THERMAL PROPERTIES

In this lecture we shall answer the following questions

- How does a material respond to heat?
- How do we define and measure...
  - heat capacity
  - coefficient of thermal expansion
  - thermal conductivity
  - thermal shock resistance
- How do ceramics, metals, and polymers rank?

Heat Capacity

The heat capacity, C, of a system is the ratio of the heat added to, or withdrawn from the system, to the resultant change in the temperature:

$$C = q/\Delta T = \delta q/dT \text{ [J/mol-K]}$$

- This definition is only valid in the absence of …………………
- Usually C is given as *specific heat capacity*, c, per gram or per mol
- New state of the system is not defined by T only, need to specify or constrain second variable:

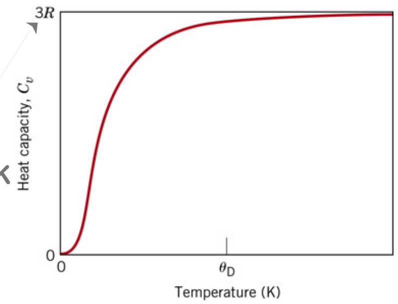
- constant-volume heat capacity $C_V = \left(\frac{\delta q}{dT}\right)_V$

- constant-pressure heat capacity $C_P = \left(\frac{\delta q}{dT}\right)_P$

cv and cp can be measured experimentally

Heat Capacity Vs T

- Heat capacity
  - increases with temperature
  - reaches a limiting value of 3R



C_V = constant

gas constant = 8.31 J/mol-K

Debye temperature (usually less than T_{room})

Adapted from Fig. 19.02, *Callister 8e.*

- Atomic view:
  - Energy is stored as atomic vibrations.
  - As T goes up, so does the avg. energy of atomic vibration.

Theoretical Calculation of the Heat Capacity

- In 1819 Dulong and Petit found experimentally that for many solids at room temperature, $c_v = 3R =$ …………...

- Although c_v for many elements (*e.g. lead and copper*) at room temp. are indeed close to 3R, c_v values of silicon and diamond are significantly lower than 25J/K.mol.
- Low temp. measurements showed a strong temperature dependence of c_v. Actually, c_v 0 as T 0 K.

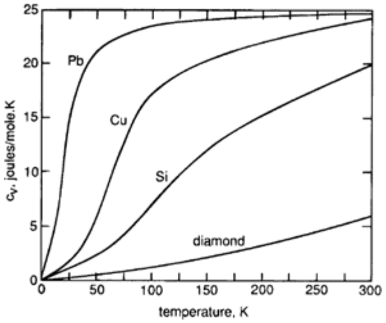


Figure 6.1: *Gaskell 3rd ed.*

Calculation of heat capacity of solids, as a f(T), was one of the early driving forces of the quantum theory. *The first explanation was proposed by ………… in 1906.*

Theoretical Calculation of the Heat Capacity

- Although Einstein's treatment agrees with the trend of the experimental values, it was not exact.
- Einstein formula predicts faster decrease of c_v as compared with experimental data.
- This discrepancy is caused by the fact that the oscillators do not vibrate with a single frequency.

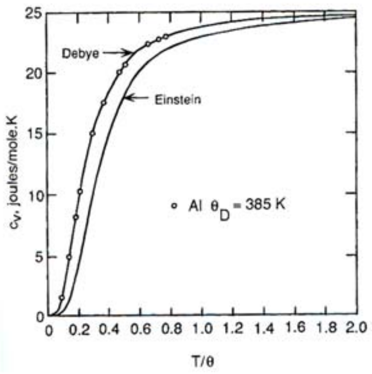
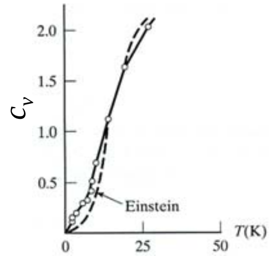


Figure 6.2: *Gaskell 3rd ed.*



Debye enhanced the model by treating the quantum oscillators as collective modes in the solid - phonons. And by considering that the oscillators vibrate with a range of frequencies.

Heat Capacity: *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

increasing c_p

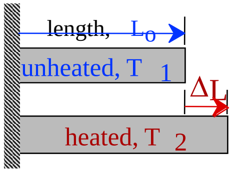
c_p : (J/kg-K) Specific Heat

C_p: (J/mol-K)

Selected values from Table 19.1, *Callister 8e*.

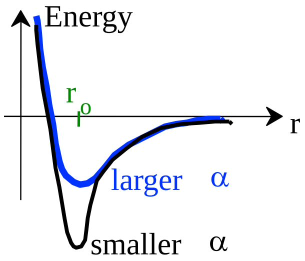
Properties From Bonding: α

- Coefficient of thermal expansion, α



coeff. thermal expansion

$$\frac{\Delta L}{L_o} = \alpha\,(T_2 - T_1)$$



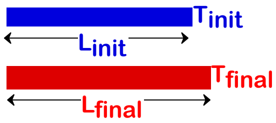
α is larger if Eₒ is smaller.

Thermal Expansion

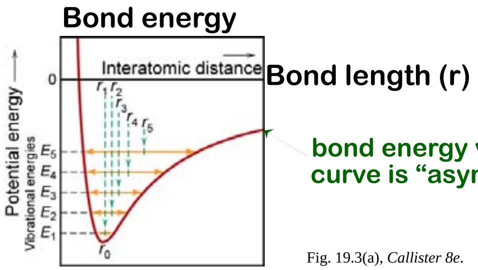
- Materials change size upon heating.

$$\frac{L_{final} - L_{initial}}{L_{initial}} = \alpha(T_{final} - T_{initial})$$

coefficient of thermal expansion (1/K)



- Atomic view: Mean bond length increases with T.



bond energy vs. bond length curve is "asymmetric"

Fig. 19.3(a), *Callister 8e*.

Thermal Expansion: Comparison

increasing α_ℓ

Material	α_ℓ (10^{-6}/°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

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

Selected values from Table 19.1, *Callister 6e*.

Thermal Conductivity

- General: The ability of a material to transfer heat.
- Quantitative:

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

heat flux (J/m^2-s)

temperature gradient

thermal conductivity (J/m-K-s)

- Atomic view: Atomic vibrations in hotter region carry energy (vibrations) to cooler regions.

Thermal Conductivity: Comparison

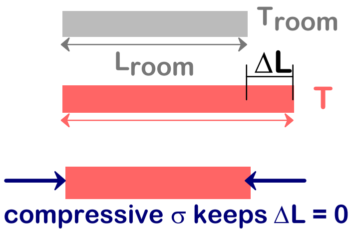
increasing *k*

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 6e*.

Example: *Thermal Stress*

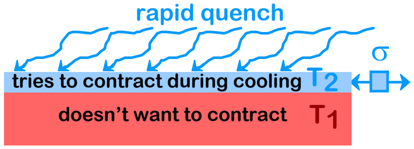
- Occurs due to:
  - uneven heating/cooling
  - mismatch in thermal expansion.
- Example:
  - A brass rod is stress-free at room temperature (20°C).
  - It is heated up, but prevented from lengthening.
  - At what T does the stress reach 172MPa (*compression*)?



$$\frac{\Delta L}{L_{room}} = \varepsilon_{thermal} = \alpha(T - T_{room})$$

Thermal Shock Resistance

- Occurs due to uneven heating/cooling.
- Example: Assume top thin layer is rapidly cooled from T_1 to T_2:



Tension develops at surface

$$\sigma = -E\alpha(T_1 - T_2)$$

Temperature difference that can be produced by cooling:

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

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

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

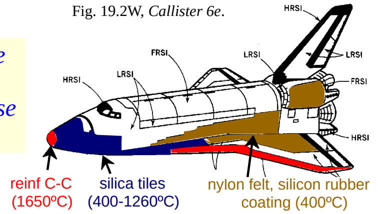
set equal

- Result: $(\text{quench rate})_{\text{for fracture}} \propto \frac{\sigma_f k}{E\alpha}$
- Large thermal shock resistance when $\frac{\sigma_f k}{E\alpha}$ is large.

Space Shuttle Thermal Protection System

Is there a single material which satisfies all these requirements?

Fig. 19.2W, *Callister 6e*.



- Materials developed previously by the aerospace industry are ………….. for the shuttle
- They are **too dense** or **non-reusable**

1. Maintain the temperature on the inner airframe below certain temp. [eg., 175°C] for a maximum outer surface temperature of 1465°C.

2. Remain usable for 100 missions, with a maximum turnaround time of 160 h.

3. Provide and maintain an aerodynamically smooth outer surface.

4. Be constructed of low-density materials.

5. Withstand temperature extremes between -110°C and 1465°C.

6. Be resistant to severe thermal gradients and rapid temperature changes.

7. Be able to withstand stresses and vibrations that are experienced during launch, as well as thermally induced stresses imposed during temperature changes.

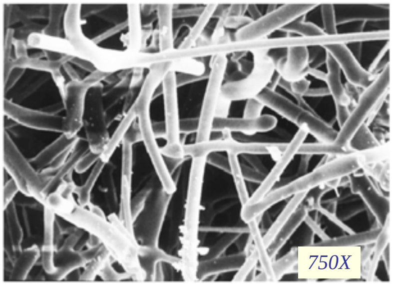
8. Experience a **minimum absorption of moisture** and other contaminants during storage between missions.

9. Be made to adhere to the airframe that is constructed of an aluminum alloy.

Space Shuttle Thermal Protection System

- For regions that are exposed to higher temperature (400 to 1260°C);
- ceramic tiles (more complex) are used
- because ceramics are thermal insulators and can withstand high temperature.
- 24,300 tiles (70% or the exterior area)
- each tile is different

FIGURE 23.17 *Photograph showing the installation of thermal protection ceramic tiles on the Space Shuttle Orbiter.*



SEM micrograph of a Space Shuttle Orbiter ceramic tile showing silica fibers after sintering

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Summary

- A material responds to heat by:
  - increased vibrational energy
  - redistribution of this energy to achieve thermal equilibrium.
- Heat capacity:
  - energy required to increase a unit mass by a unit temp.
  - polymers have the ……. values.
- Coefficient of thermal expansion:
  - the stress-free strain induced by heating by a unit T.
  - polymers have the ……… values.
- Thermal conductivity:
  - the ability of a material to transfer heat.
  - **metals** have the ……… values.
- Thermal shock resistance:
  - the ability of a material to be rapidly cooled and not crack. Maximize $\sigma_f k/E\alpha$.

Next time:

Magnetic Properties