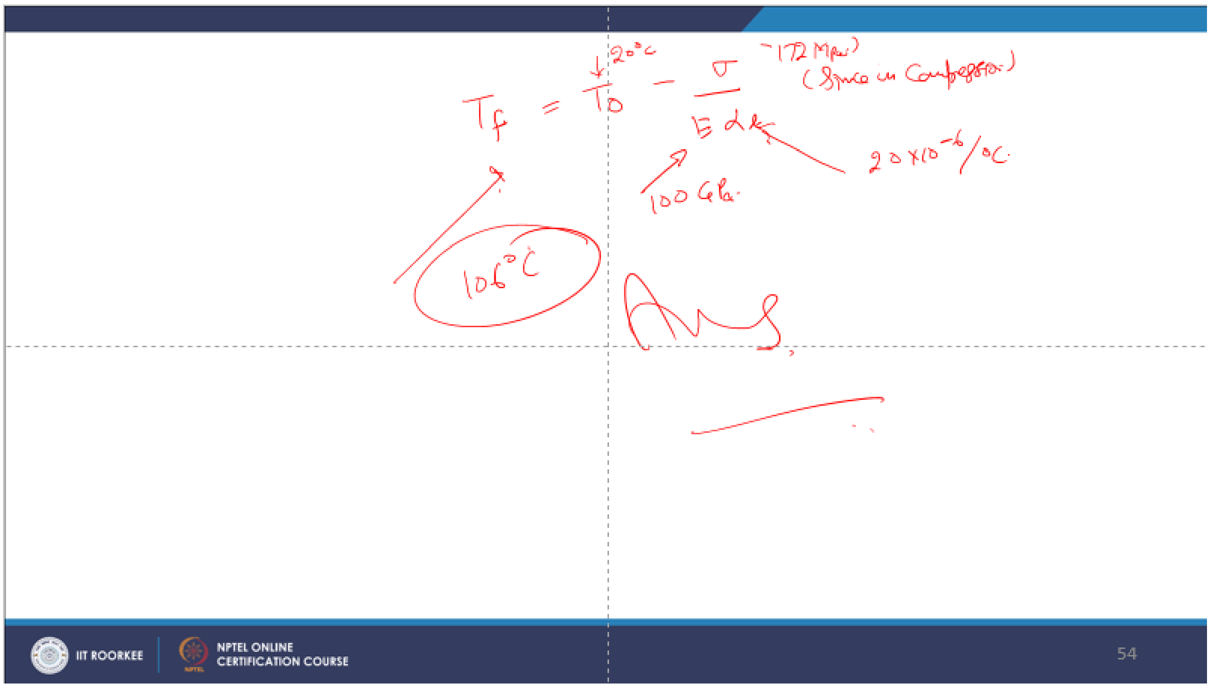

$T_f = T_0 - \frac{\sigma}{E\,\alpha_\ell}$

20°C

−172 MPa (Since in Compression)

100 GPa

20×10^{-6}/°C

106°C

Ans

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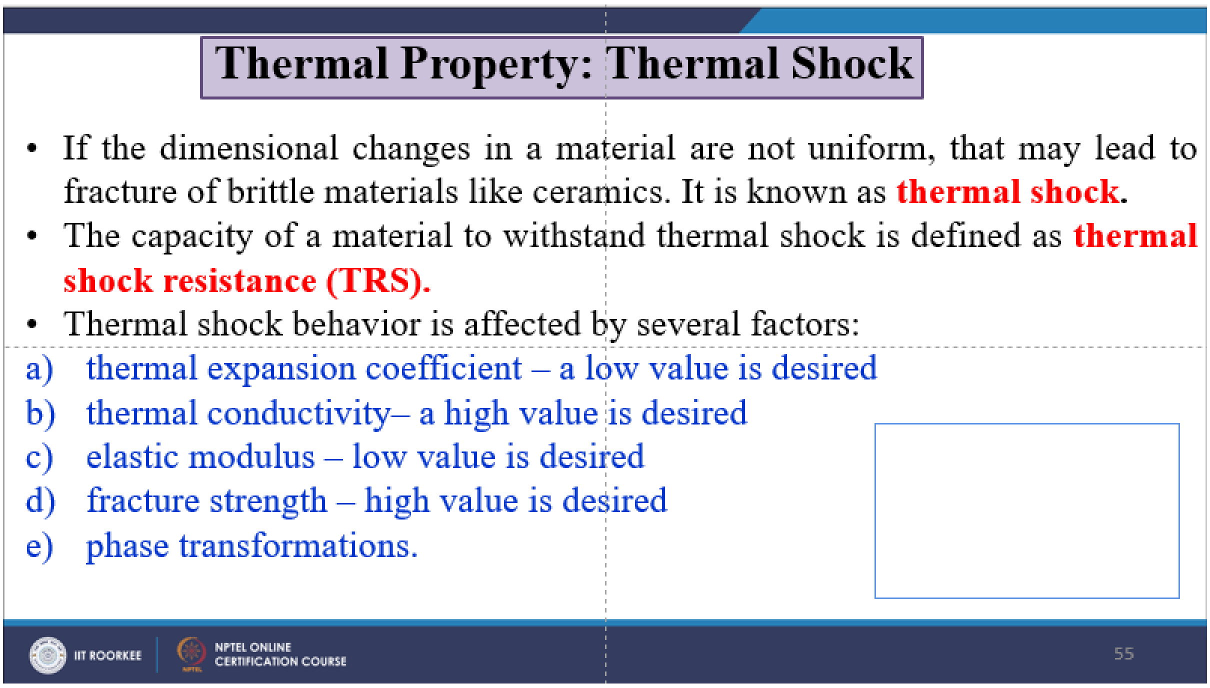
So, is equal to minus delta L over L room is equal to epsilon thermal. Now based on this particular aspect let us talk about another step this is the fourth the thermal stress. The thermal stress can be directly calculated as, this is lo. Which is equal to silent compress. Now this epsilon compress is equal to silent thermal. So, if you substitute this gives epsilon thermal which is equal to minus e alpha L T f minus T naught and which is equal to e alpha L T naught T f.

So, the T f which is the final can be calculated as T naught which is given as 20 degree Celsius minus which is calculated as minus 172 mega Pascal since in compression over e alpha L which is given as 100 GPa and this is given as 20 into 10 to the power minus 6 over degree Celsius. So, if we calculate then this comes out to be 106 degree Celsius which is your answer. So, let us talk about the thermal shocks. The dimensional changes in the material are not uniform that may lead to a fracture or a brittle material like ceramics.



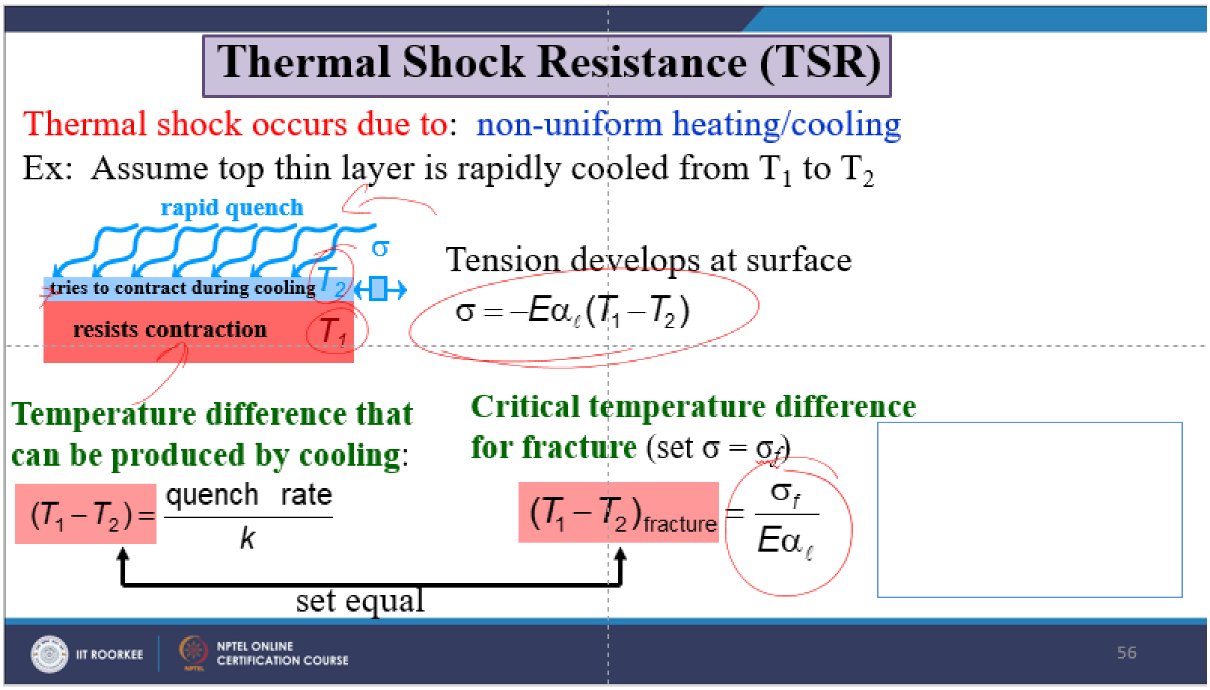
Thermal Property: Thermal Shock

- If the dimensional changes in a material are not uniform, that may lead to fracture of brittle materials like ceramics. It is known as **thermal shock**.
- The capacity of a material to withstand thermal shock is defined as **thermal shock resistance (TRS).**
- Thermal shock behavior is affected by several factors:

a) thermal expansion coefficient – a low value is desired
b) thermal conductivity– a high value is desired
c) elastic modulus – low value is desired
d) fracture strength – high value is desired
e) phase transformations.

It is known as a thermal shock. The capacity of a material to withstand thermal shock is usually defined as a thermal shock resistance or sometimes referred as a TRS. The thermal shock behaviour is affected by various factors. One is the thermal expansion coefficient a low value is desired obviously. The thermal conductivity usually a high value is desired.

Elastic modulus desired is the low value. The fracture strength usually a high value is desired and a phase transformation. Now, let us talk about this thermal how this thermal shock occurs. Now, this thermal shock occurs due to the non-uniform heating or cooling. Now, assume here you see that this is a thin layer rod which is being heated or heated rod. Now, if we apply the rapid quenching then it may this tries this particular layer which is in the direct contact tries to contract during the cooling.



Thermal Shock Resistance (TSR)

Thermal shock occurs due to: non-uniform heating/cooling

Ex: Assume top thin layer is rapidly cooled from T_1 to T_2

Tension develops at surface

$$\sigma = -E\alpha_\ell (T_1 - T_2)$$

Temperature difference that can be produced by cooling:

$$(T_1 - T_2) = \frac{\text{quench rate}}{k}$$

Critical temperature difference for fracture (set $\sigma = \sigma_f$)

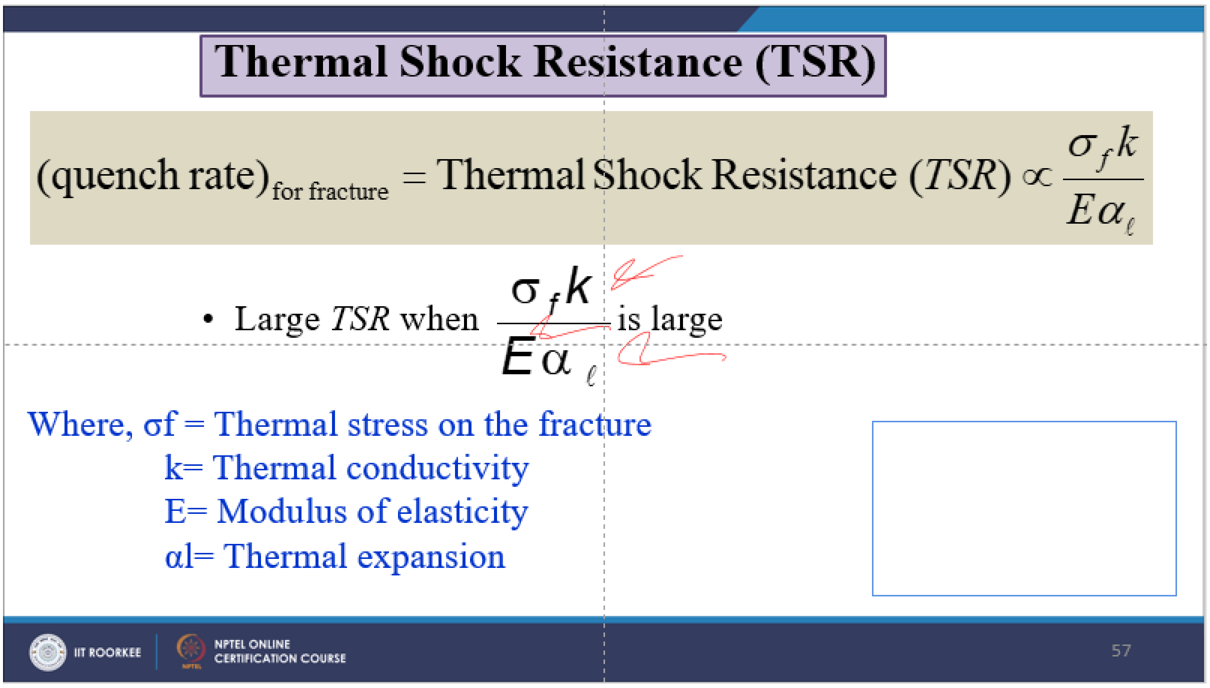
$$(T_1 - T_2)_{\text{fracture}} = \frac{\sigma_f}{E\alpha_\ell}$$

set equal

$$(T_1 - T_2)_{\text{fracture}} = \frac{\sigma_f}{E\alpha_\ell}\ , \quad (T_1 - T_2) = \frac{\text{quench rate}}{k}$$

$$\sigma = -E\alpha_\ell (T_1 - T_2)$$

However, the heated segment they try to resist the contraction. So, therefore, a tension develops at the surface and which is represented as small sigma is equal to E alpha T 1 minus T 2. So, this is the T 1 and T 2. So, T 2 is the cooling temperature at the cooled surface and T 1 is the temperature at the surface which is maintained at the higher range. Now, this temperature difference that can be produced by cooling it is T 1 minus T 2 this is equal to the quench rate over k. Now, this is the critical temperature difference for fracture this is usually set as alpha is equal to final and T 1 minus T 2 that is a fracture can be calculated by this small sigma f over E alpha l.



Thermal Shock Resistance (TSR)

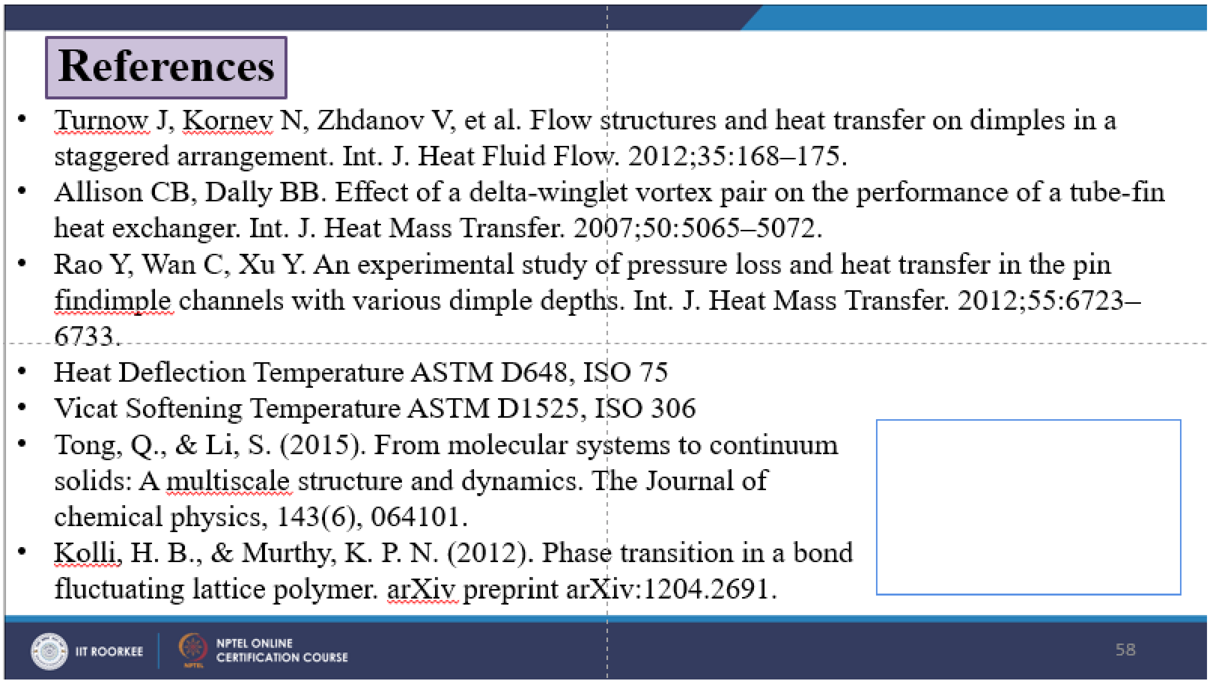
$$(\text{quench rate})_{\text{for fracture}} = \text{Thermal Shock Resistance } (TSR) \propto \frac{\sigma_f k}{E\alpha_\ell}$$

- Large *TSR* when $\frac{\sigma_f k}{E\alpha_\ell}$ is large

Where, σf = Thermal stress on the fracture
k= Thermal conductivity
E= Modulus of elasticity
αl= Thermal expansion

- Large *TSR* when $\frac{\sigma_f k}{E\alpha_\ell}$ is large

Now, the quench rate for the fracture that is a thermal shock resistance is directly proportional to the small sigma f k over E alpha l. Now, the larger TSR this is thermal shock resistance when small sigma f k E alpha l is large where small sigma is a thermal stress of on the fracture k is the thermal conductivity E is the modulus of elasticity and this is the thermal expansion.



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So, dear friends, here we discussed about the various phenomena of heat transfer especially related to the thermal expansion contraction all these things for your convenience we have enlisted couple of references you can utilize those references for further studies. Thank you very much.