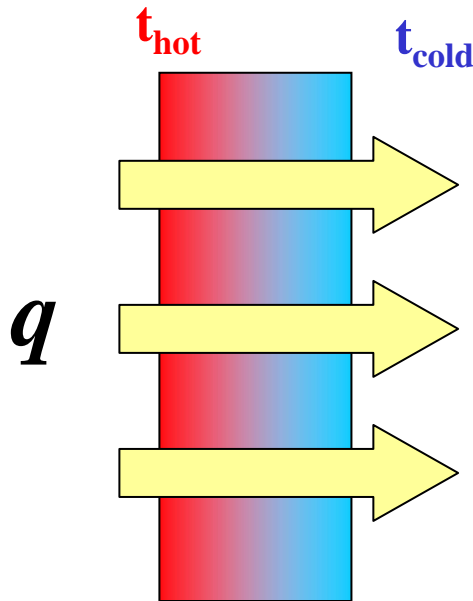


17

**CONDUCTION AND
THERMAL CONDUCTIVITY**

The Fourier Equation for Heat Conduction

The basic equation for steady-state heat conduction



$$q = -kA \frac{dt}{dx}$$

q = heat-conduction rate in x-direction

A = cross-sectional area normal to heat flow

dt/dx = temperature gradient in x direction

k = a proportionality constant known as the thermal conductivity of the conducting medium

q : does not vary with time (steady state)

k : depends on molecular state of the medium (function of T and P)

If dt/dx is large, significant variation of k with position

A : dependent on position

- sign : make q positive in the positive x direction.

Jean Baptiste Joseph Fourier

(1768-1830)



“Yesterday was my 21st birthday, at that age Newton and Pascal had already acquired many claims to immortality.”

It was during his time in Grenoble that Fourier did his important mathematical work on the theory of heat. His work on the topic began around 1804 and by 1807 he had completed his important memoir *On the Propagation of Heat in Solid Bodies*.

The memoir was read to the Paris Institute on 21 December 1807 and a committee consisting of Lagrange, Laplace, Monge and Lacroix was set up to report on the work. Now this memoir is very highly regarded but at the time it caused controversy. There were two reasons for the committee to feel unhappy with the work. The first objection, made by Lagrange and Laplace in 1808, was to Fourier's expansions of functions as trigonometrical series, what we now call Fourier series. Further clarification by Fourier still failed to convince them. The second objection was made by Biot against Fourier's derivation of the equations of transfer of heat. Fourier had not made reference to Biot's 1804 paper on this topic but Biot's paper is certainly incorrect. Laplace, and later Poisson, had similar objections.

Isotropic and nonisotropic

✿ **Isotropic** ($k_x = k_y = k_z$)

Materials having thermal conductivities which are independent of the direction of flow of heat transfer

✿ **Non-isotropics** ($k_x \neq k_y \neq k_z$)

Single crystals which have different thermal conductivities in the different directions of the crystal axes.

Laminated materials

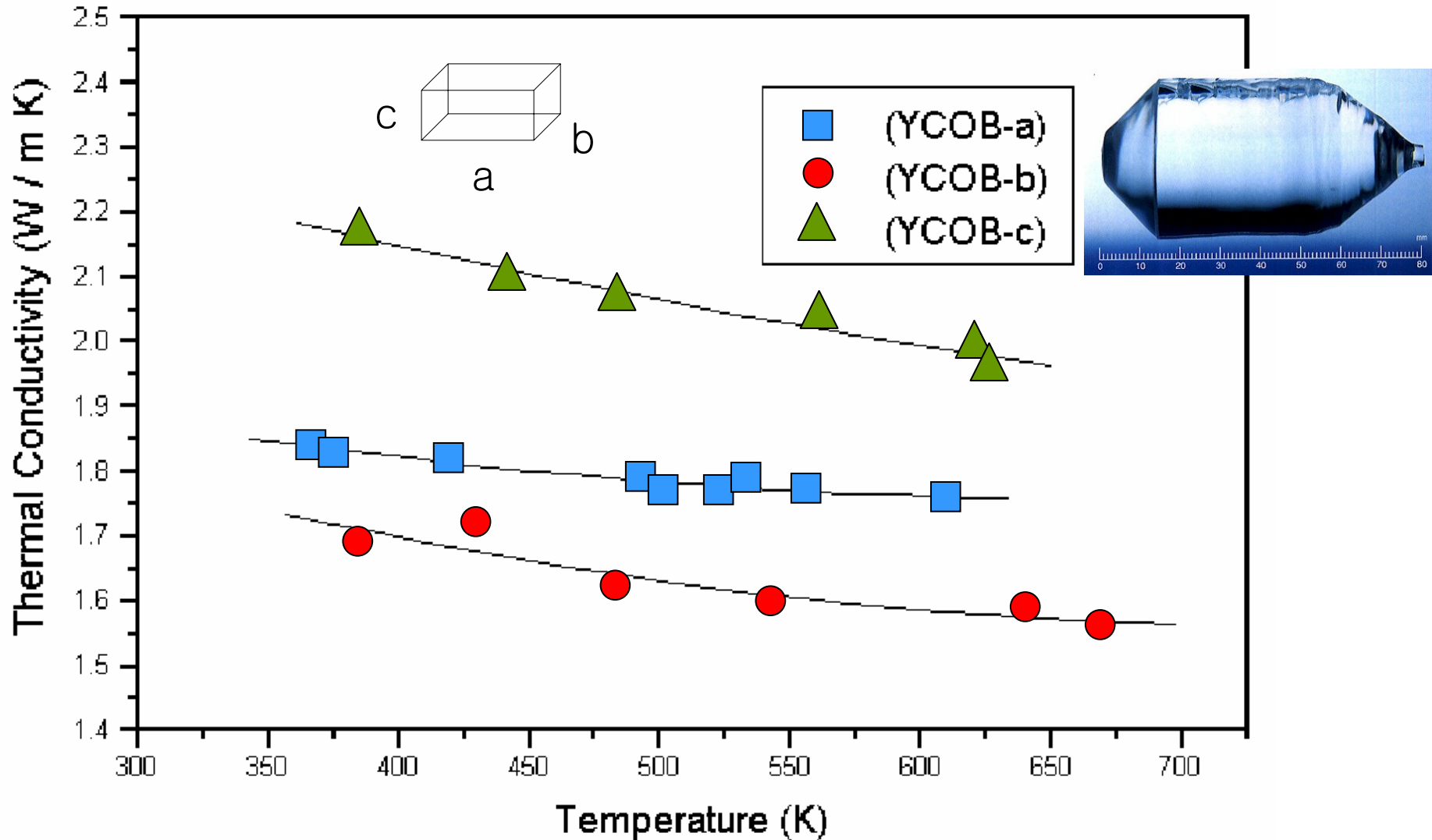
Eckert and Drake show that for these substances the heat flux vector is generally not normal to the isothermal surface

Thermal Conductivity of Purified Diamond

(Lanhua Wei et al., Physical Review Letters, 14 June 1993.)

- ❁ Natural diamond is 98.9% carbon-12 and 1.1% carbon-13.
- ❁ A team of scientists from Wayne State University and General Electric showed in 1990 that purifying the C-12 component of diamond to 99.9% increased its room-temperature thermal conductivity by 50%, a much bigger isotope effect than in other compounds.
- ❁ The same scientists have now recorded the highest thermal conductivity ever observed for a solid above liquid nitrogen temperatures, 410 W/cm-K, in 99.9%-pure C-12 at 104 K.
- ❁ The researchers predict that the thermal conductivity for 99.999%- pure C-12 diamonds would exceed 2000 W/cm-K and that integrated circuits mounted on such diamonds (cooled in liquid nitrogen) could operate at 500 times the power density of circuits mounted on copper substrates at room temperature.

Thermal Conductivity of Non-isotropics Crystal



Thermal Conductivity

*From Young, Hugh D.,
University Physics,
7th Ed. Table 15-5.

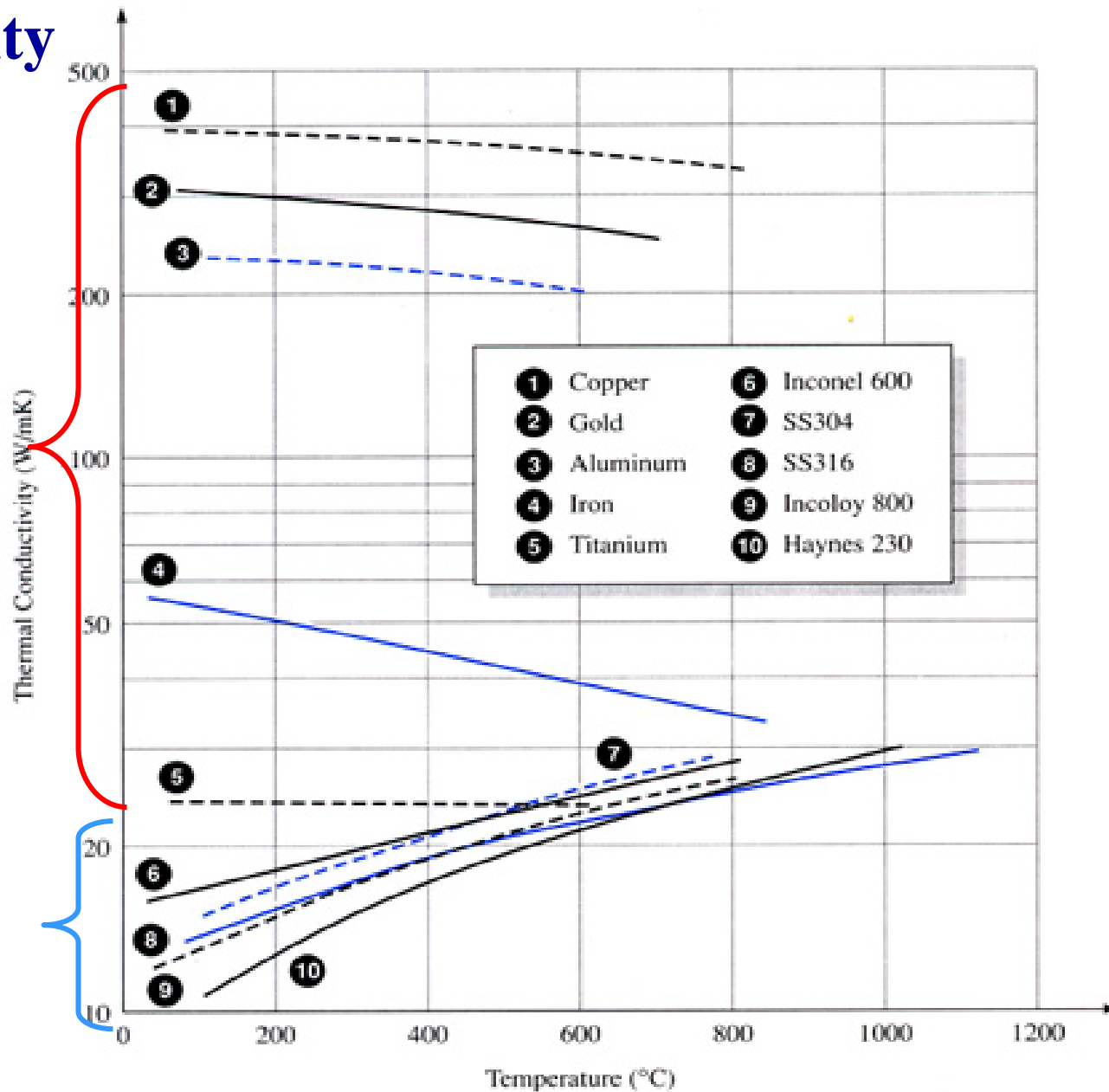
Material	Thermal conductivity (cal/sec)/(cm² C/cm)	Thermal conductivity (W/m K)*
Silver	1.01	406.0
Copper	0.99	385.0
Brass	...	109.0
Aluminum	0.50	205.0
Iron	0.163	...
Steel	...	50.2
Lead	0.083	34.7
Mercury	...	8.3
Ice	0.005	1.6
Glass,ordinary	0.0025	0.8
Concrete	0.002	0.8
Water at 20 C	0.0014	...
Asbestos	0.0004	...
Hydrogen at 0 C	0.0004	0.14
Helium at 0 C	0.0003	0.14
Oxygen	...	0.023
Snow (dry)	0.00026	...
Fiberglass	0.00015	0.04
Brick,insulating	...	0.15
Brick, red	...	0.6
Cork board	0.00011	0.04
Wool felt	0.0001	0.04
Rock wool	...	0.04
Styrofoam	...	0.01
Wood	0.0001	0.12-0.04
Air at 0 C	0.000057	0.024

Thermal Conductivity

Metals

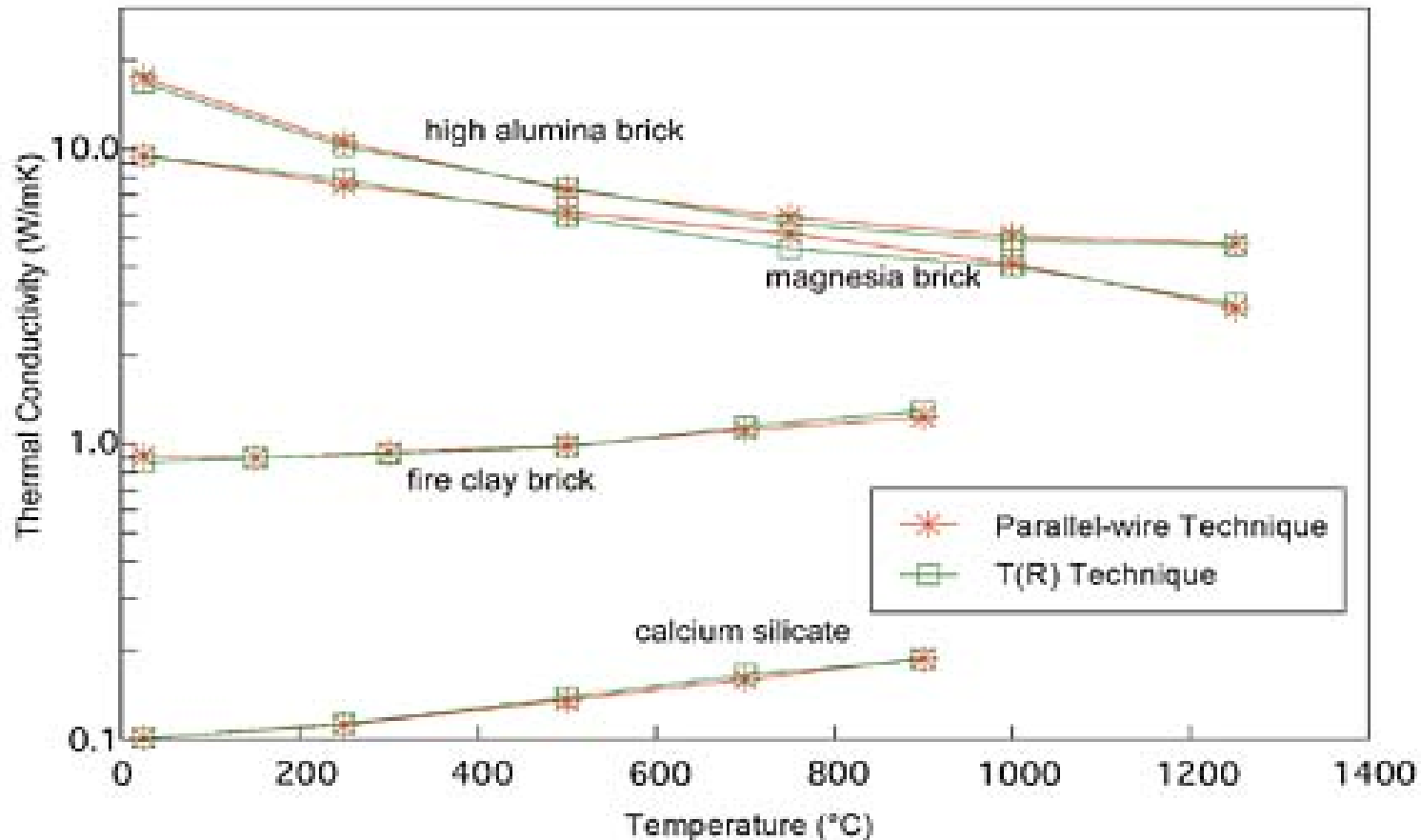
Pure metal

Alloy



Thermal Conductivity

refractory materials



Thermal Conductivity

Heat transfer by conduction involves transfer of energy within a material without any motion of the material as a whole. The rate of heat transfer depends upon the temperature gradient and the thermal conductivity of the material. More fundamental questions arise when you examine the reasons for wide variations in thermal conductivity.

Gases transfer heat by direct collisions between molecules, and as would be expected, their thermal conductivity is low compared to most solids since they are dilute media. **Non-metallic solids** transfer heat by lattice vibrations so that there is no net motion of the media as the energy propagates through. Such heat transfer is often described in terms of "phonons", quanta of lattice vibrations. **Metals** are much better thermal conductors than non-metals because the same mobile electrons which participate in electrical conduction also take part in the transfer of heat.

Four modes of transport of energy in solids

- 1. Free Electrons**
 - 2. Lattice waves (Phonons)**
 - 3. Magnetic excitations (Magnons)**
 - 4. Electromagnetic radiation (Photons)**
- } **Principal Carriers**

Thermal Conductivity by Free electron: Metals

For metals, the thermal conductivity is quite high, and those metals which are the best electrical conductors are also the best thermal conductors. At a given temperature, the thermal and electrical conductivities of metals are proportional, but raising the temperature increases the thermal conductivity while decreasing the electrical conductivity. This behavior is quantified in the **Wiedemann-Franz**

Law:

$$\frac{k}{\sigma} = LT \quad \text{or} \quad L = \frac{k}{\sigma T}$$

k = thermal conductivity, σ = electric conductivity, L = Lorenz number

Thermal Conductivity by Free electron: Metals

where the constant of proportionality L is called the **Lorenz number**.

$$L = 22\sim 29 \times 10^{-9} \text{ volts}^2/\text{K}^2$$

Qualitatively, this relationship is based upon the fact that the heat and electrical transport both involve the free electrons in the metal. **The thermal conductivity increases with the average particle velocity since that increases the forward transport of energy. However, the electrical conductivity decreases with particle velocity increases because the collisions divert the electrons from forward transport of charge.** This means that the ratio of thermal to electrical conductivity depends upon the average velocity squared, which is proportional to the **kinetic temperature**.

Thermal Conductivity by Free electron: Metals

The *electronic thermal conductivity* is proportional in magnitude to the electron mean free path. In a perfect crystal lattice this would be infinite, but in actual materials, it is limited by the electron scattering produced by chemical impurities, lattice dislocation, physical defects, and thermal vibration.

$$k_{\text{pure copper}} = 5000 \sim 7000 \text{ Btu}/(\text{h})(\text{ft})(^\circ\text{F})$$

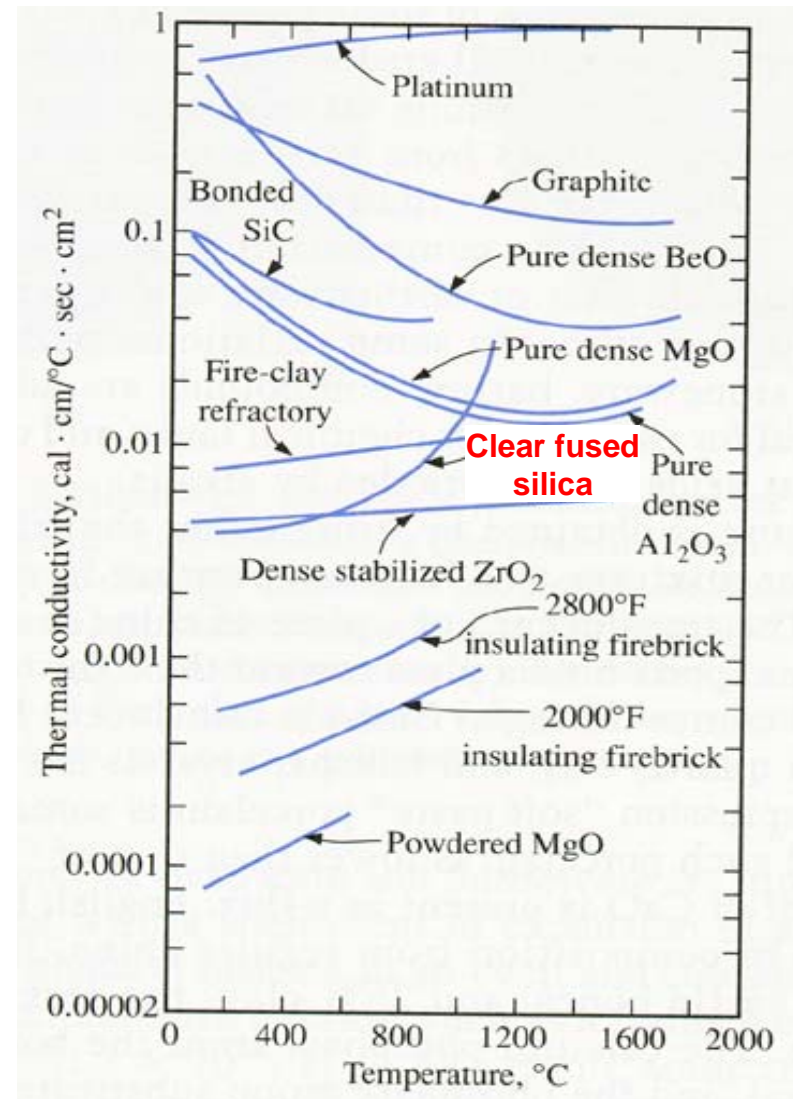
$$k_{\text{commercial copper}} = 220 \text{ Btu}/(\text{h})(\text{ft})(^\circ\text{F})$$

Thermal Conductivity by Lattice waves (Non-metallic solid)

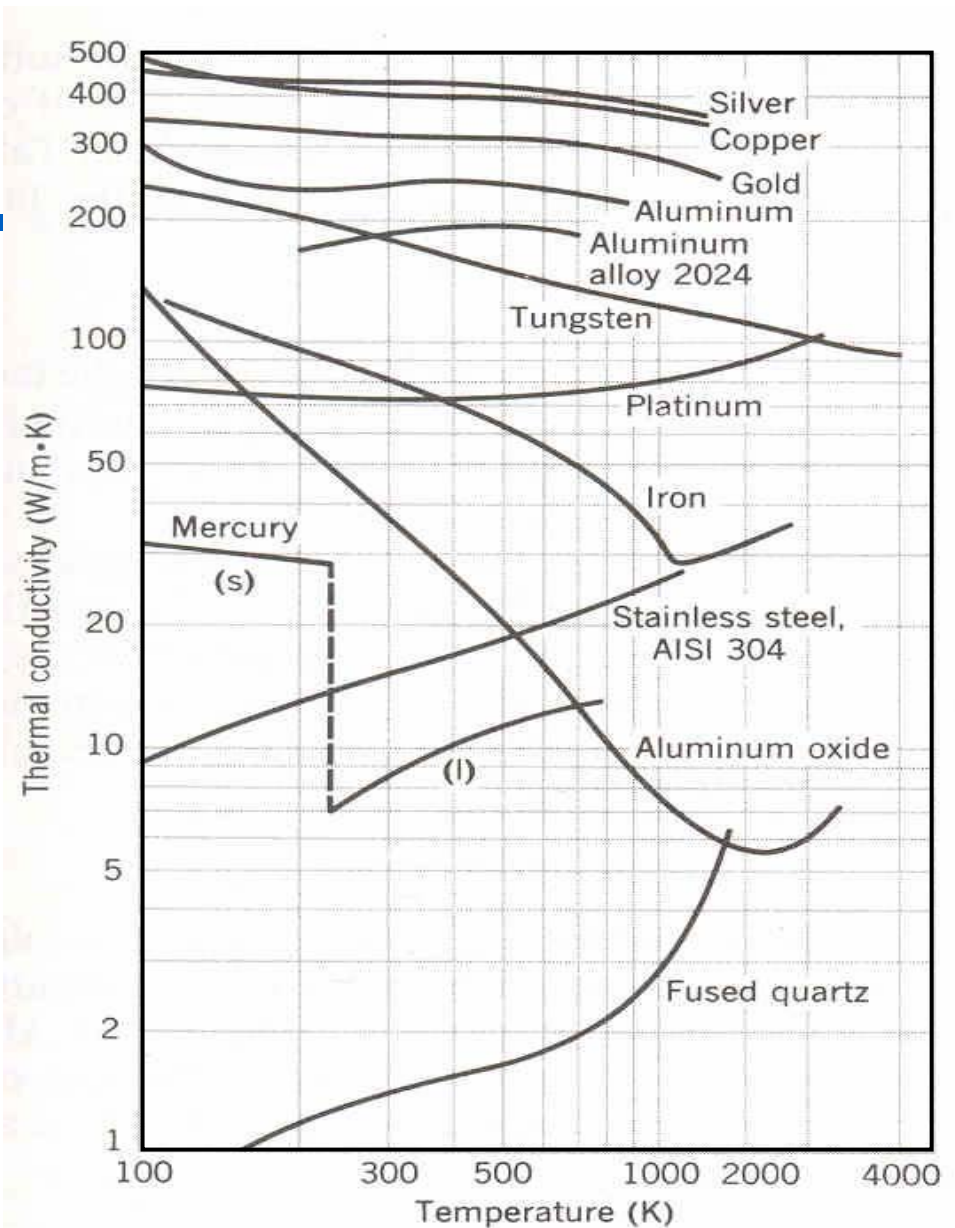
For non-metallic solids, the heat transfer is view as being transferred via lattice vibrations, as atoms vibrating more energetically at one part of a solid transfer that energy to less energetic neighboring atoms. This can be enhanced by cooperative motion in the form of propagating lattice waves, which in the quantum limit are quantized as **phonons**. Practically, there is so much variability for non-metallic solids that we normally just characterize the substance with a measured thermal conductivity when doing ordinary calculations.

Thermal Conductivity by photons

The transmission of electromagnetic radiation in translucent materials in the form of **photons** adds to the total effective thermal conductivity of solid. This energy is principally in the infrared portion of the electromagnetic spectrum. If the solid either has no absorptive capacity for the radiation, or if it is completely opaque, there will be no augmentation of thermal conductivity. In general, solid will emit, absorb, and re-radiate photons. This is considered to be the reason why the thermal conductivity of glasses tend to increase rapidly at high temperatures.



The temperature dependence of the thermal conductivity of selected solids



Thermal Conductivity: Liquids

Brigman Model (1923)

$$k = \frac{1}{3} \rho C_v \bar{u} \lambda = \rho C_v v_s a$$

Energy is handed down rows of molecules with the velocity of sound.

$$\rho C_v \cong 3 \left(\frac{N}{V} \right) k$$

Semiempirical correlation based on experimental results

$$a = \left(\frac{V}{N} \right)^{1/3}$$

$$k = 3 \left(\frac{N}{V} \right)^{2/3} \kappa v_s$$

: Brigman's equation

$$v_s = \sqrt{\frac{C_p}{C_v} \left(\frac{\partial P}{\partial \rho} \right)_T}$$

Sonic velocity

Thermal Conductivity: Liquids

Horrocks and McLaughlin Model (1960)

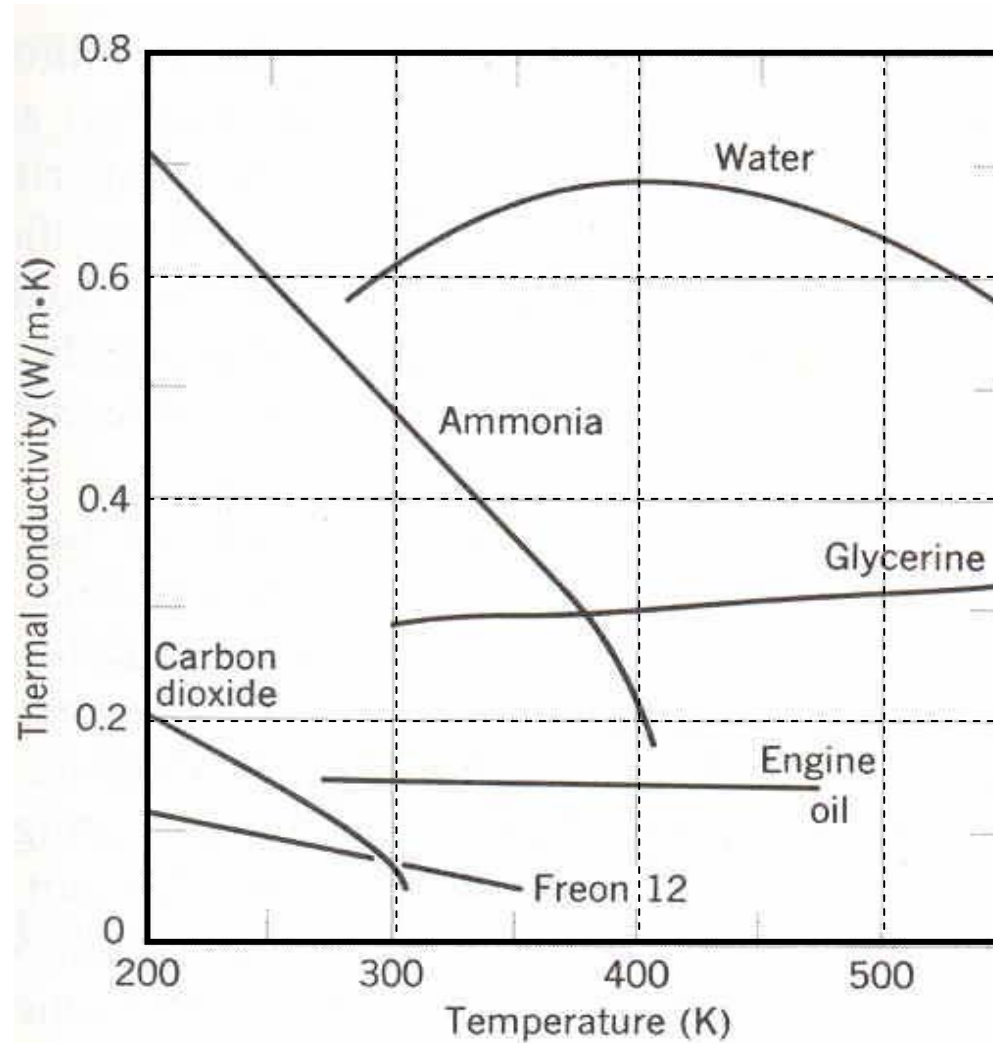
Liquid has a lattice structure through which excess energy due to a temperature gradient is transferred both

- (1) By motion of molecules from cell to cell and
- (2) By a vibrational mechanism in which the molecule vibrates within its cell.

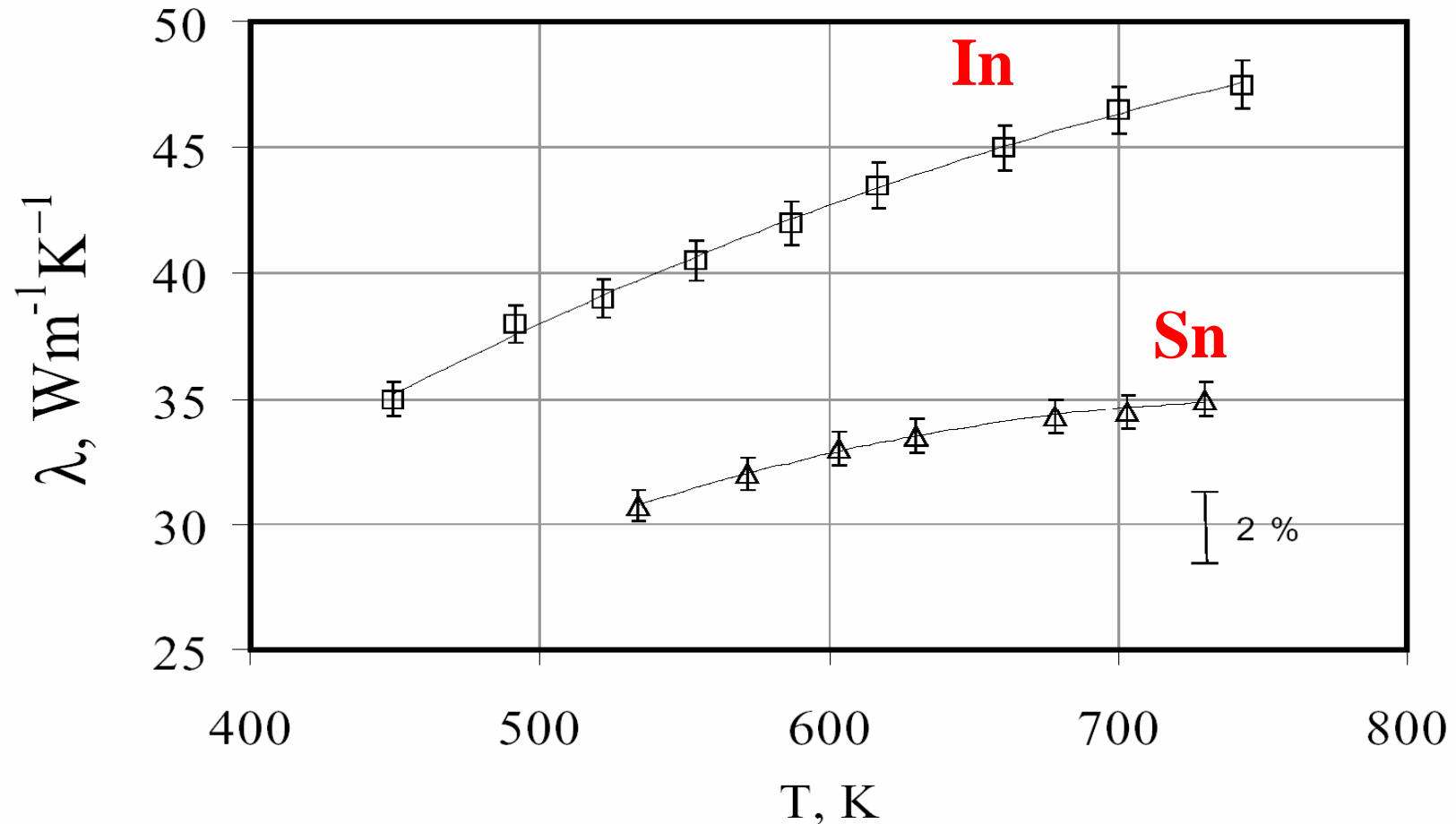
(1) \ll (2)

The intercellular contribution, calculated from intermolecular force, gives good results for simple liquids.

The temperature dependence of the thermal conductivity of selected non-metallic liquids under saturated conditions



Thermal Conductivity of Liquid Tin and Indium



Thermal Conductivity: Gas

The conduction of heat in a gas is basically the mechanism of a random walk (diffusion and collision). The molecules of high-temperature gas diffuse among the molecules of low-temperature gas, collide with them, and give up kinetic energy. For an ideal gas, the heat transfer rate is proportional to the average molecular velocity, the mean free path, and the molar heat capacity of the gas.

$$k = \frac{n \bar{v} \lambda C_P}{3 N_A}$$

Diagram illustrating the components of the thermal conductivity equation for a gas:

- n : Particle per unit volume
- \bar{v} : Mean particle speed
- λ : Mean free path
- C_P : Molar heat capacity
- $3 N_A$: Avogadro's number
- k : Thermal conductivity

If $n \uparrow$, then $P \uparrow$.

If $\lambda \uparrow$, then $P \downarrow$.

The thermal conductivity should be independent of pressure. This has been found to be approximately true of most gases (ideal gas) near atmospheric pressure.

Thermal Conductivity: Gas

The thermal conduction of gas is dependent upon pressure.

- (1) At very low pressures, where the thermal conductivity of a gas obviously must approach zero.
- (2) At even moderately low pressures, when the dimensions of the container are less than the mean free path of the gas molecules (a so-called Knudsen gas)
- (3) At high pressures, where the simple kinetic theory of gases does not apply.

Thermal Conductivity: Gas

**A relationship between
the viscosity and thermal conductivity**

Similarity:

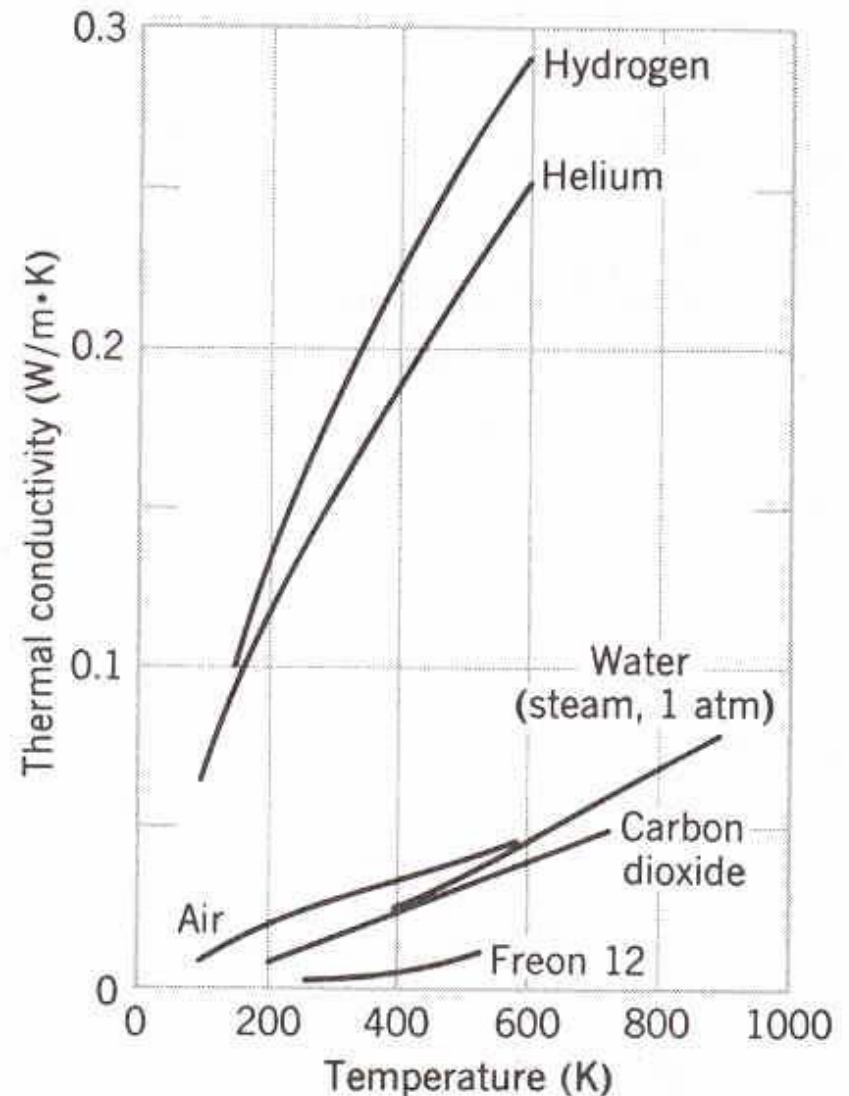
Gas viscosity is a measure of the drag exerted by diffusion of gas molecules in a zone moving at a different mean velocity.

Difference:

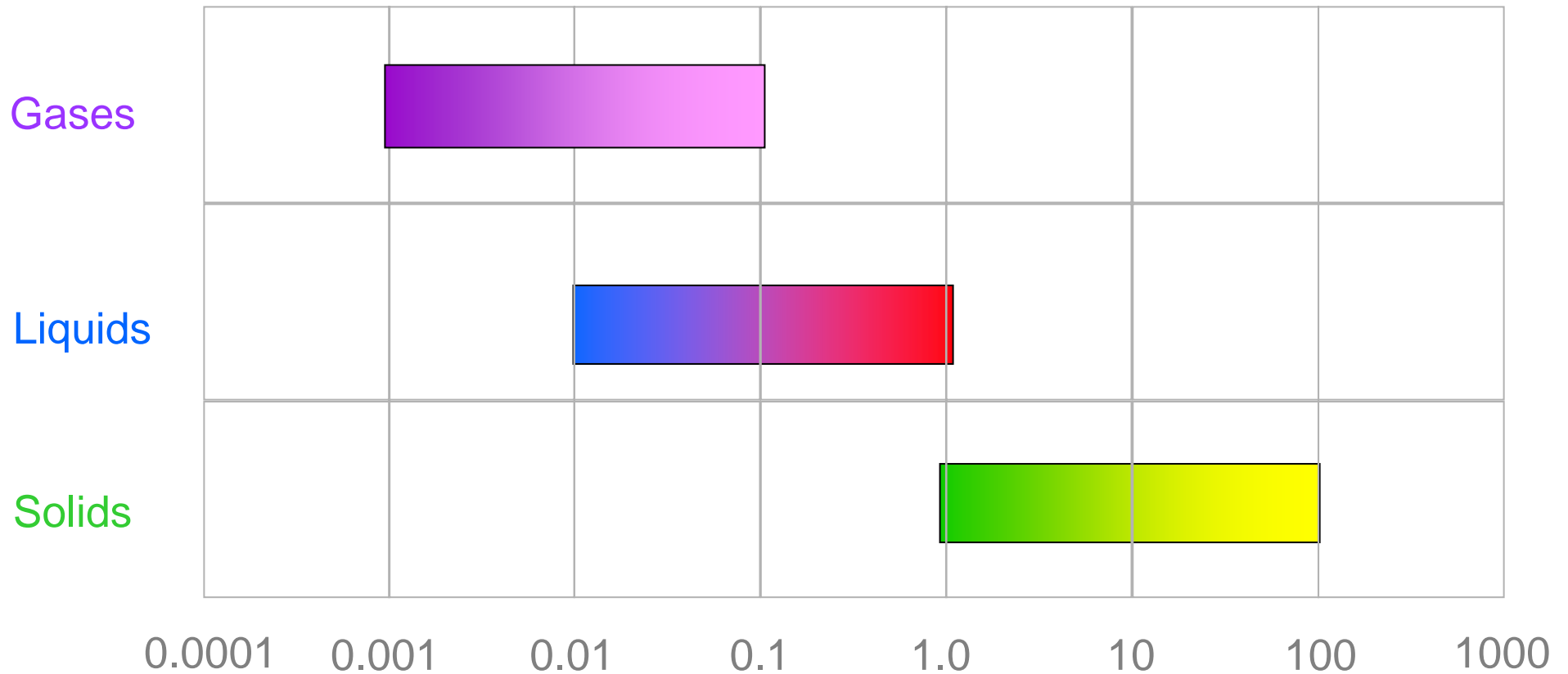
The quantity being transported is kinetic energy associated with **random motion** of the molecules rather than **directed momentum**.

Thermal Conductivity: Common Gases

Since the mechanism of heat conduction in a gas is a function of its tendency to diffuse, it is to be expected that light gases like hydrogen or helium would have relatively high thermal conductivity. This is what actually happens. The paraffin hydrocarbons show a typical decrease of thermal conductivity with increase of molecular weight in a homogeneous series.

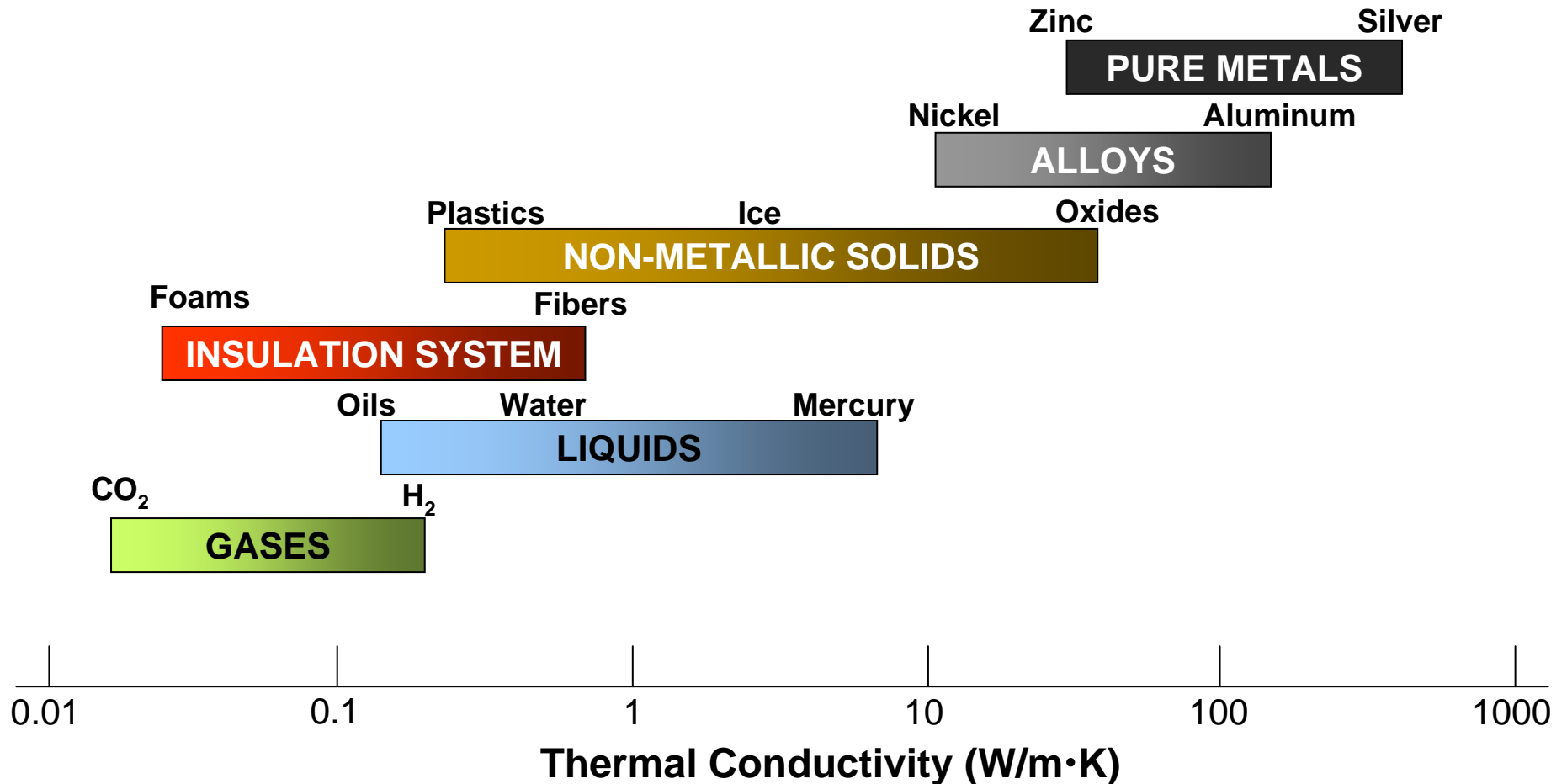


Thermal Conductivity, k [Btu/(h)(ft)(°F)]



Range of thermal conductivity for various states of matter

@normal temperature and pressure



Thermal Conductivity: Fine powder

At sufficiently high pressures, the mean free path of gas molecules is much smaller than the dimensions of the cavities in the powder and conductivity of the system lies between the values for the solid and the gas.

Below the certain pressure, which is a function of pore size, the gas in the pore behaves as a Knudsen gas, with the result that its thermal conductivity is low than the conductivity of the gas at the same pressure in a large free volume.

As a result, the conductivity of the porous system may be lower than either the conductivity of the solid or the gas at measured under ordinary conditions.

Thermal Conductivity: Estimation & Data

Estimation

Robert C. Reid, John M. Prausnitz, and Bruce E. Poling
“The properties of Gases & Liquids”
4th ed., McGraw-Hill, New York (1987)

Data

Robert H. Perry and Don Green
“Perry Chemical Engineers’ Handbook”
6th ed., McGraw-Hill, New York (1987)

David R. Lide
“CRC Handbook of Chemistry and Physics”
84th ed., CRC Press, New York (2003-2004)

Thermophysical Properties of Fluid Systems

Accurate thermophysical properties are available for several fluids. These data include the following:

- Density
- C_p
- Enthalpy
- Internal energy
- Viscosity
- Joule-Thomson coefficient
- Specific volume
- C_v
- Entropy
- Speed of Sound
- Thermal conductivity
- Surface tension (saturation curve only)

<http://webbook.nist.gov/chemistry/fluid/>