

Heat capacity is a material's ability to absorb heat from the external surroundings; it represents the amount of energy needed to increase the temperature of a substance 1 degree, so the units are J / °C. In mathematical terms, the heat capacity C is expressed as follows: $C = \Delta Q/\Delta T = dQ/dT$ [J/deg] Where dQ is the energy required to produce a dT temperature change. Ordinarily, heat capacity is specified per mole of material (e.g., J/mol-K, or cal/mol-K). Table below give the heat capacity of some materials.

When the temperature is increased, the kinetic energy of the particles in the material changes. The heat is transferred from high temperature region to low temperature region. This energy is stored as kinetic energy in case of gases and in case of solids this energy is stored as potential energy in the particles. This is because in solids the particles are tightly bound together.

Two ways to measure heat capacity:

C_p : Heat capacity at constant pressure.

C_v : Heat capacity at constant volume.

$C_p > C_v$

Heat capacity has units as J/mol-K or Cal/mol-K.

Heat capacity is not an intrinsic property i.e. It changes with material volume/mass.

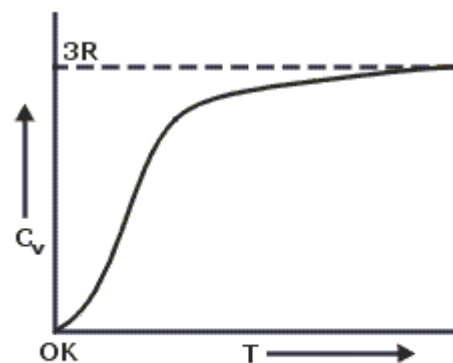
At low temperatures, vibrational heat contribution of heat capacity varies with temperature as follows:

$$C_v = AT^3$$

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

Heat capacity increases with temperature and reaches a limiting value of $3R = 25 \text{ JK}^{-1}\text{mol}^{-1}$, where R is the gas constant

Substance	$c/\text{J kg}^{-1} \text{K}^{-1}$	Substance	$c/\text{J kg}^{-1} \text{K}^{-1}$
Aluminium	900	Ice	2100
Iron/steel	450	Wood	1700
Copper	390	Nylon	1700
Brass	380	Rubber	1700
Zinc	380	Marble	880
Silver	230	Concrete	850
Mercury	140	Granite	840
Tungsten	135	Sand	800
Platinum	130	Glass	670
Lead	130	Carbon	500
Hydrogen	14000	Ethanol	2400
Air	718	Paraffin	2100
Nitrogen	1040	Water	4186
Steam	2000	Sea water	3900



Variation of C_v with T

Specific heat:

A more useful procedure is to compare heat capacities for one gram of material. This is called the *specific heat capacity* or simply *specific heat*. Specific heat is the quantity of heat required to raise the temperature of one gram of material one degree Celsius (or one kelvin). We get the specific heat when we divide the heat capacity of a material by its mass.

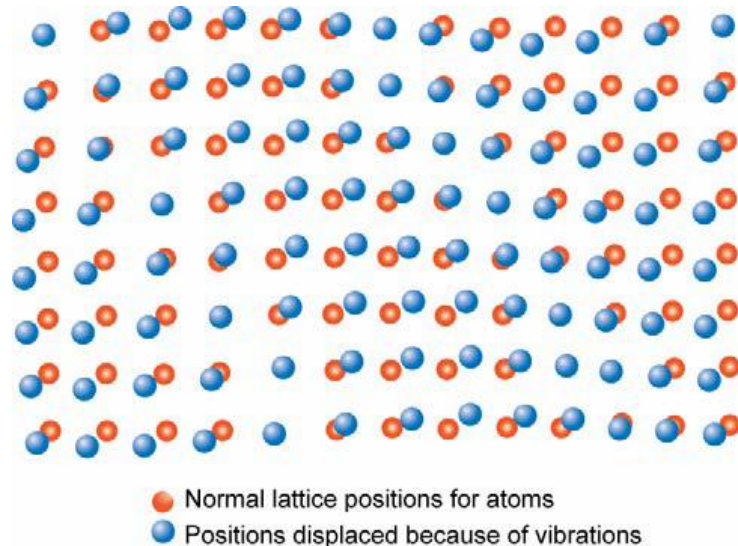
$$\text{Specific heat} = \text{heat capacity} / \text{mass} = C / m$$

- Specific heat is heat capacity per unit mass. It has units as J/kg-K or Cal/kg-K.
- With increase of heat energy, dimensional changes may occur. Hence, two heat capacities are usually defined, C_p and C_v
- Heat is absorbed through different mechanisms: lattice vibrations and electronic contribution (in that electrons absorb energy by increasing their kinetic energy).

Vibrations of individual atoms in solids are not independent from each other. The coupling of atomic vibrations of adjacent atoms results in waves of atomic displacements. Each wave is characterized by its

wavelength and frequency. For a wave of a given frequency ν , there is the smallest “quantum” of vibrational energy, $h\nu$, called **phonon**. (A quantum of sound. A phonon is the sound particle equivalent of a photon, which is a light particle. While photons travel in space, long wave phonons travel within the atomic lattice of solid matter)

Thus, the thermal energy is the energy of all phonons (or all vibrational waves) present in the crystal at a given temperature.



Example: (a) Determine the room temperature heat capacities at constant pressure for the following materials: copper, iron, gold, and nickel. (b) How do these values compare with one another? How do you explain this? If C_p for Cu, Fe, Au, Ni are 386, 448, 128, and 443 J/kg-K respectively.

for Cu	$C_p = (386 \text{ J/kg-K})(1 \text{ kg}/1000 \text{ g})(63.55 \text{ g/mol}) = 24.5 \text{ J/mol-K}$
For Fe	$C_p = (448 \text{ J/kg-K})(1 \text{ kg}/1000 \text{ g})(55.85 \text{ g/mol}) = 25.0 \text{ J/mol-K}$
For Au	$C_p = (128 \text{ J/kg-K})(1 \text{ kg}/1000 \text{ g})(196.97 \text{ g/mol}) = 25.2 \text{ J/mol-K}$
For Ni	$C_p = (443 \text{ J/kg-K})(1 \text{ kg}/1000 \text{ g})(58.69 \text{ g/mol}) = 26.0 \text{ J/mol-K}$

(b) These values of C_p are very close to one another because room temperature is considerably above the Debye temperature for these metals; therefore, the values of C_p should be about equal to $3R$ [$(3)(8.31 \text{ J/mol-K}) = 24.9 \text{ J/mol-K}$], which is indeed the case for all four of these metals.

Thermal expansion:

Most solid materials expand upon heating and contract when cooled. The change in length with temperature for a solid material may be expressed as follows:

$$\frac{l_f - l_0}{l_0} = \alpha_l (T_f - T_0) = \frac{\Delta l}{l_0} = \alpha_l \Delta T$$

$$\alpha = \varepsilon / \Delta T$$

α values:

- for metals $5\text{-}25 \times 10^{-6}$
- for ceramics $0.5\text{-}15 \times 10^{-6}$
- for polymers $50\text{-}400 \times 10^{-6}$ The highest values are found in linear and branched polymers because the secondary intermolecular bonds are weak, and there is a minimum of crosslinking. With increased crosslinking, the magnitude of the expansion coefficient diminishes; the lowest coefficients are found in the thermosetting network polymers such as phenol-formaldehyde, in which the bonding is almost entirely covalent.

where l_f and l_0 represent, respectively, final and initial lengths with the temperature change from T_0 to T_f . The parameter α_l is called the **linear coefficient of thermal expansion**; it is a material property that is indicative of the extent to which a material expands upon heating, and has units of reciprocal emperature [$(^\circ\text{C})^{-1}$ or $(^\circ\text{F})^{-1}$]

A volume coefficient of thermal expansion, $\alpha_v = 3\alpha_l$ is used to describe the volume change with temperature.

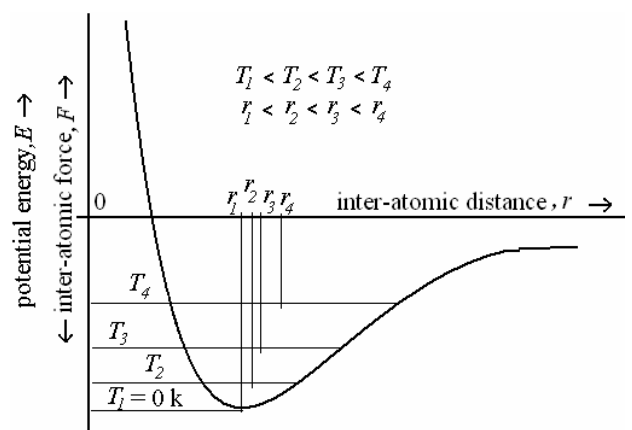
$$\alpha_v = \frac{\Delta v}{v_0 \Delta T}$$

Where Δv and v_0 are the volume change and the original volume.

- An instrument known as dilatometer is used to measure the thermal expansion coefficient.
- At microscopic level, because of asymmetric nature of the potential energy trough, changes in dimensions with temperature are due to change in inter-atomic distance, rather than increase in vibrational amplitude.

If a very deep energy trough caused by strong atomic bonding is characteristic of the material, the atoms separate to a lesser and the material has low linear coefficient of thermal expansion. This relationship also suggests that materials having a high melting temperature – also due to strong atomic bonds – have low thermal expansion coefficients.

For each class of materials (metals, ceramics, and polymers), the greater the atomic bonding energy, the deeper and more narrow this potential energy trough.



Thermal expansion of various materials

<i>Material</i>	α_l [(°C) ⁻¹ × 10 ⁻⁶] ^b
Metals	
Aluminum	23.6
Copper	17.0
Gold	14.2
Iron	11.8
Nickel	13.3
Silver	19.7
Tungsten	4.5
1025 Steel	12.0
316 Stainless steel	16.0
Brass (70Cu–30Zn)	20.0
Kovar (54Fe–29Ni–17Co)	5.1
Invar (64Fe–36Ni)	1.6
Super Invar (63Fe–32Ni–5Co)	0.72
Ceramics	
Alumina (Al ₂ O ₃)	7.6
Magnesia (MgO)	13.5 ^d
Spinel (MgAl ₂ O ₄)	7.6 ^d
Fused silica (SiO ₂)	0.4
Soda–lime glass	9.0
Borosilicate (Pyrex) glass	3.3
Polymers	
Polyethylene (high density)	106–198
Polypropylene	145–180
Polystyrene	90–150
Polytetrafluoroethylene (Teflon)	126–216
Phenol-formaldehyde, phenolic	122
Nylon 6,6	144
Polyisoprene	220

Example: A 0.4 m rod of a metal elongates 0.48 mm on heating from 20 to 100 °C . Determine the value of the linear coefficient of thermal expansion for this material.

$$\alpha_l = \Delta l / l_0 \Delta T = \Delta l / l_0 (T_f - T_0) = 0.48 \times 10^{-3} \text{ m} / (0.4 \text{ m})(100^\circ\text{C} - 20^\circ\text{C}) = 15.0 \times 10^{-6} (\text{°C})^{-1}$$

Example: Compute the density for iron at 700 °C given that its room-temperature density is 7.870 g/cm³. Assume that the volume coefficient of thermal expansion, α_v is equal to $3\alpha_l$

$$\begin{aligned} \Delta V / V_0 &= \alpha_v \Delta T \quad \text{or} \quad \Delta V = V_0 \alpha_v \Delta T \\ V &= V_0 + \Delta V = V_0 (1 + \alpha_v \Delta T) = V_0 (1 + 3\alpha_l \Delta T) \\ &= (1 \text{ cm}^3) \{ 1 + (3) [11.8 \times 10^{-6} (\text{°C})^{-1}] (700^\circ\text{C} - 20^\circ\text{C}) \} = 1.02471 \text{ cm}^3 \\ \rho &= 7.870 \text{ g} / 1.02471 \text{ cm}^3 = 7.680 \text{ g/cm}^3 \end{aligned}$$

Example: To what temperature must a cylindrical rod of tungsten 15.025 mm in diameter and a plate of 1025 steel having a circular hole 15.000 mm in diameter have to be heated for the rod to just fit into the hole? Assume that the initial temperature is 25 °C.

$$d_f - d_0 / d_0 = \alpha_l (T_f - T_0)$$

$$d_f = d_0 [1 + \alpha_l (T_f - T_0)]$$

Now all we need do is to establish expressions for $d_f(\text{steel})$ and $d_f(\text{W})$, set them equal to one another, and solve for T_f . from Tables , $\alpha_l(\text{steel}) = 12.0 \times 10^{-6} (\text{°C})^{-1}$ and $\alpha_l(\text{W}) = 4.5 \times 10^{-6} (\text{°C})^{-1}$. Thus

$$d_f(\text{steel}) = d_f(\text{W})$$

$$(15.000 \text{ mm}) [1 + \{12.0 \times 10^{-6} (\text{°C})^{-1}\} (T_f - 25 \text{°C})]$$

$$= (15.025 \text{ mm}) [1 + \{4.5 \times 10^{-6} (\text{°C})^{-1}\} (T_f - 25 \text{°C})]$$

Now solving for T_f gives $T_f = 222.4 \text{°C}$

Implications and applications of thermal expansion:

Thermostats based on bimetal strips made of two metals with different coefficient of thermal expansion:

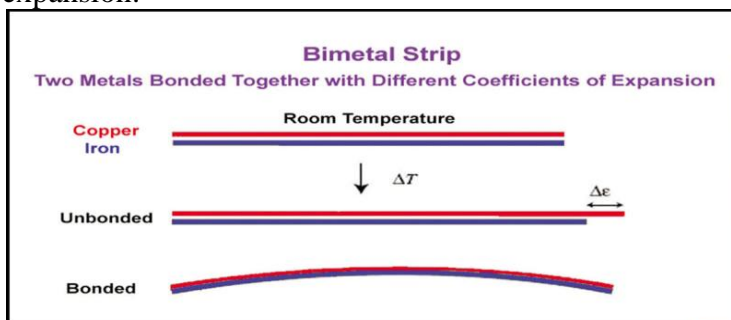
Railway tracks are built from steel rails laid with a gap between the ends



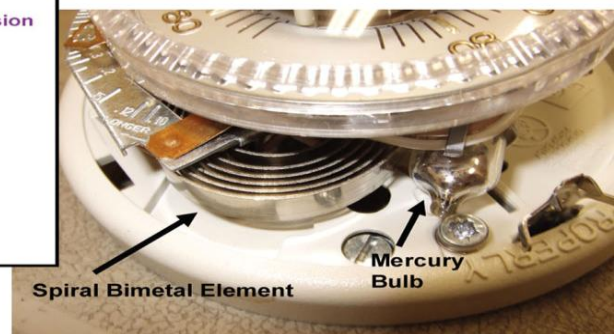
Joints such as this one are used in bridges to accommodate thermal expansion.



Thermostats based on bimetal strips made of two metals with different coefficient of thermal expansion:



(a)



(b)

Thermal conductivity

- *Thermal conductivity* is ability of a material to transport heat energy through it from high temperature region to low temperature region.
- q is the heat flux or heat flow, per unit time per unit area (area being taken as that perpendicular to the flow direction), is given by:

$$q = -k \frac{dT}{dx}$$

- where k is the thermal conductivity of the material. It has units as W/m.K.
- q has units as W/m^2 .
- It is a microstructure sensitive property.
- Its value range
 - o for metals 20-400 W/m-K
 - o for ceramics 2-50 W/m-K
 - o for polymers order of 0.3 W/m-K
- The above equation is valid only for steady-state heat flow—that is, for situations in which the heat flux does not change with time.
- The minus sign in the expression indicates that the direction of heat flow is from hot to cold, or down the temperature gradient.

Mechanisms Of Thermal conductivity:

- Heat is transported in solids by two ways – lattice vibration waves (phonons) and free electrons. Thus; $k = k_l + k_e$
 - The k_l contribution results from a net movement of phonons from high- to lowtemperature regions of a body across which a temperature gradient exists.
 - The relative contribution of k_e to the total thermal conductivity increases with increasing free electron concentrations, since more electrons are available to participate in this heat transference process.
 - In high-purity metals, the electron mechanism of heat transport is much more efficient than the phonon contribution because electrons are not as easily scattered as phonons and have higher velocities. Furthermore, metals are extremely good conductors of heat because relatively large numbers of free electrons exist that participate in thermal conduction.
 - It is same as electrical conduction. Both electrical and thermal conductivities are related through Wiedemann-Franz law:

$$L = k / \sigma T$$

- where L – Lorentz constant ($2.44 \times 10^{-8} \Omega \cdot W / K^2$) should be independent of temperature and the same for all metals if the heat energy is transported entirely by free electrons.

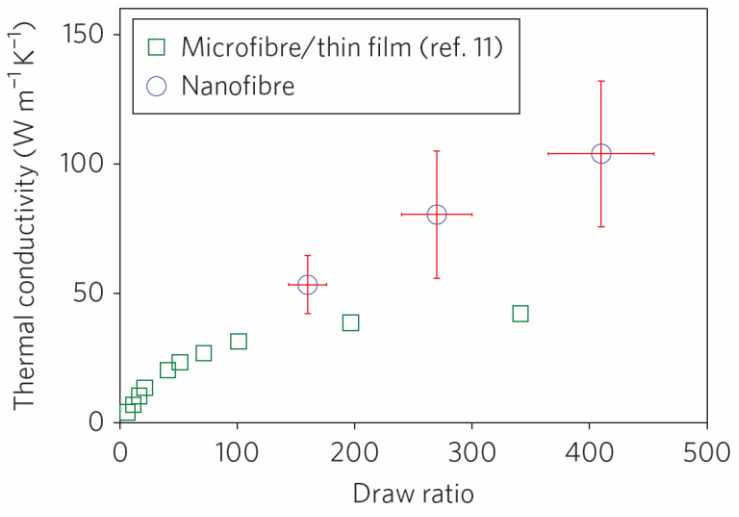
Alloying metals with impurities results in a reduction in the thermal conductivity, for the same reason that the electrical conductivity is diminished namely, the impurity atoms, especially if in solid solution, act as scattering centers, lowering the efficiency of electron motion.

- As different contributions to conduction vary with temperature, the above relation is valid to a limited extension for many metals.
- With increase in temperature, both number of carrier electrons and contribution of lattice vibrations increase. Thus thermal conductivity of a metal is expected to increase.
- However, because of greater lattice vibrations, electron mobility decreases.
- The combined effect of these factors leads to very different behavior for different metals.

- Eg: thermal conductivity of iron initially decreases then increases slightly; thermal conductivity decreases with increase in temperature for aluminium; while it increases for platinum
 - Nonmetallic materials are thermal insulators inasmuch as they lack large numbers of free electrons. Thus the phonons are primarily responsible for thermal conduction: k_e is much smaller than k_l
 - Glass and other amorphous ceramics have lower conductivities than crystalline ceramics, since the phonon scattering is much more effective when the atomic structure is highly disordered and irregular.
 - Many ceramics that are used for thermal insulation are porous. Heat transfer across pores is ordinarily slow and inefficient. Internal pores normally contain still air, which has an extremely low thermal conductivity—approximately 0.02 W/m. Also, gaseous convection within the pores is also comparatively ineffective.
 - polymer with a highly crystalline and ordered structure will have a greater conductivity than the equivalent amorphous material.
 - This is due to the more effective coordinated vibration of the molecular chains for the crystalline state.

Thermal conductivity of individual polymer chains can be very high. Experimental study of high-quality ultra-drawn polyethylene nanofibers with diameters of 50-500 nm and lengths up to tens of millimeters demonstrated that the nanofibers conducts heat just as well as most metals, yet remain electrical insulators.

104 $\text{Wm}^{-1}\text{K}^{-1}$, 300 times higher than k of bulk polyethylene!



Example: (a) Calculate the heat flux through a sheet of brass 7.5 mm thick if the temperatures at the two faces are 150 and 50 °C ; assume steady-state heat flow. (b) What is the heat loss per hour if the area of the sheet is 0.5 m²? (c) What will be the heat loss per hour if soda-lime glass instead of brass is used? (d) Calculate the heat loss per hour if brass is used and the thickness is increased to 15 mm . If the thermal conductivity for brass and soda-lime glass are 120 W/m-K and $k = 1.7 \text{ W/m-K}$ respectively

$$q = -k \Delta T / \Delta x$$

$$= -(120 \text{ W/m-K}) [(50+273\text{K}) - (150+273\text{K}) / 7.5 \times 10^{-3} \text{m}]$$

$$= 1.60 \times 10^6 \text{ W/m}^2$$

(b) Let dQ/dt represent the total heat loss such that $dQ / dt = qAt$ where A and t are the cross-sectional area and time, respectively. Thus,

$$dQ / dt = (1.60 \times 10^6 \text{ J/s-m}^2)(0.5 \text{ m}^2)(60 \text{ s/min})(60 \text{ min/h}) = 2.88 \times 10^9 \text{ J/h}$$

$$(c) \frac{dQ}{dt} = -k A \frac{\Delta T}{\Delta x} = -(1.7 \text{ J/s-m-K})(0.5 \text{ m}^2)(3600 \text{ s/h}) \left(\frac{-100\text{K}}{7.5 \times 10^{-3} \text{ m}} \right) = 4.08 \times 10^7 \text{ J/h}$$

(d) If the thickness of the brass is increased to 15 mm, then

$$\frac{dQ}{dt} = -k A \frac{\Delta T}{\Delta x} = -(120 \text{ W/m-K})(0.5 \text{ m}^2)(3600 \text{ s/h}) \left(\frac{-100\text{K}}{15 \times 10^{-3} \text{ m}} \right) = 1.44 \times 10^9 \text{ J/h}$$

Example: Briefly explain why the thermal conductivities are higher for crystalline than noncrystalline ceramics.

Thermal conductivities are higher for crystalline than for noncrystalline ceramics because, for noncrystalline, phonon scattering, and thus the resistance to heat transport, is much more effective due to the highly disordered and irregular atomic structure.

Thermal stresses :

- Stresses due to change in temperature or due to temperature gradient are termed as *thermal stresses*

$$\sigma_{thermal} = \alpha E \Delta T$$

Thermal stresses is important because these stresses can lead to fracture or undesirable plastic deformation.

- Thermal stress 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.
 - Eg.: Zerodur – a glass-ceramic material that consists of 70-80% crystalline quartz, and the remaining as glassy phase.
 - Sodium-zirconium-phosphate (NZP) have a near-zero thermal expansion coefficient.

Thermal shock:

Thermal shock is the fracture of a body resulting from thermal stresses induced by rapid temperature changes. Because ceramic materials are brittle, they are especially susceptible to this type of failure. The **thermal shock resistance** of many materials is proportional to the fracture strength and thermal conductivity, and inversely proportional to both the modulus of elasticity and the coefficient of thermal expansion as given in equation:

$$TSR = \frac{\sigma_f k}{E \alpha_l}$$

Example: (a) If a rod of brass 0.35 m long is heated from 15 to 85 °C while its ends are maintained rigid, determine the type and magnitude of stress that develops. Assume that at 15 °C the rod is stress free. (b) What will be the stress magnitude if a rod 1 m long is used? (c) If the rod in part (a) is cooled from 15 °C to -15 °C to what type and magnitude of stress will result? 97 GPa the modulus of elasticity of brass and $\alpha_l = 20.0 \times 10^{-6} (\text{°C})^{-1}$ for brass.

$$\sigma = E\alpha_l (T_0 - T_f) = (97 \times 10^3 \text{ MPa}) [20.0 \times 10^{-6} (\text{°C})^{-1}] (15\text{°C} - 85\text{°C}) = -136 \text{ MPa}$$

The stress will be compressive since its sign is negative.

(b) The stress will be the same [-136 MPa], since stress is independent of bar length.

(c) Upon cooling the indicated amount, the stress becomes

$$\begin{aligned} \sigma &= E\alpha_l (T_0 - T_f) \\ &= (97 \times 10^3 \text{ MPa}) [20.0 \times 10^{-6} (\text{°C})^{-1}] [(15\text{°C} - (-15\text{°C}))] \\ &= +58 \text{ MPa} \end{aligned}$$

This stress will be tensile since its sign is positive.

Example: (a) Briefly explain why thermal stresses may be introduced into a structure by rapid heating

or cooling. (b) For cooling, what is the nature of the surface stresses? (c) For heating, what is the nature of the surface stresses?

(a) Thermal stresses may be introduced into a structure by rapid heating or cooling because temperature gradients will be established across the cross section due to more rapid temperature changes at the surface than within the interior; thus, the surface will expand or contract at a different rate than the interior and since this surface expansion or contraction will be restrained by the interior, stresses will be introduced.

(b) For cooling, the surface stresses will be tensile in nature since the interior contracts to a lesser degree than the cooler surface.

(c) For heating, the surface stresses will be compressive in nature since the interior expands to a lesser degree than the hotter surface.

Example: A steel wire is stretched with a stress of 70 MPa at (20 °C). If the length is held constant, to what temperature must the wire be heated to reduce the stress to 17 MPa? If values for E and α_l for steel of 207 GPa and $12.0 \times 10^{-6} (\text{°C})^{-1}$, respectively

We want to heat the steel wire in order to reduce the stress level from 70 MPa to 17 MPa; in doing so, we reduce the stress in the wire by $70 \text{ MPa} - 17 \text{ MPa} = 53 \text{ MPa}$, which stress will be a compressive one (i.e., $\sigma = -53 \text{ MPa}$)

$$\begin{aligned} T_f &= T_0 - (\sigma / E\alpha_l) \\ &= 20\text{°C} - [-53\text{MPa} / (207 \times 10^3 \text{MPa}) (12.0 \times 10^{-6} (\text{°C})^{-1})] \\ &= 20\text{°C} + 21.3\text{°C} = 41.3\text{°C} \end{aligned}$$

Example: The two ends of a cylindrical rod of nickel 120.00 mm long and 12.000 mm in diameter are maintained rigid. If the rod is initially at 70⁰C to what temperature must it be cooled in order to have a 0.023-mm reduction in diameter? If the values of ν and α_l for nickel are 0.31 and $13.3 \times 10^{-6} (\text{°C})^{-1}$, respectively

$$\Delta d_1 = d_0 \alpha_l (T_f - T_0)$$

Now, let Δd_2 is related to the transverse strain (ϵ_x)

$$\Delta d_2 / d_0 = \epsilon_x$$

Also, transverse strain and longitudinal strain (ϵ_z) are related according to Equation below:

$$\epsilon_x = -\nu \epsilon_z$$

where ν is Poisson's ratio. Substitution of this expression for ϵ_x into the first equation above leads to

$$\Delta d_2 / d_0 = -\nu \epsilon_z$$

Furthermore, the longitudinal strain is related to the modulus of elasticity through Equation below:

$$\epsilon_z = \sigma / E$$

And, therefore, $\Delta d_2 / d_0 = -\nu \sigma / E$

Now, $\sigma = E \alpha_l (T_0 - T_f)$

which, when substituted into the preceding equation leads to

$$\Delta d_2 / d_0 = -\nu E \alpha_l (T_0 - T_f) / E = -\nu \alpha_l (T_0 - T_f)$$

And, solving for Δd_2 from this expression $\Delta d_2 = -d_0 \nu \alpha_l (T_0 - T_f)$

The total Δd is just $\Delta d = \Delta d_1 + \Delta d_2$, and

$$\Delta d = d_0 \alpha_l (T_f - T_0) + d_0 \nu \alpha_l (T_f - T_0) = d_0 \alpha_l (T_f - T_0) (1 + \nu)$$

$$-(0.023 \text{ mm}) = (12.000 \text{ mm}) [13.3 \times 10^{-6} (\text{°C})^{-1}] (T_f - 70 \text{°C}) (1 + 0.31)$$

And, finally, solving the above expression for T_f yields $T_f = -40 \text{°C}$.