

Chapter 19 Thermal Properties

This photograph shows a white-hot cube of a silica fiber insulation material, which, only seconds after having been removed from a hot furnace, can be held by its edges with the bare hands. Initially, the heat transfer from the surface is relatively rapid; however, the thermal conductivity of this material is so small that heat conduction from the interior [maximum temperature approximately 1250°C (2300°F)] is extremely slow.

This material was developed especially for the tiles that cover the Space Shuttle Orbiters and protect and insulate them during their fiery reentry into the atmosphere. Other attractive features of this *high-temperature reusable surface insulation (HRSI)* include low density and a low coefficient of thermal expansion. (Photograph courtesy of Lockheed Missiles & Space Company, Inc.)



WHY STUDY *the Thermal Properties of Materials*?

Materials selection decisions for components that are exposed to elevated/subambient temperatures, temperature changes, and/or thermal gradients require the design engineer to have an understanding of the thermal responses of materials, as well as access to the thermal properties of a wide variety of materials. For example, in the discussion on materials that are used for the leadframe component of an integrated circuit package (Section 22.16), we note restrictions

that are imposed on the thermal characteristics of the adhesive material that attaches the integrated circuit chip to the leadframe plate. This adhesive must be thermally conductive so as to facilitate the dissipation of heat generated by the chip. In addition, its thermal expansion/contraction on heating/cooling must match that of the chip such that the integrity of the adhesive-chip bond is maintained during thermal cycling.

Learning Objectives

After careful study of this chapter you should be able to do the following:

1. Define *heat capacity* and *specific heat*.
2. Note the primary mechanism by which thermal energy is assimilated in solid materials.
3. Determine the linear coefficient of thermal expansion given the length alteration that accompanies a specified temperature change.
4. Briefly explain the phenomenon of thermal expansion from an atomic perspective using a potential energy-versus-interatomic separation plot.
5. Define *thermal conductivity*.
6. Note the two principal mechanisms of heat conduction in solids, and compare the relative magnitudes of these contributions for each of metals, ceramics, and polymeric materials.

19.1 INTRODUCTION

By “thermal property” is meant the response of a material to the application of heat. As a solid absorbs energy in the form of heat, its temperature rises and its dimensions increase. The energy may be transported to cooler regions of the specimen if temperature gradients exist, and ultimately, the specimen may melt. Heat capacity, thermal expansion, and thermal conductivity are properties that are often critical in the practical utilization of solids.

19.2 HEAT CAPACITY

heat capacity

A solid material, when heated, experiences an increase in temperature signifying that some energy has been absorbed. **Heat capacity** is a property that is indicative of a material’s ability to absorb heat from the external surroundings; it represents the amount of energy required to produce a unit temperature rise. In mathematical terms, the heat capacity C is expressed as follows:

$$C = \frac{dQ}{dT} \quad (19.1)$$

Definition of heat capacity—ratio of energy change (energy gained or lost) and the resulting temperature change

specific heat

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). **Specific heat** (often denoted by a lowercase c) is sometimes used; this represents the heat capacity per unit mass and has various units (J/kg-K, cal/g-K, Btu/lb_m-°F).

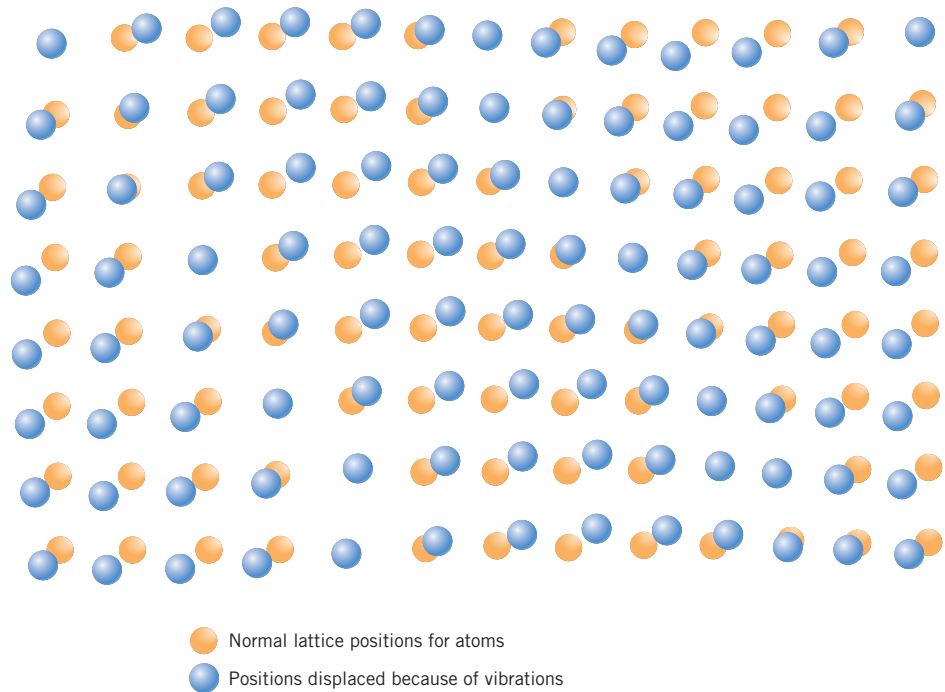
There are really two ways in which this property may be measured, according to the environmental conditions accompanying the transfer of heat. One is the heat capacity while maintaining the specimen volume constant, C_v ; the other is for constant external pressure, which is denoted C_p . The magnitude of C_p is almost always greater than C_v ; however, this difference is very slight for most solid materials at room temperature and below.

Vibrational Heat Capacity

In most solids the principal mode of thermal energy assimilation is by the increase in vibrational energy of the atoms. Again, atoms in solid materials are constantly vibrating at very high frequencies and with relatively small amplitudes. Rather than being independent of one another, the vibrations of adjacent atoms are coupled by virtue of the atomic bonding. These vibrations are coordinated in such a way that traveling lattice waves are produced, a phenomenon represented in Figure 19.1.

Figure 19.1

Schematic representation of the generation of lattice waves in a crystal by means of atomic vibrations. (Adapted from “The Thermal Properties of Materials” by J. Ziman. Copyright © 1967 by Scientific American, Inc. All rights reserved.)



These may be thought of as elastic waves or simply sound waves, having short wavelengths and very high frequencies, which propagate through the crystal at the velocity of sound. The vibrational thermal energy for a material consists of a series of these elastic waves, which have a range of distributions and frequencies. Only certain energy values are allowed (the energy is said to be quantized), and a single quantum of vibrational energy is called a **phonon**. (A phonon is analogous to the quantum of electromagnetic radiation, the **photon**.) On occasion, the vibrational waves themselves are termed phonons.

The thermal scattering of free electrons during electronic conduction (Section 18.7) is by these vibrational waves, and these elastic waves also participate in the transport of energy during thermal conduction (see Section 19.4).

Temperature Dependence of the Heat Capacity

The variation with temperature of the vibrational contribution to the heat capacity at constant volume for many relatively simple crystalline solids is shown in Figure 19.2. The C_v is zero at 0 K, but it rises rapidly with temperature; this corresponds to an increased ability of the lattice waves to enhance their average energy with ascending temperature. At low temperatures the relationship between C_v and the absolute temperature T is

$$C_v = AT^3 \quad (19.2)$$

where A is a temperature-independent constant. Above what is called the *Debye temperature* θ_D , C_v levels off and becomes essentially independent of temperature at a value of approximately $3R$, R being the gas constant. Thus even though the total energy of the material is increasing with temperature, the quantity of energy required to produce a one-degree temperature change is constant. The value of θ_D is

Dependence of heat capacity (at constant volume) on temperature, at low temperatures (near 0 K)

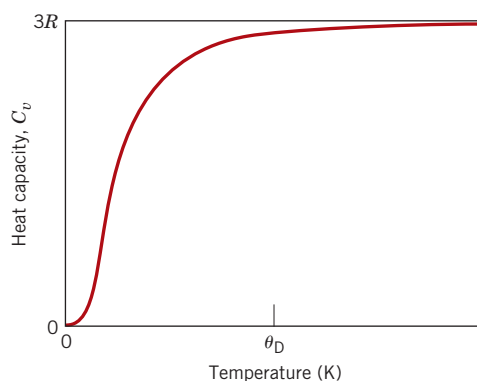


Figure 19.2 The temperature dependence of the heat capacity at constant volume; θ_D is the Debye temperature.

below room temperature for many solid materials, and 25 J/mol-K is a reasonable room-temperature approximation for C_v . Table 19.1 presents experimental specific heats for a number of materials; c_p values for still more materials are tabulated in Table B.8 of Appendix B.

Other Heat Capacity Contributions

Other energy-absorptive mechanisms also exist that can add to the total heat capacity of a solid. In most instances, however, these are minor relative to the magnitude of the vibrational contribution. There is an electronic contribution in that electrons absorb energy by increasing their kinetic energy. However, this is possible only for free electrons—those that have been excited from filled states to empty states above the Fermi energy (Section 18.6). In metals, only electrons at states near the Fermi energy are capable of such transitions, and these represent only a very small fraction of the total number. An even smaller proportion of electrons experiences excitations in insulating and semiconducting materials. Hence, this electronic contribution is ordinarily insignificant, except at temperatures near 0 K.

Furthermore, in some materials other energy-absorptive processes occur at specific temperatures—for example, the randomization of electron spins in a ferromagnetic material as it is heated through its Curie temperature. A large spike is produced on the heat capacity-versus-temperature curve at the temperature of this transformation.

19.3 THERMAL EXPANSION

For thermal expansion, dependence of fractional length change on the linear coefficient of thermal expansion and the temperature change

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:

$$\frac{l_f - l_0}{l_0} = \alpha_l(T_f - T_0) \quad (19.3a)$$

or

$$\frac{\Delta l}{l_0} = \alpha_l \Delta T \quad (19.3b)$$

linear coefficient of thermal expansion

where l_0 and l_f represent, respectively, initial and final lengths with the temperature change from T_0 to T_f . The parameter α_l is called the **linear coefficient of**

Table 19.1 Tabulation of the Thermal Properties for a Variety of Materials

Material	c_p (J/kg-K) ^a	α_l [(°C) ⁻¹ × 10 ⁻⁶] ^b	k (W/m-K) ^c	L [Ω-W/(K) ² × 10 ⁻⁸]
Metals				
Aluminum	900	23.6	247	2.20
Copper	386	17.0	398	2.25
Gold	128	14.2	315	2.50
Iron	448	11.8	80	2.71
Nickel	443	13.3	90	2.08
Silver	235	19.7	428	2.13
Tungsten	138	4.5	178	3.20
1025 Steel	486	12.0	51.9	—
316 Stainless steel	502	16.0	15.9	—
Brass (70Cu–30Zn)	375	20.0	120	—
Kovar (54Fe–29Ni–17Co)	460	5.1	17	2.80
Invar (64Fe–36Ni)	500	1.6	10	2.75
Super Invar (63Fe–32Ni–5Co)	500	0.72	10	2.68
Ceramics				
Alumina (Al ₂ O ₃)	775	7.6	39	—
Magnesia (MgO)	940	13.5 ^d	37.7	—
Spinel (MgAl ₂ O ₄)	790	7.6 ^d	15.0 ^e	—
Fused silica (SiO ₂)	740	0.4	1.4	—
Soda–lime glass	840	9.0	1.7	—
Borosilicate (Pyrex™) glass	850	3.3	1.4	—
Polymers				
Polyethylene (high density)	1850	106–198	0.46–0.50	—
Polypropylene	1925	145–180	0.12	—
Polystyrene	1170	90–150	0.13	—
Polytetrafluoroethylene (Teflon™)	1050	126–216	0.25	—
Phenol-formaldehyde, phenolic	1590–1760	122	0.15	—
Nylon 6,6	1670	144	0.24	—
Polyisoprene	—	220	0.14	—

^a To convert to cal/g-K, multiply by 2.39×10^{-4} ; to convert to Btu/lb_m-°F, multiply by 2.39×10^{-4} .

^b To convert to (°F)⁻¹, multiply by 0.56.

^c To convert to cal/s-cm-K, multiply by 2.39×10^{-3} ; to convert to Btu/ft-h-°F, multiply by 0.578.

^d Value measured at 100°C.

^e Mean value taken over the temperature range 0–1000°C.

For thermal expansion, dependence of fractional volume change on the volume coefficient of thermal expansion and the temperature change

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 temperature [(°C)⁻¹ or (°F)⁻¹]. Of course, heating or cooling affects all the dimensions of a body, with a resultant change in volume. Volume changes with temperature may be computed from

$$\frac{\Delta V}{V_0} = \alpha_v \Delta T \quad (19.4)$$

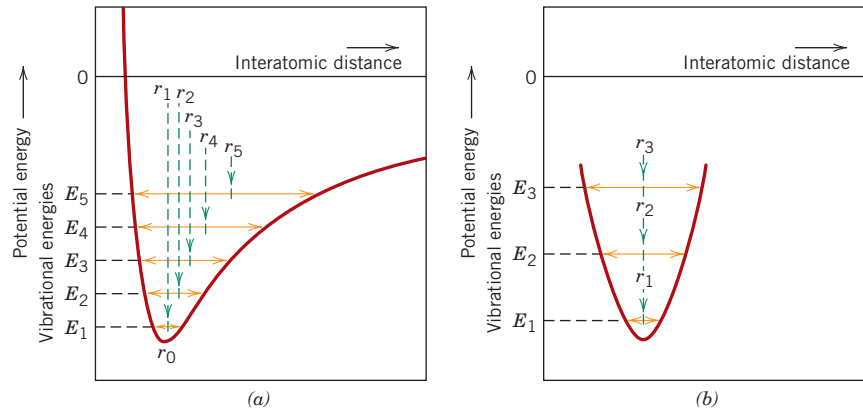


Figure 19.3 (a) Plot of potential energy versus interatomic distance, demonstrating the increase in interatomic separation with rising temperature. With heating, the interatomic separation increases from r_0 to r_1 to r_2 , and so on. (b) For a symmetric potential energy-versus-interatomic distance curve, there is no increase in interatomic separation with rising temperature (i.e., $r_1 = r_2 = r_3$). (Adapted from R. M. Rose, L. A. Shepard, and J. Wulff, *The Structure and Properties of Materials*, Vol. 4, *Electronic Properties*. Copyright © 1966 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

where ΔV and V_0 are the volume change and the original volume, respectively, and α_v symbolizes the volume coefficient of thermal expansion. In many materials, the value of α_v is anisotropic; that is, it depends on the crystallographic direction along which it is measured. For materials in which the thermal expansion is isotropic, α_v is approximately $3\alpha_l$.

From an atomic perspective, thermal expansion is reflected by an increase in the average distance between the atoms. This phenomenon can best be understood by consultation of the potential energy-versus-interatomic spacing curve for a solid material introduced previously (Figure 2.8b), and reproduced in Figure 19.3a. The curve is in the form of a potential energy trough, and the equilibrium interatomic spacing at 0 K, r_0 , corresponds to the trough minimum. Heating to successively higher temperatures (T_1 , T_2 , T_3 , etc.) raises the vibrational energy from E_1 to E_2 to E_3 , and so on. The average vibrational amplitude of an atom corresponds to the trough width at each temperature, and the average interatomic distance is represented by the mean position, which increases with temperature from r_0 to r_1 to r_2 , and so on.

Thermal expansion is really due to the asymmetric curvature of this potential energy trough, rather than the increased atomic vibrational amplitudes with rising temperature. If the potential energy curve were symmetric (Figure 19.3b), there would be no net change in interatomic separation and, consequently, no thermal expansion.

For each class of materials (metals, ceramics, and polymers), the greater the atomic bonding energy, the deeper and more narrow this potential energy trough. As a result, the increase in interatomic separation with a given rise in temperature will be lower, yielding a smaller value of α_l . Table 19.1 lists the linear coefficients of thermal expansion for several materials. With regard to temperature dependence, the magnitude of the coefficient of expansion increases with rising temperature. The values in Table 19.1 are taken at room temperature unless indicated otherwise. A more comprehensive list of coefficients of thermal expansion is provided in Table B.6 of Appendix B.

Metals

As noted in Table 19.1, linear coefficients of thermal expansion for some of the common metals range between about 5×10^{-6} and $25 \times 10^{-6} (\text{°C})^{-1}$; these values are intermediate in magnitude between those for ceramic and polymeric materials. As the following Materials of Importance piece explains, several low-expansion and controlled-expansion metal alloys have been developed, which are used in applications requiring dimensional stability with temperature variations.

Ceramics

Relatively strong interatomic bonding forces are found in many ceramic materials as reflected in comparatively low coefficients of thermal expansion; values typically range between about 0.5×10^{-6} and $15 \times 10^{-6} (\text{°C})^{-1}$. For noncrystalline ceramics and also those having cubic crystal structures, α_l is isotropic. Otherwise, it is anisotropic; and, in fact, some ceramic materials, upon heating, contract in some crystallographic directions while expanding in others. For inorganic glasses, the coefficient of expansion is dependent on composition. Fused silica (high-purity SiO_2 glass) has a small expansion coefficient, $0.4 \times 10^{-6} (\text{°C})^{-1}$. This is explained by a low atomic packing density such that interatomic expansion produces relatively small macroscopic dimensional changes.

Ceramic materials that are to be subjected to temperature changes must have coefficients of thermal expansion that are relatively low, and in addition, isotropic. Otherwise, these brittle materials may experience fracture as a consequence of nonuniform dimensional changes in what is termed **thermal shock**, as discussed later in the chapter.

thermal shock

Polymers

Some polymeric materials experience very large thermal expansions upon heating as indicated by coefficients that range from approximately 50×10^{-6} to $400 \times 10^{-6} (\text{°C})^{-1}$. The highest α_l 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.



Concept Check 19.1

- (a) Explain why a brass lid ring on a glass canning jar will loosen when heated.
- (b) Suppose the ring is made of tungsten instead of brass. What will be the effect of heating the lid and jar? Why?

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

19.4 THERMAL CONDUCTIVITY

thermal conductivity

For steady-state heat flow, dependence of heat flux on the thermal conductivity and the temperature gradient

Thermal conduction is the phenomenon by which heat is transported from high- to low-temperature regions of a substance. The property that characterizes the ability of a material to transfer heat is the **thermal conductivity**. It is best defined in terms of the expression

$$q = -k \frac{dT}{dx} \quad (19.5)$$

MATERIALS OF IMPORTANCE

Invar and Other Low-Expansion Alloys

In 1896, Charles-Edouard Guillaume of France made an interesting and important discovery that earned him the 1920 Nobel Prize in Physics; his discovery: an iron–nickel alloy that has a very low (near-zero) coefficient of thermal expansion between room temperature and approximately 230°C. This material became the forerunner of a family of “low-expansion” (also sometimes called “controlled-expansion”) metal alloys. Its composition is 64 wt% Fe–36 wt% Ni, and it has been given the trade-name of “Invar” since the length of a specimen of this material is virtually invariable with changes in temperature. Its coefficient of thermal expansion near room temperature is $1.6 \times 10^{-6} (\text{°C})^{-1}$.

One might surmise that this near zero expansion is explained by a symmetrical potential energy-versus-interatomic distance curve [Figure 19.3(b)]. Such is not so; rather, this behavior relates to the magnetic characteristics of Invar. Both iron and nickel are ferromagnetic materials (Section 20.4). A ferromagnetic material may be made to form a permanent and strong magnet; upon heating, this property disappears at a specific temperature, called the “Curie temperature,” which temperature varies from one ferromagnetic material to another (Section 20.6). As a specimen of Invar is heated, its tendency to expand is counteracted by a contraction phenomenon that is associated with its ferromagnetic properties (which is termed “magnetostriction”). Above its Curie temperature (approximately 230°C), Invar expands in a normal manner, and its coefficient of thermal expansion assumes a much greater value.

Heat treating and processing of Invar will also affect its thermal expansion characteristics. The lowest α_l values result for specimens quenched from elevated temperatures (near 800°C) that are then cold worked. Annealing leads to an increase in α_l .

Other low-expansion alloys have been developed. One of these is called “Super-Invar” because its thermal expansion coefficient [$0.72 \times 10^{-6} (\text{°C})^{-1}$] is lower than the value for Invar. However, the temperature range over which its low expansion characteristics persist is relatively narrow. Compositionally, for Super-Invar some of the nickel in Invar is replaced by another ferromagnetic metal, cobalt; Super-Invar contains 63 wt% Fe, 32 wt% Ni, and 5 wt% Co.

Another such alloy, with the trade-name of “Kovar,” has been designed to have expansion characteristics close to those of borosilicate (or Pyrex) glass; when joined to Pyrex and subjected to temperature variations, thermal stresses and possible fracture at the junction are avoided. The composition of Kovar is 54 wt% Fe, 29 wt% Ni, and 17 wt% Co.

These low-expansion alloys are employed in applications that require dimensional stability with temperature fluctuations; these include the following:

- Compensating pendulums and balance wheels for mechanical clocks and watches.
- Structural components in optical and laser measuring systems that require dimensional stabilities on the order of a wavelength of light.
- Bimetallic strips that are used to actuate microswitches in water heating systems.
- Shadow masks on cathode ray tubes that are used for television and display screens; higher contrast, improved brightness, and sharper definition are possible using low-expansion materials.
- Vessels and piping for the storage and piping of liquefied natural gas.



Photograph showing tubular products that have glass-to-metal junctions. The thermal expansion coefficient of the metal alloy (Kovar) is approximately the same as that of the Pyrex glass. Thus, with changes in temperature, the likelihood of the establishment of thermal stresses and fracture at the junction are minimized. [Photograph courtesy of Moores (EVIC) Glassworks, Ltd., Walton-on-Thames, England.]

where q denotes the *heat flux*, or heat flow, per unit time per unit area (area being taken as that perpendicular to the flow direction), k is the thermal conductivity, and dT/dx is the *temperature gradient* through the conducting medium.

The units of q and k are W/m^2 ($\text{Btu/ft}^2\text{-h}$) and W/m-K ($\text{Btu/ft-h-}^\circ\text{F}$), respectively. Equation 19.5 is valid only for steady-state heat flow—that is, for situations in which the heat flux does not change with time. Also, the minus sign in the expression indicates that the direction of heat flow is from hot to cold, or down the temperature gradient.

Equation 19.5 is similar in form to Fick's first law (Equation 5.3) for steady-state diffusion. For these expressions, k is analogous to the diffusion coefficient D , and the temperature gradient parallels the concentration gradient, dC/dx .

Mechanisms of Heat Conduction

Heat is transported in solid materials by both lattice vibration waves (phonons) and free electrons. A thermal conductivity is associated with each of these mechanisms, and the total conductivity is the sum of the two contributions, or

$$k = k_l + k_e \quad (19.6)$$

where k_l and k_e represent the lattice vibration and electron thermal conductivities, respectively; usually one or the other predominates. The thermal energy associated with phonons or lattice waves is transported in the direction of their motion. The k_l contribution results from a net movement of phonons from high- to low-temperature regions of a body across which a temperature gradient exists.

Free or conducting electrons participate in electronic thermal conduction. To the free electrons in a hot region of the specimen is imparted a gain in kinetic energy. They then migrate to colder areas, where some of this kinetic energy is transferred to the atoms themselves (as vibrational energy) as a consequence of collisions with phonons or other imperfections in the crystal. 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 transfer process.

Metals

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. The thermal conductivities of several of the common metals are given in Table 19.1; values generally range between about 20 and 400 W/m-K .

Since free electrons are responsible for both electrical and thermal conduction in pure metals, theoretical treatments suggest that the two conductivities should be related according to the *Wiedemann–Franz law*:

$$L = \frac{k}{\sigma T} \quad (19.7)$$

where σ is the electrical conductivity, T is the absolute temperature, and L is a constant. The theoretical value of L , $2.44 \times 10^{-8} \text{ } \Omega\text{-W}/(\text{K})^2$, should be independent of temperature and the same for all metals if the heat energy is transported entirely by free electrons. Included in Table 19.1 are the experimental L values for these

Weidemann-Franz law—for metals, the ratio of thermal conductivity and the product of the electrical conductivity and temperature should be a constant

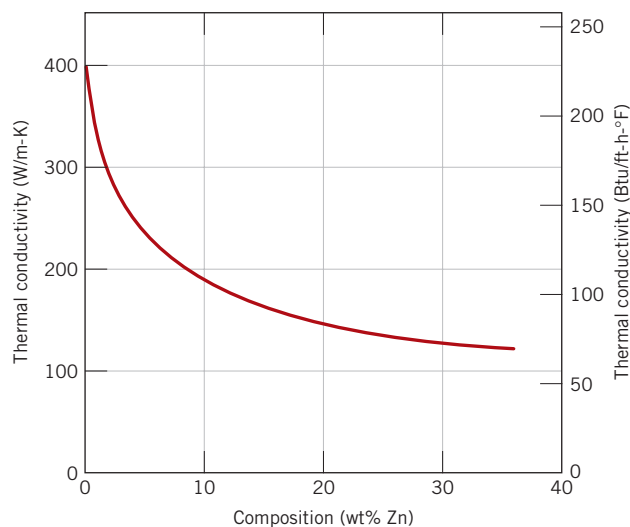


Figure 19.4 Thermal conductivity versus composition for copper–zinc alloys. [Adapted from *Metals Handbook: Properties and Selection: Nonferrous Alloys and Pure Metals*, Vol. 2, 9th edition, H. Baker (Managing Editor), American Society for Metals, 1979, p. 315.]

several metals; note that the agreement between these and the theoretical value is quite reasonable (well within a factor of 2).

Alloying metals with impurities results in a reduction in the thermal conductivity, for the same reason that the electrical conductivity is diminished (Section 18.8); namely, the impurity atoms, especially if in solid solution, act as scattering centers, lowering the efficiency of electron motion. A plot of thermal conductivity versus composition for copper–zinc alloys (Figure 19.4) displays this effect.



Concept Check 19.2

The thermal conductivity of a plain carbon steel is greater than for a stainless steel. Why is this so? *Hint:* you may want to consult Section 11.2.

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

Ceramics

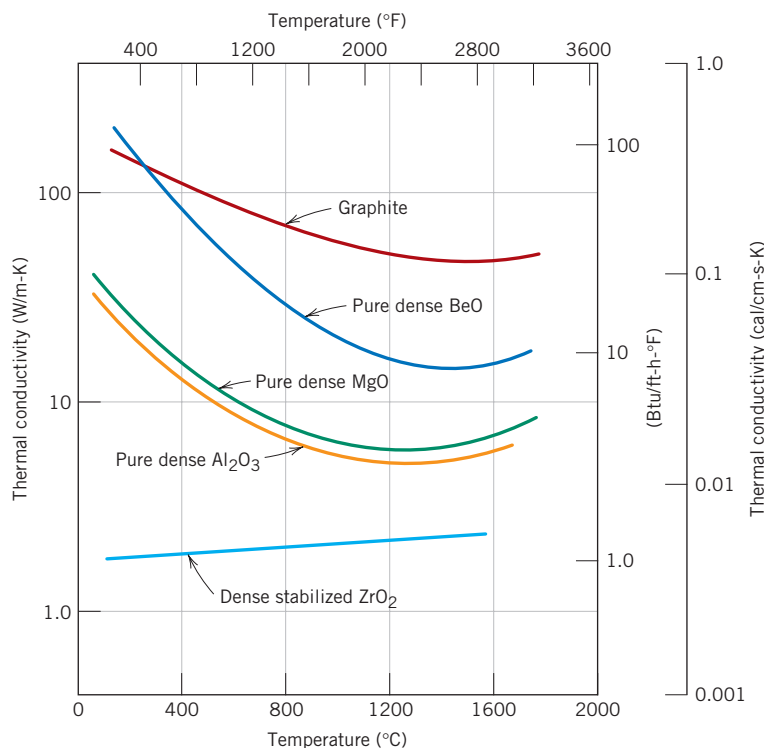
Nonmetallic materials are thermal insulators inasmuch as they lack large numbers of free electrons. Thus the phonons are primarily responsible for thermal conduction: k_e is much smaller than k_l . Again, the phonons are not as effective as free electrons in the transport of heat energy as a result of the very efficient phonon scattering by lattice imperfections.

Thermal conductivity values for a number of ceramic materials are contained in Table 19.1; room-temperature thermal conductivities range between approximately 2 and 50 W/m-K. 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.

The scattering of lattice vibrations becomes more pronounced with rising temperature; hence, the thermal conductivity of most ceramic materials normally diminishes with increasing temperature, at least at relatively low temperatures (Figure 19.5). As Figure 19.5 indicates, the conductivity begins to increase at higher temperatures, which is due to radiant heat transfer: significant quantities of infrared radiant heat may be transported through a transparent ceramic material. The efficiency of this process increases with temperature.

Figure 19.5

Dependence of thermal conductivity on temperature for several ceramic materials. (Adapted from W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd edition. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)



Porosity in ceramic materials may have a dramatic influence on thermal conductivity; increasing the pore volume will, under most circumstances, result in a reduction of the thermal conductivity. In fact, 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-K. Furthermore, gaseous convection within the pores is also comparatively ineffective.



Concept Check 19.3

The thermal conductivity of a single-crystal ceramic specimen is slightly greater than a polycrystalline one of the same material. Why is this so?

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

Polymers

As noted in Table 19.1, thermal conductivities for most polymers are on the order of 0.3 W/m-K. For these materials, energy transfer is accomplished by the vibration and rotation of the chain molecules. The magnitude of the thermal conductivity depends on the degree of crystallinity; a 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.

Polymers are often utilized as thermal insulators because of their low thermal conductivities. As with ceramics, their insulative properties may be further enhanced by the introduction of small pores, which are ordinarily introduced by foaming

during polymerization (Section 15.18). Foamed polystyrene (Styrofoam) is commonly used for drinking cups and insulating chests.



Concept Check 19.4

Which of a linear polyethylene ($\bar{M}_n = 450,000$ g/mol) and a lightly branched polyethylene ($\bar{M}_n = 650,000$ g/mol) has the higher thermal conductivity? Why? *Hint:* you may want to consult Section 14.11.

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]



Concept Check 19.5

Explain why, on a cold day, the metal door handle of an automobile feels colder to the touch than a plastic steering wheel, even though both are at the same temperature.

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

19.5 THERMAL STRESSES

thermal stress

Thermal stresses are stresses induced in a body as a result of changes in temperature. An understanding of the origins and nature of thermal stresses is important because these stresses can lead to fracture or undesirable plastic deformation.

Stresses Resulting From Restrained Thermal Expansion and Contraction

Let us first consider a homogeneous and isotropic solid rod that is heated or cooled uniformly; that is, no temperature gradients are imposed. For free expansion or contraction, the rod will be stress free. If, however, axial motion of the rod is restrained by rigid end supports, thermal stresses will be introduced. The magnitude of the stress σ resulting from a temperature change from T_0 to T_f is

$$\sigma = E\alpha_l(T_0 - T_f) = E\alpha_l\Delta T \quad (19.8)$$

where E is the modulus of elasticity and α_l is the linear coefficient of thermal expansion. Upon heating ($T_f > T_0$), the stress is compressive ($\sigma < 0$), since rod expansion has been constrained. Of course, if the rod specimen is cooled ($T_f < T_0$), a tensile stress will be imposed ($\sigma > 0$). Also, the stress in Equation 19.8 is the same as the stress that would be required to elastically compress (or elongate) the rod specimen back to its original length after it had been allowed to freely expand (or contract) with the $T_0 - T_f$ temperature change.

Dependence of thermal stress on elastic modulus, linear coefficient of thermal expansion, and temperature change

EXAMPLE PROBLEM 19.1

Thermal Stress Created Upon Heating

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 (25,000 psi)? Assume a modulus of elasticity of 100 GPa (14.6×10^6 psi) for brass.

Solution

Use Equation 19.8 to solve this problem, where the stress of 172 MPa is taken to be negative. Also, the initial temperature T_0 is 20°C, and the magnitude of the linear coefficient of thermal expansion from Table 19.1 is $20.0 \times 10^{-6} (\text{°C})^{-1}$. Thus, solving for the final temperature T_f yields

$$\begin{aligned} T_f &= T_0 - \frac{\sigma}{E\alpha_l} \\ &= 20^\circ\text{C} - \frac{-172 \text{ MPa}}{(100 \times 10^3 \text{ MPa})[20 \times 10^{-6} (\text{°C})^{-1}]} \\ &= 20^\circ\text{C} + 86^\circ\text{C} = 106^\circ\text{C} \text{ (223°F)} \end{aligned}$$

Stresses Resulting From Temperature Gradients

When a solid body is heated or cooled, the internal temperature distribution will depend on its size and shape, the thermal conductivity of the material, and the rate of temperature change. Thermal stresses may be established as a result of temperature gradients across a body, which are frequently caused by rapid heating or cooling, in that the outside changes temperature more rapidly than the interior; differential dimensional changes serve to restrain the free expansion or contraction of adjacent volume elements within the piece. For example, upon heating, the exterior of a specimen is hotter and, therefore, will have expanded more than the interior regions. Hence, compressive surface stresses are induced and are balanced by tensile interior stresses. The interior–exterior stress conditions are reversed for rapid cooling such that the surface is put into a state of tension.

Thermal Shock of Brittle Materials

For ductile metals and polymers, alleviation of thermally induced stresses may be accomplished by plastic deformation. However, the nonductility of most ceramics enhances the possibility of brittle fracture from these stresses. Rapid cooling of a brittle body is more likely to inflict such thermal shock than heating, since the induced surface stresses are tensile. Crack formation and propagation from surface flaws are more probable when an imposed stress is tensile (Section 12.8).

The capacity of a material to withstand this kind of failure is termed its *thermal shock resistance*. For a ceramic body that is rapidly cooled, the resistance to thermal shock depends not only on the magnitude of the temperature change, but also on the mechanical and thermal properties of the material. The thermal shock resistance is best for ceramics that have high fracture strengths σ_f and high thermal conductivities, as well as low moduli of elasticity and low coefficients of thermal expansion. The resistance of many materials to this type of failure may be approximated by a thermal shock resistance parameter *TSR*:

$$TSR \cong \frac{\sigma_f k}{E\alpha_l} \quad (19.9)$$

Definition of
thermal shock
resistance parameter

Thermal shock may be prevented by altering the external conditions to the degree that cooling or heating rates are reduced and temperature gradients across a body are minimized. Modification of the thermal and/or mechanical characteristics in Equation 19.9 may also enhance the thermal shock resistance of a material. Of

these parameters, the coefficient of thermal expansion is probably most easily changed and controlled. For example, common soda–lime glasses, which have an α_l of approximately $9 \times 10^{-6} (\text{°C})^{-1}$, are particularly susceptible to thermal shock, as anyone who has baked can probably attest. Reducing the CaO and Na₂O contents while at the same time adding B₂O₃ in sufficient quantities to form borosilicate (or Pyrex) glass will reduce the coefficient of expansion to about $3 \times 10^{-6} (\text{°C})^{-1}$; this material is entirely suitable for kitchen oven heating and cooling cycles. The introduction of some relatively large pores or a ductile second phase may also improve the thermal shock characteristics of a material; both serve to impede the propagation of thermally induced cracks.

It is often necessary to remove thermal stresses in ceramic materials as a means of improving their mechanical strengths and optical characteristics. This may be accomplished by an annealing heat treatment, as discussed for glasses in Section 13.9.

SUMMARY

Heat Capacity

This chapter discussed heat absorption, thermal expansion, and thermal conduction—three important thermal phenomena. Heat capacity represents the quantity of heat required to produce a unit rise in temperature for one mole of a substance; on a per-unit mass basis, it is termed specific heat. Most of the energy assimilated by many solid materials is associated with increasing the vibrational energy of the atoms; contributions to the total heat capacity by other energy-absorptive mechanisms (i.e., increased free-electron kinetic energies) are normally insignificant.

For many crystalline solids and at temperatures within the vicinity of 0 K, the heat capacity measured at constant volume varies as the cube of the absolute temperature; in excess of the Debye temperature, C_v becomes temperature independent, assuming a value of approximately $3R$.

Thermal Expansion

Solid materials expand when heated and contract when cooled. The fractional change in length is proportional to the temperature change, the constant of proportionality being the coefficient of thermal expansion. Thermal expansion is reflected by an increase in the average interatomic separation, which is a consequence of the asymmetric nature of the potential energy versus interatomic spacing curve trough. The larger the interatomic bonding energy, the lower is the coefficient of thermal expansion.

Thermal Conductivity

The transport of thermal energy from high- to low-temperature regions of a material is termed thermal conduction. For steady-state heat transport, the flux is proportional to the temperature gradient along the direction of flow; the proportionality constant is the thermal conductivity.

For solid materials, heat is transported by free electrons and by vibrational lattice waves, or phonons. The high thermal conductivities for relatively pure metals are due to the large numbers of free electrons, and also the efficiency with which these electrons transport thermal energy. By way of contrast, ceramics and polymers are poor thermal conductors because free-electron concentrations are low and phonon conduction predominates.

Thermal Stresses

Thermal stresses, which are introduced in a body as a consequence of temperature changes, may lead to fracture or undesirable plastic deformation. The two prime sources of thermal stresses are restrained thermal expansion (or contraction) and temperature gradients established during heating or cooling.

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.

IMPORTANT TERMS AND CONCEPTS

Heat capacity
Linear coefficient of thermal expansion
Phonon

Specific heat
Thermal conductivity

Thermal shock
Thermal stress

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QUESTIONS AND PROBLEMS

Heat Capacity

- 19.1** Estimate the energy required to raise the temperature of 5 kg (11.0 lb_m) of the following materials from 20 to 150°C (68 to 300°F): aluminum, brass, aluminum oxide (alumina), and polypropylene.
- 19.2** 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?
- 19.3** (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?
- 19.4** For copper, the heat capacity at constant volume C_v at 20 K is 0.38 J/mol-K, and the Debye temperature is 340 K. Estimate the specific heat (a) at 40 K and (b) at 400 K.

- 19.5** The constant A in Equation 19.2 is $12\pi^4 R/5\theta_D^3$, where R is the gas constant and θ_D is the Debye temperature (K). Estimate θ_D for aluminum, given that the specific heat is 4.60 J/kg-K at 15 K.

- 19.6** (a) Briefly explain why C_v rises with increasing temperature at temperatures near 0 K. (b) Briefly explain why C_v becomes virtually independent of temperature at temperatures far removed from 0 K.

Thermal Expansion

- 19.7** A bimetallic strip is constructed from strips of two different metals that are bonded along their lengths. Explain how such a device may be used in a thermostat to regulate temperature.
- 19.8** 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?

- 19.9** A 0.4 m (15.7 in.) rod of a metal elongates 0.48 mm (0.019 in.) on heating from 20 to 100°C (68 to 212°F). Determine the value of the linear coefficient of thermal expansion for this material.
- 19.10** Briefly explain thermal expansion using the potential energy-versus-interatomic spacing curve.
- 19.11** 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 $3\alpha_l$.
- 19.12** When a metal is heated its density decreases. There are two sources that give rise to this diminishment of ρ : (1) the thermal expansion of the solid, and (2) the formation of vacancies (Section 4.2). Consider a specimen of gold at room temperature (20°C) that has a density of 19.320 g/cm³. **(a)** Determine its density upon heating to 800°C when only thermal expansion is considered. **(b)** Repeat the calculation when the introduction of vacancies is taken into account. Assume that the energy of vacancy formation is 0.98 eV/atom, and that the volume coefficient of thermal expansion, α_v is equal to $3\alpha_l$.
- 19.13** The difference between the specific heats at constant pressure and volume is described by the expression

$$c_p - c_v = \frac{\alpha_v^2 v_0 T}{\beta} \quad (19.10)$$

where α_v is the volume coefficient of thermal expansion, v_0 is the specific volume (i.e., volume per unit mass, or the reciprocal of density), β is the compressibility, and T is the absolute temperature. Compute the values of c_v at room temperature (293 K) for aluminum and iron using the data in Table 19.1, assuming that $\alpha_v = 3\alpha_l$ and given that the values of β for Al and Fe are 1.77×10^{-11} and 2.65×10^{-12} (Pa)⁻¹, respectively.

- 19.14** 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.

Thermal Conductivity

- 19.15** **(a)** Calculate the heat flux through a sheet of brass 7.5 mm (0.30 in.) thick if the temperatures at the two faces are 150 and 50°C (302 and 122°F); assume steady-state heat flow. **(b)** What is the heat loss per hour if the area of the sheet is 0.5 m² (5.4 ft²)? **(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 (0.59 in.).
- 19.16** **(a)** Would you expect Equation 19.7 to be valid for ceramic and polymeric materials? Why or why not? **(b)** Estimate the value for the Wiedemann–Franz constant L [in $\Omega\text{-W}/(\text{K})^2$] at room temperature (293 K) for the following nonmetals: zirconia (3 mol% Y₂O₃), diamond (synthetic), gallium arsenide (intrinsic), poly(ethylene terephthalate) (PET), and silicone. Consult Tables B.7 and B.9 in Appendix B.
- 19.17** Briefly explain why the thermal conductivities are higher for crystalline than noncrystalline ceramics.
- 19.18** Briefly explain why metals are typically better thermal conductors than ceramic materials.
- 19.19** **(a)** Briefly explain why porosity decreases the thermal conductivity of ceramic and polymeric materials, rendering them more thermally insulative. **(b)** Briefly explain how the degree of crystallinity affects the thermal conductivity of polymeric materials and why.
- 19.20** For some ceramic materials, why does the thermal conductivity first decrease and then increase with rising temperature?
- 19.21** For each of the following pairs of materials, decide which has the larger thermal conductivity. Justify your choices.
- (a)** Pure silver; sterling silver (92.5 wt% Ag–7.5 wt% Cu).
- (b)** Fused silica; polycrystalline silica.
- (c)** Linear and syndiotactic poly(vinyl chloride) ($DP = 1000$); linear and syndiotactic polystyrene ($DP = 1000$).
- (d)** Atactic polypropylene ($\bar{M}_w = 10^6$ g/mol); isotactic polypropylene ($\bar{M}_w = 5 \times 10^5$ g/mol).

19.22 We might think of a porous material as being a composite wherein one of the phases is a pore phase. Estimate upper and lower limits for the room-temperature thermal conductivity of an aluminum oxide material having a volume fraction of 0.25 of pores that are filled with still air.

19.23 Nonsteady-state heat flow may be described by the following partial differential equation:

$$\frac{\partial T}{\partial t} = D_T \frac{\partial^2 T}{\partial x^2}$$

where D_T is the thermal diffusivity; this expression is the thermal equivalent of Fick's second law of diffusion (Equation 5.4b). The thermal diffusivity is defined according to

$$D_T = \frac{k}{\rho c_p}$$

In this expression, k , ρ , and c_p represent the thermal conductivity, the mass density, and the specific heat at constant pressure, respectively.

(a) What are the SI units for D_T ?

(b) Determine values of D_T for copper, brass, magnesia, fused silica, polystyrene, and polypropylene using the data in Table 19.1. Density values are included in Table B.1, Appendix B. (*Note:* the density of magnesia (MgO) is 3.58 g/cm³.)

Thermal Stresses

19.24 Beginning with Equation 19.3, show that Equation 19.8 is valid.

19.25 (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?

19.26 (a) If a rod of brass 0.35 m (13.8 in.) long is heated from 15 to 85°C (60 to 185°F) 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 (39.4 in.) long is used? **(c)** If the rod in part (a) is cooled from 15°C to −15°C (60°F to 5°F), what type and magnitude of stress will result?

19.27 A steel wire is stretched with a stress of 70 MPa (10,000 psi) at 20°C (68°F). If the length is held constant, to what temperature must the wire be heated to reduce the stress to 17 MPa (2500 psi)?

19.28 If a cylindrical rod of brass 150.00 mm long and 10.000 mm in diameter is heated from 20°C to 160°C while its ends are maintained rigid, determine its change in diameter. You may want to consult Table 6.1.

19.29 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 70°C, to what temperature must it be cooled in order to have a 0.023-mm reduction in diameter?

19.30 What measures may be taken to reduce the likelihood of thermal shock of a ceramic piece?

DESIGN PROBLEMS

Thermal Expansion

19.D1 Railroad tracks made of 1025 steel are to be laid during the time of year when the temperature averages 4°C (40°F). If a joint space of 5.4 mm (0.210 in.) is allowed between the standard 11.9-m (39-ft) long rails, what is the hottest possible temperature that can be tolerated without the introduction of thermal stresses?

Thermal Stresses

19.D2 The ends of a cylindrical rod 6.4 mm (0.25 in.) in diameter and 250 mm (10 in.) long are mounted between rigid supports. The rod is stress free at room temperature [20°C (68°F)]; and upon cooling to −60°C (−76°F), a maximum thermally induced tensile stress of 138 MPa (20,000 psi) is possible. Of which of the following metals

or alloys may the rod be fabricated: aluminum, copper, brass, 1025 steel, and tungsten? Why?

19.D3 (a) What are the units for the thermal shock resistance parameter (*TSR*)? **(b)** Rank the following ceramic materials according to their thermal shock resistance: soda–lime glass, fused silica, and silicon [$\langle 100 \rangle$ direction and $\{100\}$ orientation, as-cut surface]. Appropriate data may be found in Tables B.2, B.4, B.6, and B.7 of Appendix B.

19.D4 Equation 19.9, for the thermal shock resistance of a material, is valid for relatively low

rates of heat transfer. When the rate is high, then, upon cooling of a body, the maximum temperature change allowable without thermal shock, ΔT_f , is approximately

$$\Delta T_f \cong \frac{\sigma_f}{E\alpha_l}$$

where σ_f is the fracture strength. Using the data in Tables B.2, B.4, and B.6 (Appendix B), determine ΔT_f for a soda–lime glass, borosilicate (Pyrex) glass, aluminum oxide (96% pure), and gallium arsenide [$\langle 100 \rangle$ direction and $\{100\}$ orientation, as-cut surface].