Chapter 19:
Thermal Properties

ISSUES TO ADDRESS...

- How do **materials respond to the application of heat**?

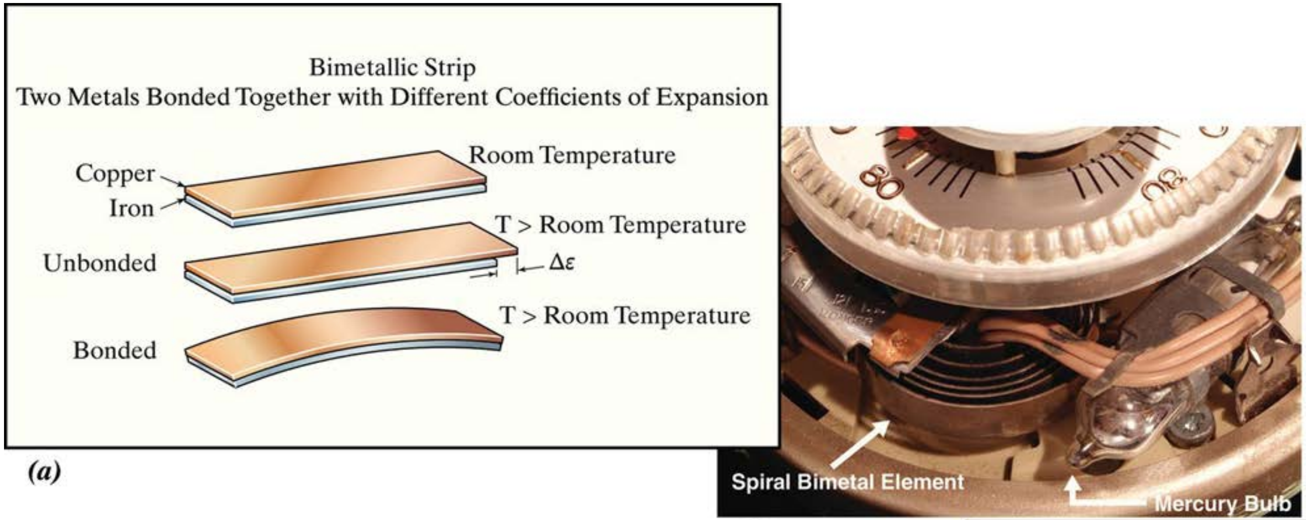
- How do we define and measure...
  -- heat capacity?
  -- thermal expansion?
  -- thermal conductivity?
  -- thermal shock resistance?

- How do the thermal properties of ceramics, metals, and polymers differ?

- **1. Introduction**
- **2. Heat Capacity**
- **3. Thermal Expansion**
- **4. Thermal Conductivity**
- **5. Thermal Stresses**
- **Summary**

1. Introduction

- Thermal property refers to 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 temp. gradients exist. (Zeroth law of thermodynamics)
- Heat capacity, thermal expansion, thermal conductivity are important



(a)

(b)

© Steven Langerman

Thermostat
– a device used to regulate temperature

Use the phenomenon of thermal expansion

(c)

© Kameleon007/iStockphoto

The consequence of unseasonably
high temperatures on July 24, 1978

(d)

ASSOCIATED PRESS/© AP/Wide World Photos

Heat Capacity

The ability of a material to absorb heat; ratio of energy change and the resulting temperature change.

- 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.

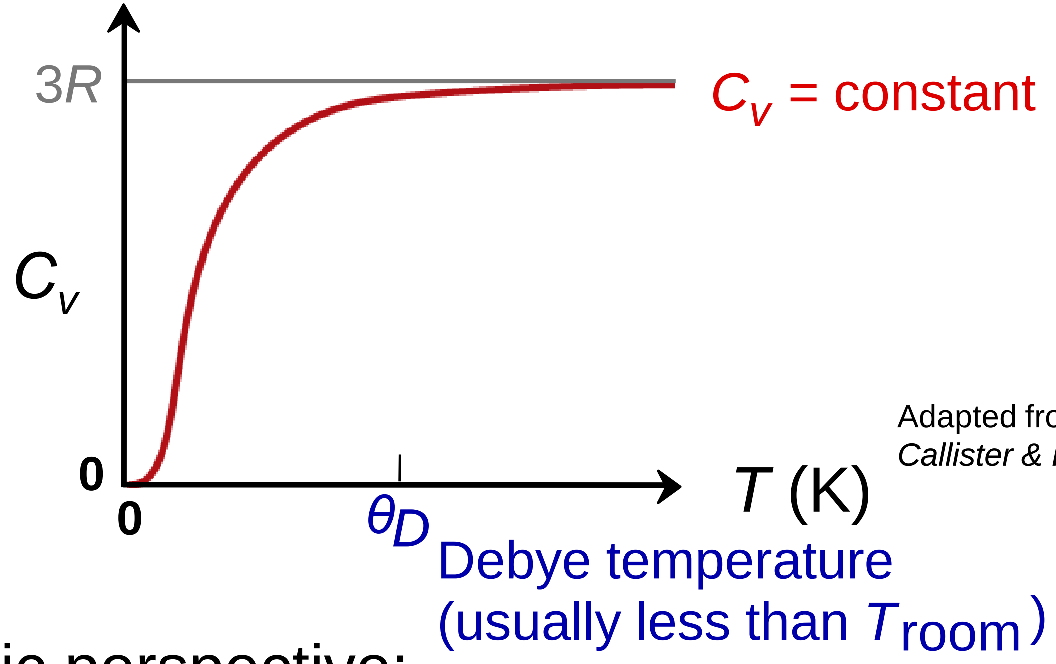
  C_p usually > C_v

- Heat capacity has units of $\frac{\text{J}}{\text{mol}\cdot\text{K}}$ $\left(\frac{\text{Btu}}{\text{lb}-\text{mol}\cdot{}^{\circ}\text{F}}\right)$

Dependence of Heat Capacity on Temperature

- Heat capacity...
  - -- increases with temperature
  - -- for solids it reaches a limiting value of $3R$

R = gas constant
= 8.31 J/mol-K



Adapted from Fig. 19.2, *Callister & Rethwisch 10e*.

- From atomic perspective:
  - -- Energy is stored as atomic vibrations.
  - -- As temperature increases, the average energy of atomic vibrations increases.

Atomic Vibrations

Atomic vibrations are in the form of lattice waves or phonons

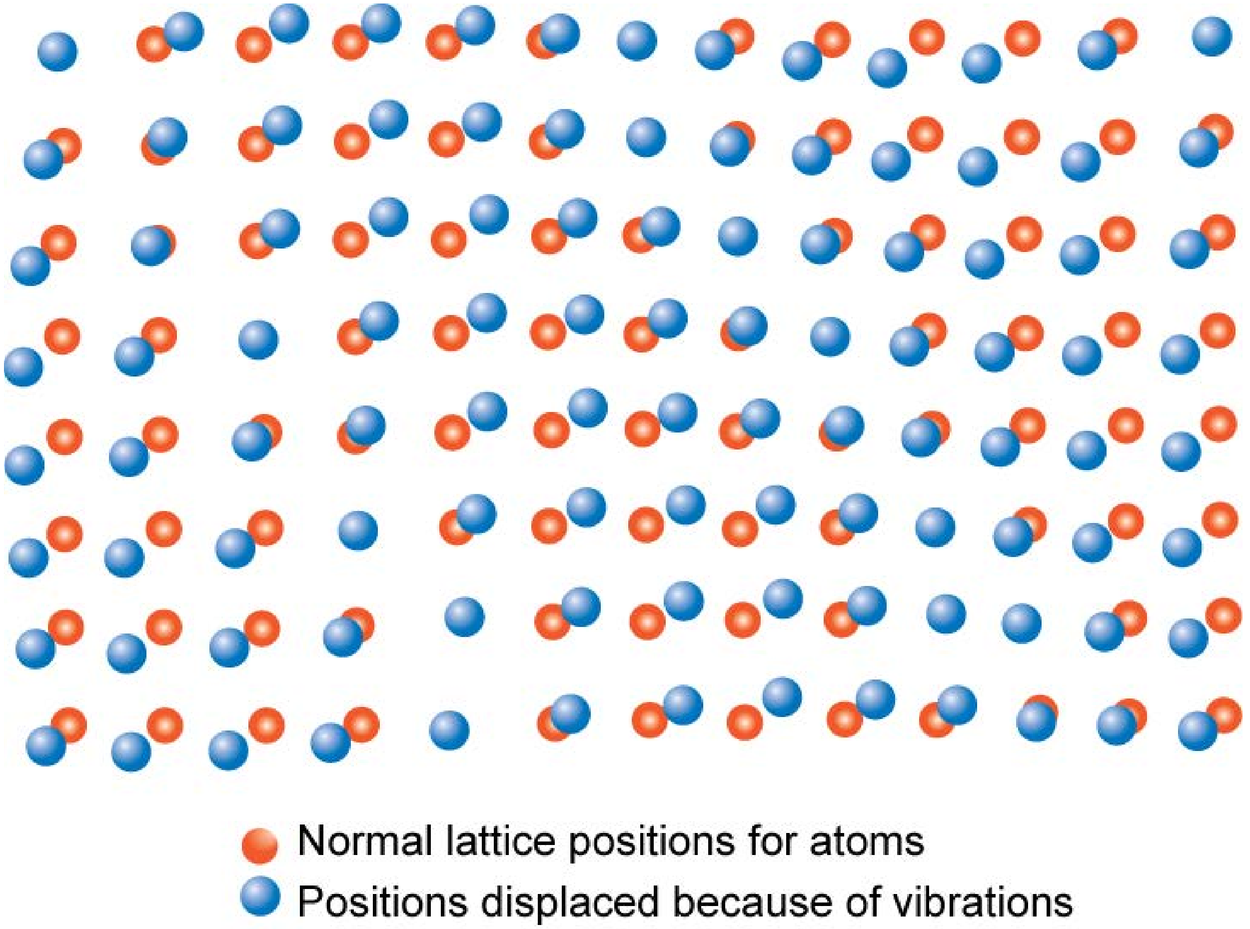
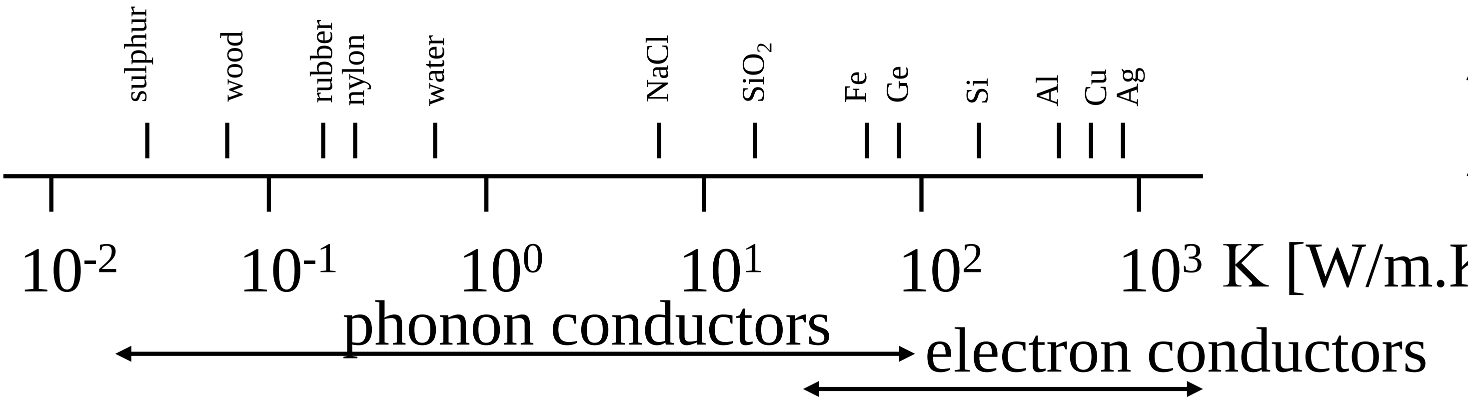
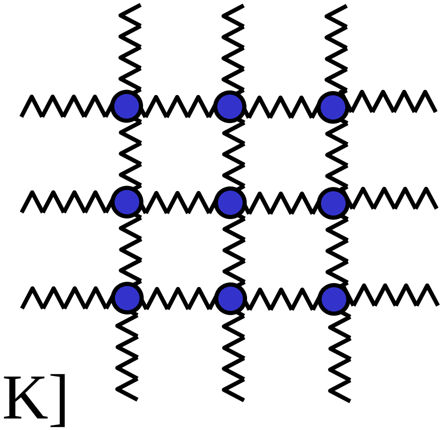


Fig. 19.1, *Callister & Rethwisch 10e*. (Adapted from "The Thermal Properties of Materials" by J. Ziman. Copyright © 1967 by Scientific American, Inc. All rights reserved.)

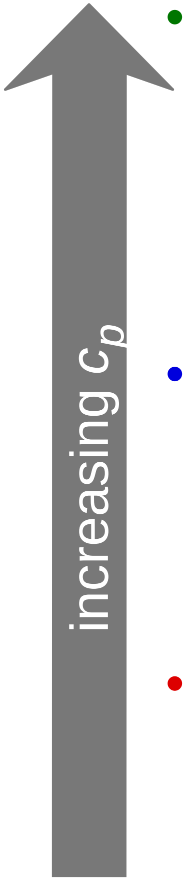
Phonons

- In 1932 Soviet physicist Igor Tamm proposed that the energies of the “atomic oscillators” was quantized, called phonons
- When we think of atoms vibrating due to their thermal energy, we assumed they moved independently
- However, ∵bonding, ∴the motions are connected
  - – leading to a wave behavior
- Materials are divided into phonon conductors and electron conductors of heat:





Specific Heat: Comparison



Material	c_p (J/kg-K) at room T
• Polymers	
Polypropylene	1925
Polyethylene	1850
Polystyrene	1170
Teflon	1050
• Ceramics	
Magnesia (MgO)	940
Alumina (Al_2O_3)	775
Glass	840
• Metals	
Aluminum	900
Steel	486
Tungsten	138
Gold	128

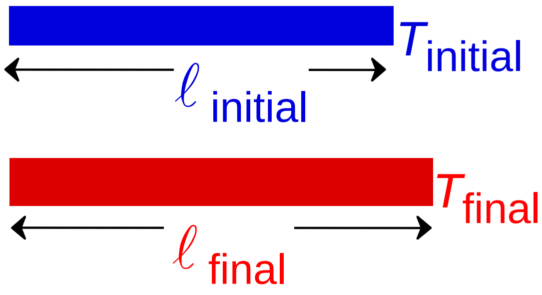
c_p (specific heat): (J/kg-K)
C_p (heat capacity): (J/mol-K)

- Why is c_p significantly larger for polymers?

Selected values from Table 19.1, *Callister & Rethwisch 10e*.

Thermal Expansion

Materials change size when temperature is changed

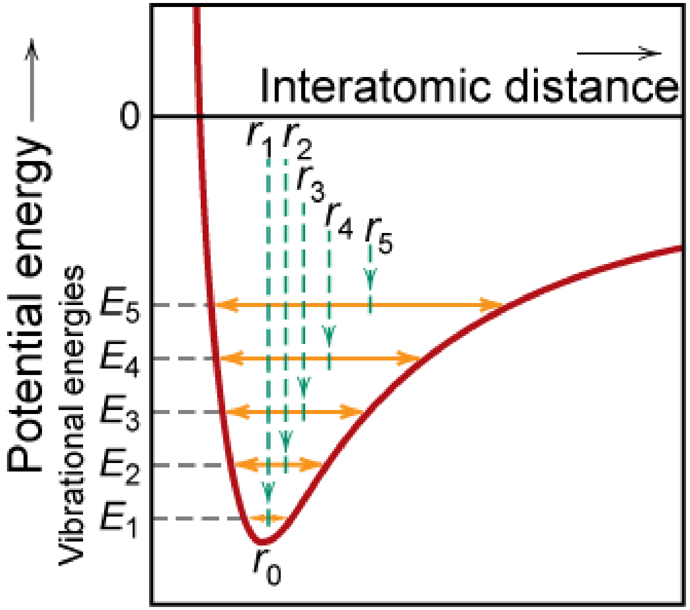


$T_{\text{final}} > T_{\text{initial}}$

$$\frac{\ell_{\text{final}} - \ell_{\text{initial}}}{\ell_{\text{initial}}} = \alpha_{\ell}(T_{\text{final}} - T_{\text{initial}})$$

linear coefficient of thermal expansion (1/K or 1/° C)

Atomic Perspective: Thermal Expansion

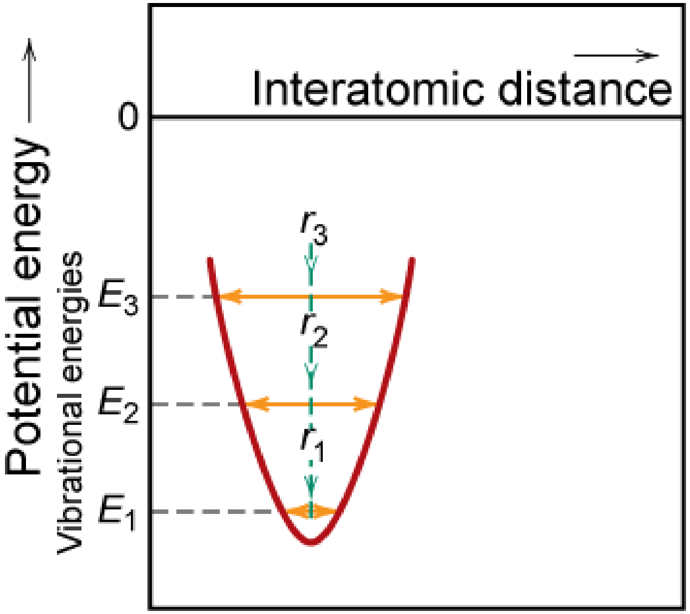


Asymmetric curve:

-- increase temperature,

-- increase in interatomic separation

-- thermal expansion



Symmetric curve:

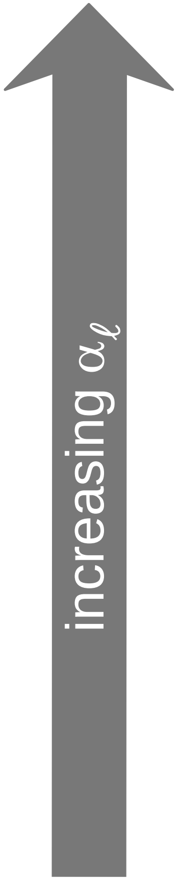
-- increase temperature,

-- no increase in interatomic separation

-- no thermal expansion

Fig. 19.3, *Callister & Rethwisch 10e*. (Adapted from R. M. Rose, L. A. Shepard, and J. Wulff, The Structure and Properties of Materials, Vol. IV, Electronic Properties, John Wiley & Sons, 1966. Reproduced with permission of Robert M. Rose.)

Coefficient of Thermal Expansion: Comparison



Material	α_ℓ $(10^{-6}/°\mathrm{C})$ at room T
• Polymers	
Polypropylene	145-180
Polyethylene	106-198
Polystyrene	90-150
Teflon	126-216
• Metals	
Aluminum	23.6
Steel	12
Tungsten	4.5
Gold	14.2
• Ceramics	
Magnesia (MgO)	13.5
Alumina (Al_2O_3)	7.6
Soda-lime glass	9
Silica (cryst. SiO_2)	0.4

Polymers have larger α_ℓ values because of weak secondary bonds

- **Q: Why does α_ℓ generally decrease with increasing bond energy?**

Selected values from Table 19.1, *Callister & Rethwisch 10e*.

Thermal Expansion: Example

Ex: A copper wire 15 m long is cooled from 40 to -9° C. How much change in length will it experience?

- Answer: For Cu $\alpha_\ell = 16.5 \text{ x } 10^{-6}\ (°\text{C})^{-1}$

rearranging Equation 17.3b

$$\Delta\ell = \alpha_\ell \ell_0 \Delta T = [16.5 \text{ x } 10^{-6} (1/°\text{C})](15 \text{ m})\,[40°\text{C} - (-9°\text{C})]$$

$$\boxed{\Delta\ell = 0.012 \text{ m} = 12 \text{ mm}}$$

Invar (Fe-Ni alloys) and

other low-expansion alloys (Be-Cu-Fe alloys), Gluecydur

Courtesy of Montres Breguet SA Switzerland

Figun_20_p741

Thermal Conductivity

The ability of a material to transport heat.

Fourier's Law

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

heat flux (J/m^2•s)

temperature gradient

thermal conductivity (J/m•K•s)

$T_2 > T_1$

- Atomic perspective: Atomic vibrations and free electrons in hotter regions transport energy to cooler regions.

$$k = k_l + k_e$$

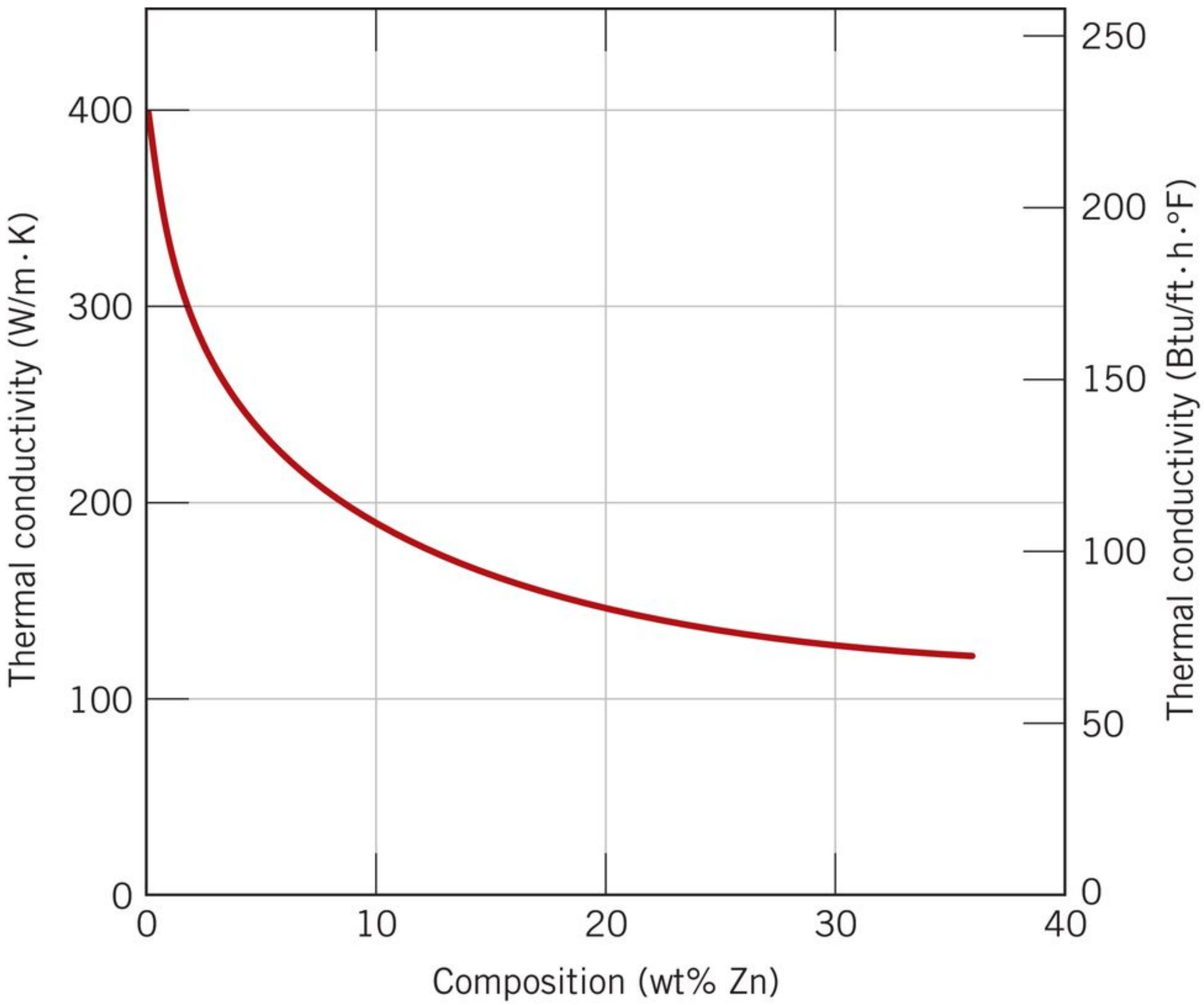
Thermal Conductivity: Comparison

increasing *k*

Material	*k* (W/m-K)	Energy Transfer Mechanism
Metals		
Aluminum	247	atomic vibrations and motion of free electrons
Steel	52	
Tungsten	178	
Gold	315	
Ceramics		
Magnesia (MgO)	38	atomic vibrations
Alumina (Al_2O_3)	39	
Soda-lime glass	1.7	
Silica (cryst. SiO_2)	1.4	
Polymers		
Polypropylene	0.12	vibration/rotation of chain molecules
Polyethylene	0.46-0.50	
Polystyrene	0.13	
Teflon	0.25	

Selected values from Table 19.1, *Callister & Rethwisch 10e*.

Thermal conductivity versus composition of Cu-Zn alloys



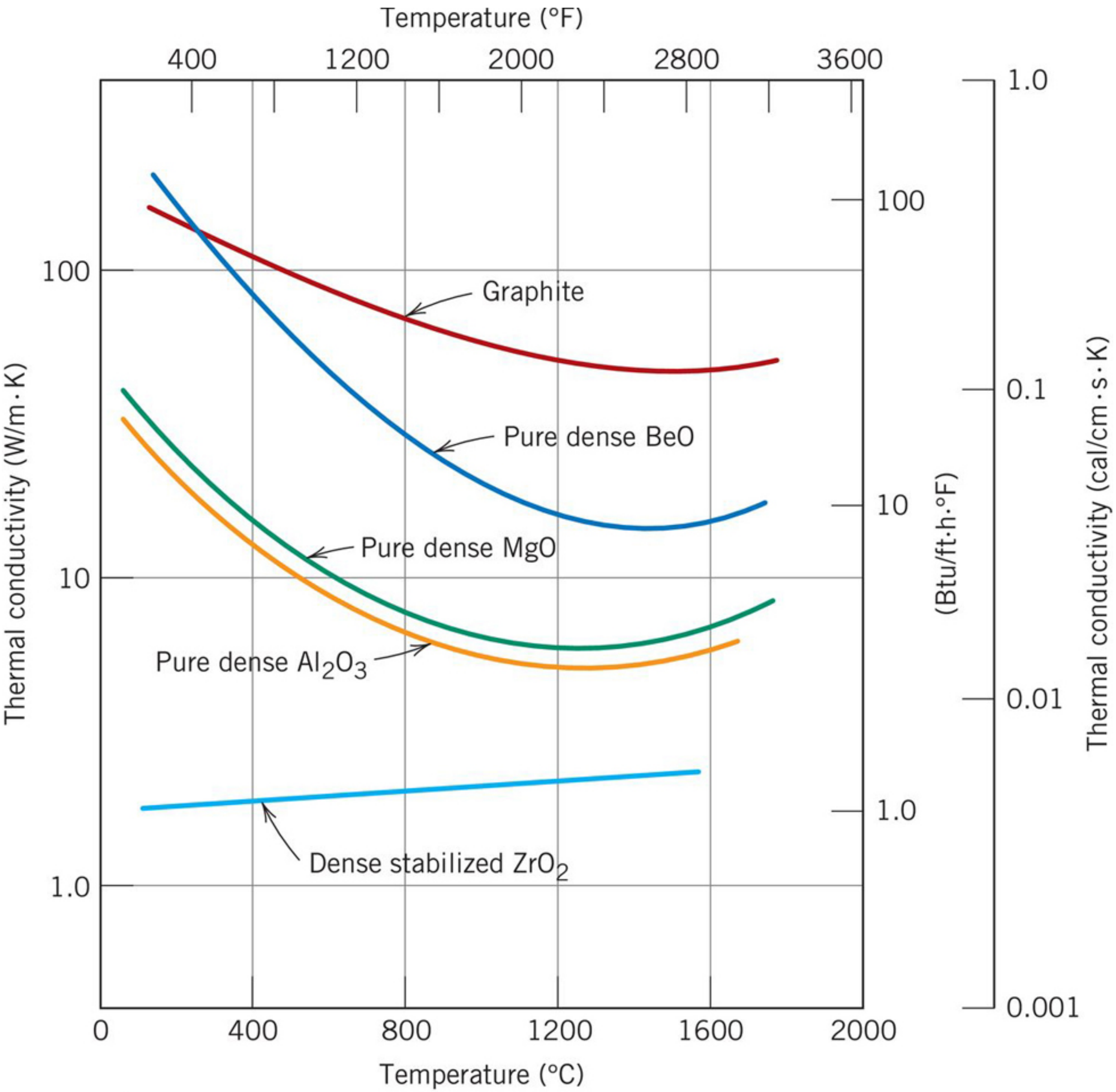
Adapted from *Metals Handbook: Properties and Selection: Nonferrous Alloys and Pure Metals,* Vol. 2, 9th edition, H. Baker (Managing Editor), 1979. Reproduced by permission of ASM International, Materials Park, OH.

WILEY

Wiedemann-Franz law

- For metals, the ratio of thermal conductivity and the product of the electrical conductivity and temperature should be a constant
- $L = k / (\sigma T) = 2.44 \times 10^{-8}\ \Omega.W/K^2$

- Because free electrons are responsible for both electrical and thermal conductivity for pure metals.



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.

Thermal Stresses

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

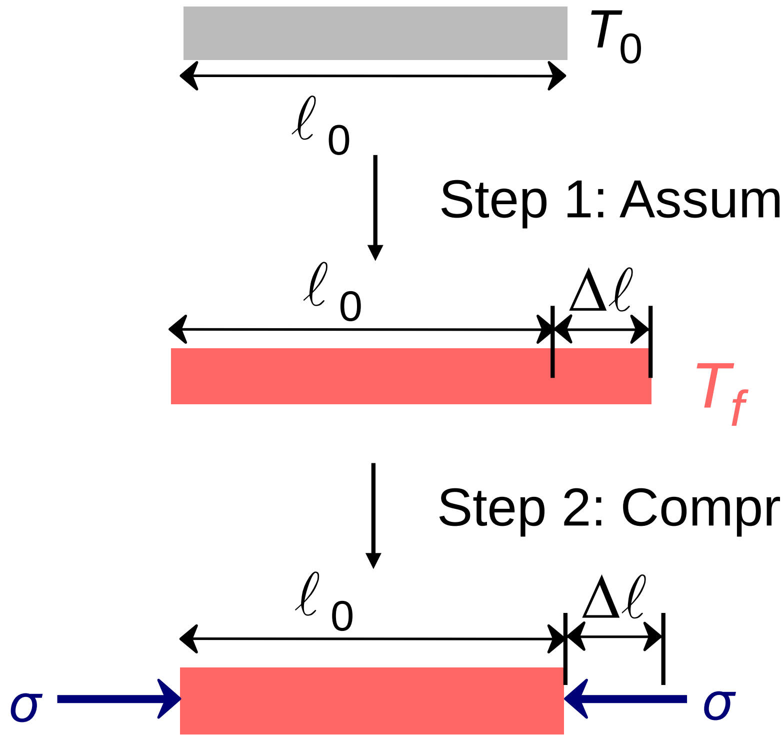
Thermal stress $= \sigma$

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

Example Problem

-- A brass rod is stress-free at room temperature (20° C).
-- It is heated up, but prevented from lengthening.
-- At what temperature does the stress reach -172 MPa?

Solution:



Original conditions

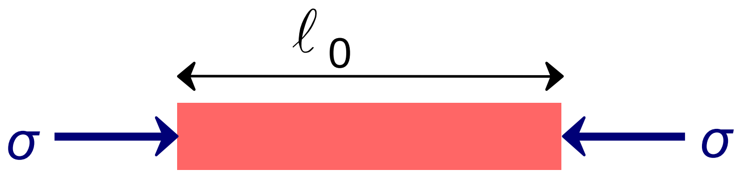
Step 1: Assume unconstrained thermal expansion

$$\frac{\Delta \ell}{\ell_{\text{room}}} = \varepsilon_{\text{thermal}} = \alpha_{\ell}(T_f - T_0)$$

Step 2: Compress specimen back to original length

$$\varepsilon_{\text{compress}} = \frac{-\Delta \ell}{\ell_{\text{room}}} = -\varepsilon_{\text{thermal}}$$

Example Problem (cont.)



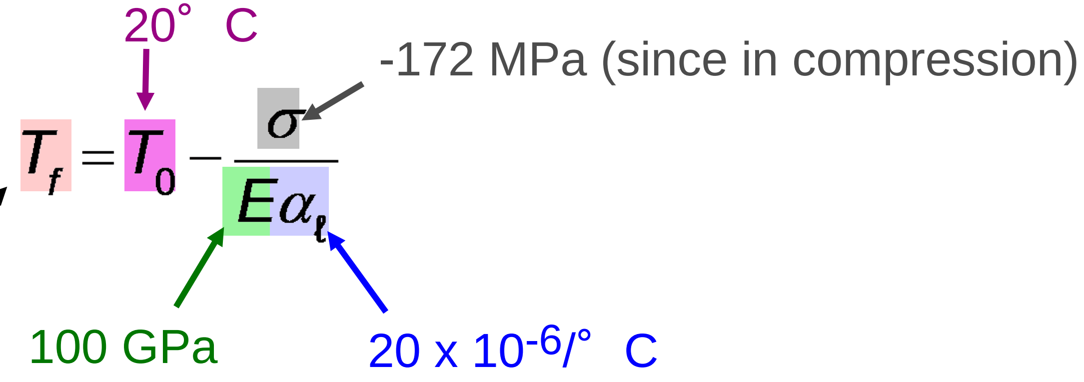
The thermal stress can be directly calculated as

$$\sigma = E(\varepsilon_{\text{compress}})$$

Noting that $\varepsilon_{\text{compress}} = -\varepsilon_{\text{thermal}}$ and substituting gives

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

Rearranging and solving for T_f gives



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

20° C

-172 MPa (since in compression)

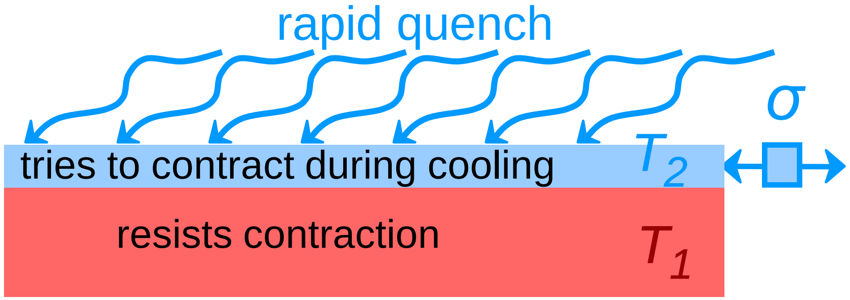
100 GPa

20 x 10^{-6}/° C

Answer: 106° C

Thermal Shock Resistance

- Occurs due to: nonuniform 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:

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

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

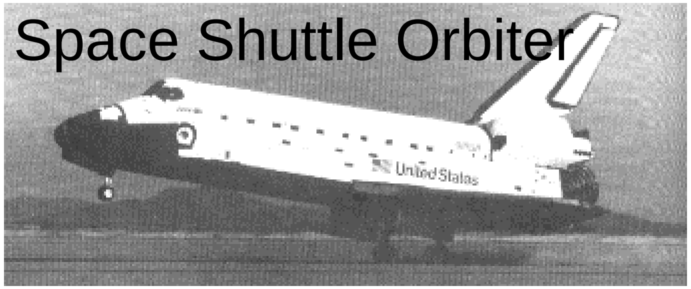
$$\boxed{(T_1 - T_2)_{\text{fracture}}} = \frac{\sigma_f}{E\alpha_\ell}$$

set equal

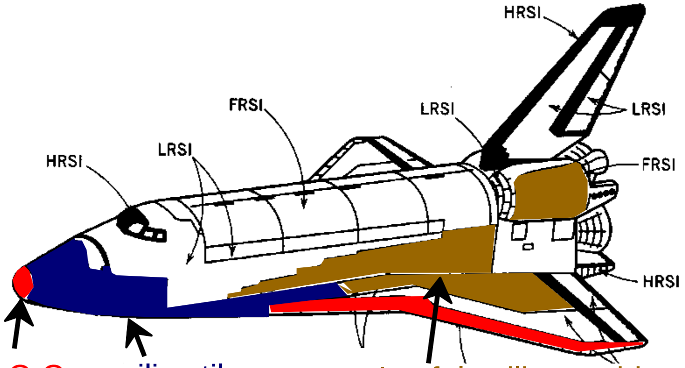
- $(\text{quench rate})_{\text{for fracture}} = \text{Thermal Shock Resistance } (TSR) \propto \dfrac{\sigma_f k}{E\alpha_\ell}$
- Large *TSR* when $\dfrac{\sigma_f k}{E\alpha_\ell}$ is large

Thermal Protection System

- Application:


Space Shuttle Orbiter

Chapter-opening photograph, Chapter 23, *Callister 5e* (courtesy of the National Aeronautics and Space Administration.)



reinf C-C (1650° C)

silica tiles (400-1260° C)

nylon felt, silicon rubber coating (400° C)

Fig. 19.2W, *Callister 6e*. (Fig. 19.2W adapted from L.J. Korb, C.A. Morant, R.M. Calland, and C.S. Thatcher, "The Shuttle Orbiter Thermal Protection System", *Ceramic Bulletin*, No. 11, Nov. 1981, p. 1189.)

- Silica tiles (400-1260°C):

-- large scale application

-- microstructure:

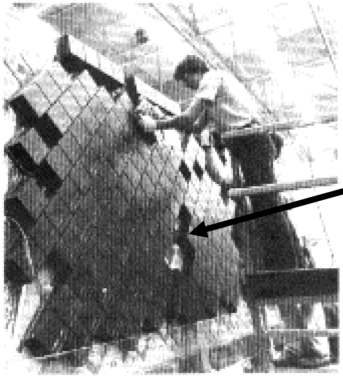
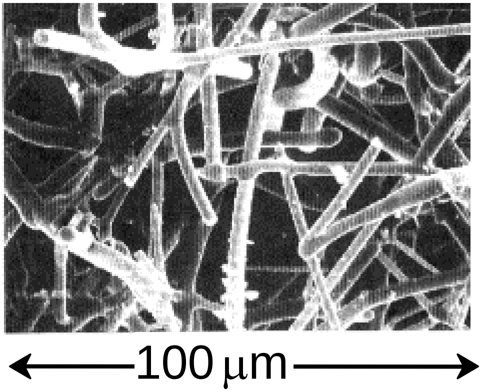


Fig. 19.3W, *Callister 5e*. (Fig. 19.3W courtesy the National Aeronautics and Space Administration.)



~90% porosity!
Si fibers bonded to one another during heat treatment.

Fig. 19.4W, *Callister 5e*. (Fig. 219.4W courtesy Lockheed Aerospace Ceramics Systems, Sunnyvale, CA.)

Table 20.1 Thermal Properties for a Variety of Materials

Material	c_p (J/kg·K)[a]	α_l $[(^\circ C)^{-1} \times 10^{-6}]$	k (W/m·K)[b]	L $[\Omega \cdot W/(K)^2 \times 10^{-8}]$
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_2O_3)	775	7.6	39	—
Magnesia (MgO)	940	13.5[c]	37.7	—
Spinel ($MgAl_2O_4$)	790	7.6[c]	15.0[d]	—
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}.

[b] To convert to cal/s·cm·K, multiply by 2.39×10^{-3}.

[c] Value measured at 100°C.

[d] Mean value taken over the temperature range 0°C to 1000°C.

Thermodynamics

- **Pretty much everything to do with heat and heat flow is covered by thermodynamics**
- **When two bodies of different temperatures are brought in contact heat, Q, flows from the hotter to the cooler**
- **Alternatively, a temperature increase can be achieved by doing work, W, on the system**
  - **e.g. electrical heating, friction, …**
- **In either case, there is a change of energy of the "system"**
  - □ **$\Delta E = W + Q$**
  - **where Q is the heat received from the environment**
  - **The first law of thermodynamics**

Summary

The thermal properties of materials include:

- **Heat capacity**:
  - -- energy required to increase a mole of material by a unit *T*
  - -- energy is stored as atomic vibrations
- **Coefficient of thermal expansion**:
  - -- the size of a material changes with a change in temperature
  - -- polymers have the largest values
- **Thermal conductivity**:
  - -- the ability of a material to transport heat
  - -- metals have the largest values
- **Thermal stresses**: --introduced by temperature change
  - **--Thermal shock resistance**:
  - -- the ability of a material to be rapidly cooled and not fracture
  - -- is proportional to $\dfrac{\sigma_f k}{E\alpha_\ell}$

Summary II

- Thermal properties of materials are connected with atomic bonding and electronic effects
- Energy is stored in ‘atomic oscillators’
  - classical treatments lead to an approximate value for the heat capacity
  - a full treatment involves phonons
- Phonons are quantized units of lattice vibration
  - effectively heat particles
- Thermal conductivity takes place either by electrons or phonons, depending on the material
- Thermal expansion is related to atomic bonding

Homework Questions

- **20.1**
- **20.7**
- **20.10**
- **20.14**
- **20.25**