



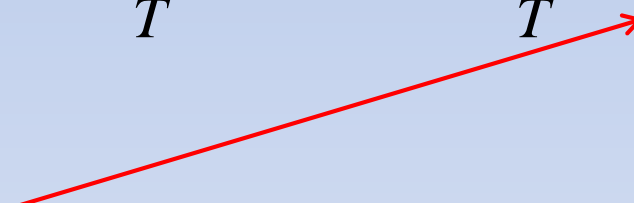
The Thermodynamic Processes

The Foundation Course on Physics
Professor Vojtěch Mornstein

Glencoe pp. 318 – 355, 368-371

Back to Ideal Gas Law

- **Ideal gas law:**
- The state parameters (quantities which values determine/describe a thermodynamic state) are interrelated by the state equations.
- The simplest state equation: the **ideal gas law (= state equation of ideal gas)**, which can be written in different ways e.g.:

$$pV = nRT \quad \frac{pV}{T} = nR \quad \Rightarrow \quad \frac{pV}{T} = \text{const.} \quad \Rightarrow \quad \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$


(for **constant amount** of substance n – this value becomes a component of the constant) ,

- where p is the gas pressure given in [Pa], V is the volume of the gas [m^3], T is the Kelvin temperature* [K], R the **molar** or **universal gas constant** (= $8.32 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), and n is amount of substance in moles [mol].

*Kelvin temperature = absolute temperature = thermodynamic temperature

Normal values of p and T

- For many calculations in thermodynamics, it is necessary to know what are the values of normal **molar volume** V_n , normal pressure p_n and normal temperature T_n :
- $p_n = 1.01325 \times 10^5 \text{ Pa} = 101,325 \text{ kPa} = 1013,25 \text{ hPa} \approx 1 \text{ atm}$
- $T_n = 273.15 \text{ K}^*$ (0 °C)
- $V_n = 22.4 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} = 22.4 \text{ litres}$



- (Note: All gases have the same molar volume at the same temperature and pressure!!!!!!)

Normal **molar volume** is a volume occupied by one mole of perfect gas at normal pressure p_n and temperature T_n . Based on the equation of ideal gas law, it is possible to derive** simply other laws which are applicable only under some specific conditions. Processes described by these laws are reversible and can be presented as curves of a typical shape in a **pV-diagram** (Fig.).

*It can be also 293.15 K, but it will influence the molar volume too.

**The historical development was different!

Thermodynamic processes

a) Boyle's law (Boyle – Mariotte law):

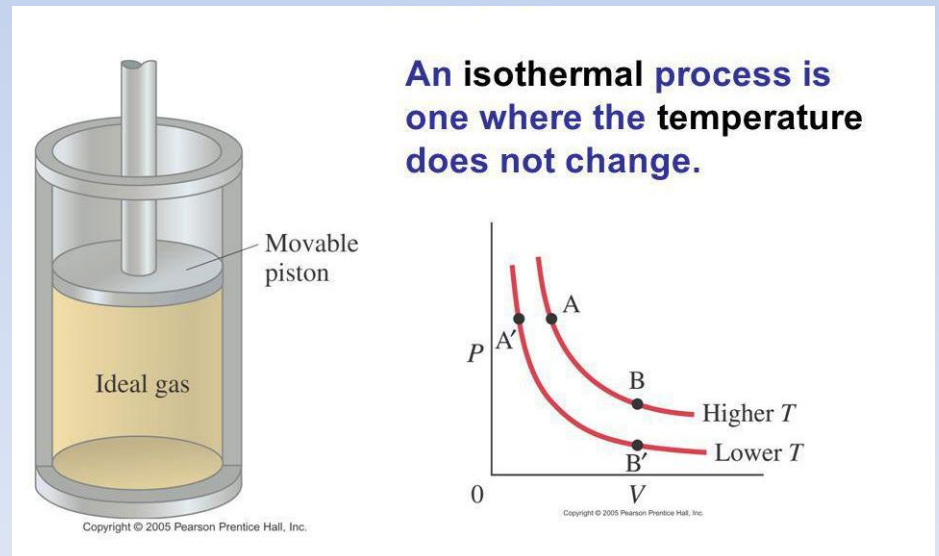
During an **isothermal process**, temperature T has a constant value (does not change). Value of temperature is included in the constant below.

$$\frac{pV}{T} = \text{const.} \Rightarrow pV = T \cdot \text{const.} = \text{const.}$$

$$p_1V_1 = p_2V_2 = \text{const.}$$

A gas is **slowly** compressed (or expanded) and the heat can be transferred to/from the surrounding: slowly inflating a rubber balloon, bubbles ascending in water

In homoeothermic organisms most processes take place at constant temperature!



Thermodynamic processes

- **b) Gay-Lussac's law:**
- Pressure p is constant – an **isobaric process** takes place. Value of pressure is included in the constant:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{const.}$$

A gas is slowly heated and its volume increases at a constant pressure: most processes around us take place under constant pressure...

like in the most living organisms!!!



The weight exerts always the same force on the gas under the movable piston. Volume and temperature are changing but pressure is constant

Thermodynamic processes

- **c) Charles's law:**

Volume V is constant – an **isochoric** (i.e. **isosteric**) **process** takes place. Value of volume is included in the constant:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \text{const.}$$

A system consisting of water and water vapour is slowly heated and its volume is kept constant: cooking in a pressure cooker autoclave used for sterilization in labs is similar.



The piston does not move, pressure and temperature increases.

Pressure cooker and Autoclave



kitchen



Small lab

What are the advantages?

industry

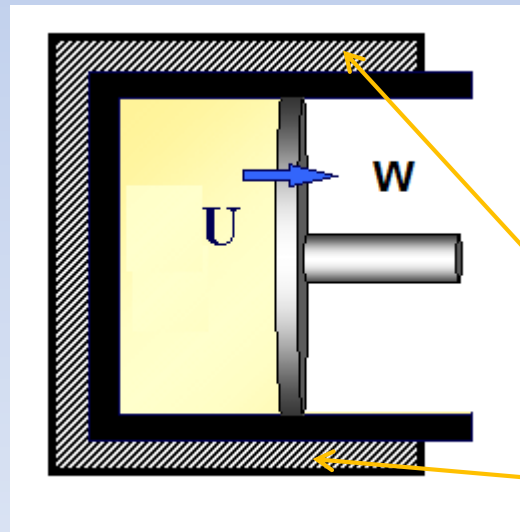


Thermodynamic processes (optional)

- A special case – **adiabatic process**. The system is thermally insulated. In the following equation the κ (kappa) is the Poisson constant which has different values for different gases.

$$pV^{\kappa} = \text{const.}$$

In real conditions, adiabatic-like processes are fast enough to avoid heat exchange with surroundings.

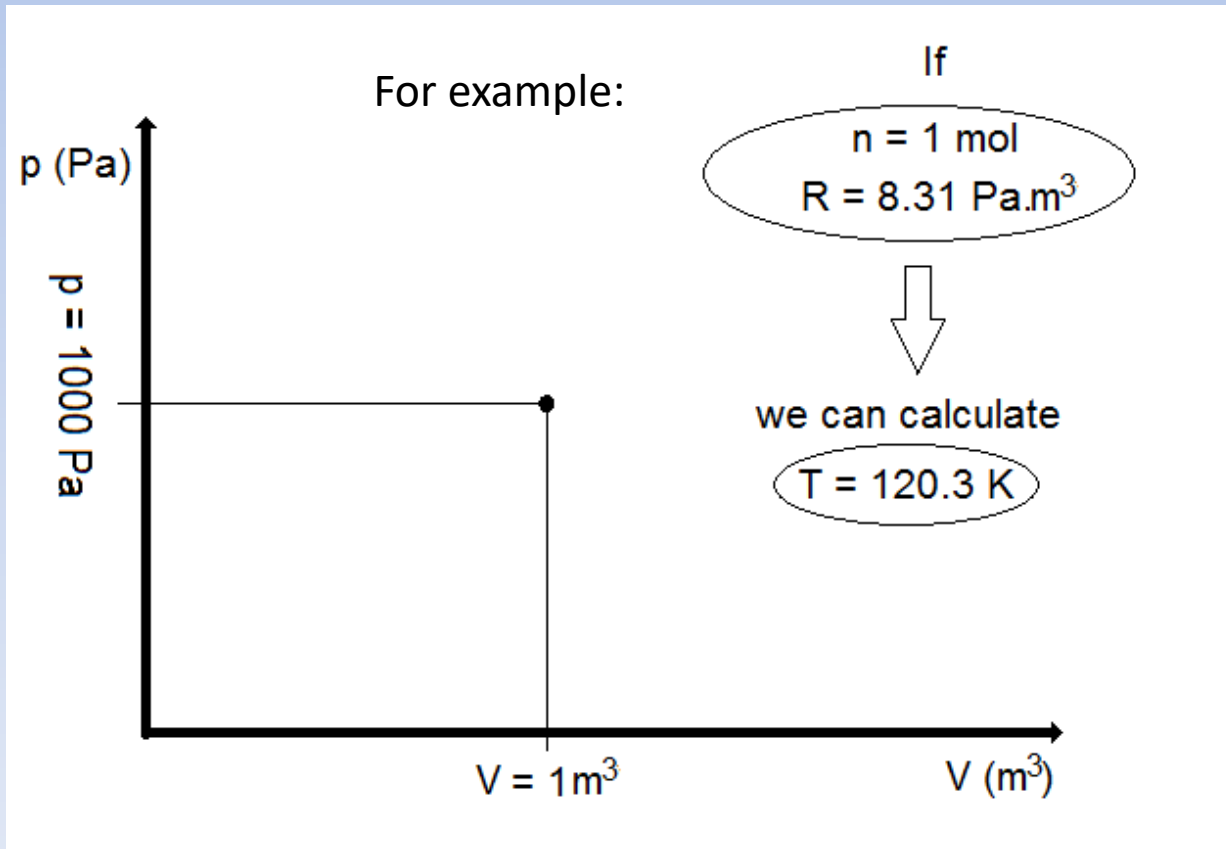


Only internal energy U can be transformed into useful work W !

Thermal insulation

p-V diagram

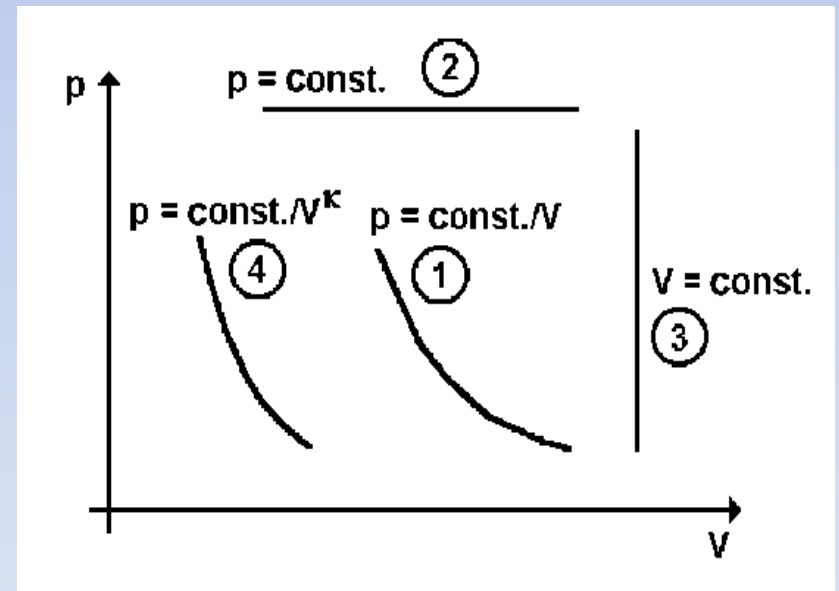
The pV-diagram is the most often used graphic representation of the reversible thermodynamic processes (see also the slide about the isothermal process!). What is the meaning of any *single point* in a p-V diagram? For an ideal gas and $n = \text{const.}$, this point represents a *single* thermodynamic state!



**A reversible
TMD process
can be
represented by
a line (point by
point = state by
state) !!!**

pV - diagram

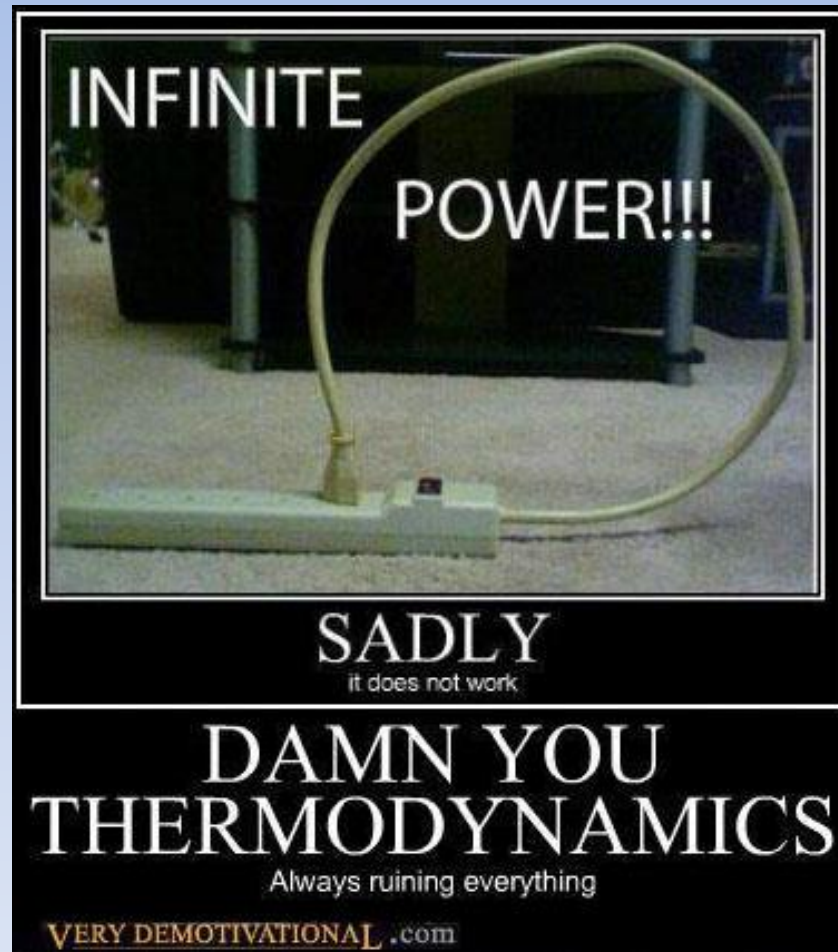
- Different thermodynamic processes are represented by different shapes of $p(V)$ function – it means they have different pV-diagrams.
- 1 – isothermal,
The line is an isotherm
- 2 – isobaric,
The line is an isobar
- 3 – isochoric*
The line is an isochore
- 4 – adiabatic (also isoentropic**).
The line is an adiabat



*called also isovolumetric or isosteric

**entropy – see next lecture

Thermodynamic systems can do some work!



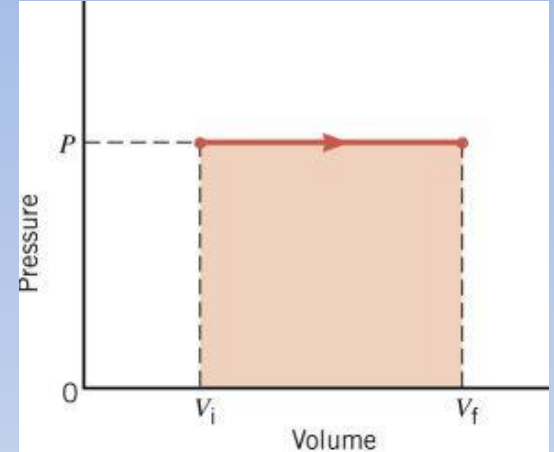
Work done in TMD processes

- 1 – isothermal $W = nRT \ln \frac{V_2}{V_1}$

- 2 – isobaric $W = p\Delta V$

- 3 – isochoric $W = 0 \quad (\Delta V = 0)$

- 4 – adiabatic process $W = \frac{p_1V_1 - p_2V_2}{\kappa - 1}$



Work done is always equal to the area below the $p(V)$ curve! It can be seen best in case of isobaric process.

Heat and Heat Capacity

We know already: *Heat energy Q is the energy related to thermal motion of molecules*. It is interchanged between thermodynamic systems during thermodynamic processes.* The thermal motion is chaotic movement of particles which move accidentally in all possible directions.

Vector sum of vectors of their velocities would be equal to zero (which is not so when we summarise or average absolute values of particle velocities or their second powers).

The unit of heat energy is joule [J]. An often used old unit of heat, the calorie** (amount of the heat necessary for heating 1 g of water by 1 °C) is:

1 cal (calorie) = 4.186 J

British thermal unit 1 BTU = 1 055,05585 J (In Czechia, BTU is almost unknown)

*Heat can be interchanged also in the form of **radiation**

**Calories used for description of energetic content of the food are the so-called big calories (kilocalories)

Heat and Heat Capacity

Heat capacity. Heat interchange can cause a change of body temperature. Heat capacity K of a body is the amount of heat causing a temperature increase of 1 °C. We can write:

$$K = \frac{Q}{\Delta T} \qquad Q = K \cdot \Delta T$$

Specific heat capacity C is the heat capacity of unit mass of a substance:

$$C = \frac{Q}{m\Delta T} \qquad Q = C \cdot m \cdot \Delta T,$$

where C is given in [$\text{Jkg}^{-1}\text{K}^{-1}$], m is mass of substance [kg], ΔT is the temperature change [K], and Q – heat interchanged [J].

C depends on the kind of thermodynamic process.

C_p – heat capacity measured in an isobaric process (at constant pressure) – is greater than

C_v – heat capacity measured in an isochoric process (at constant volume).

In the first case it can be explained by doing work, which consumed a part of absorbed heat. In the second case (C_v) no work can be done because the “piston” cannot move ($\Delta V = 0$).

Some specific heat capacities

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

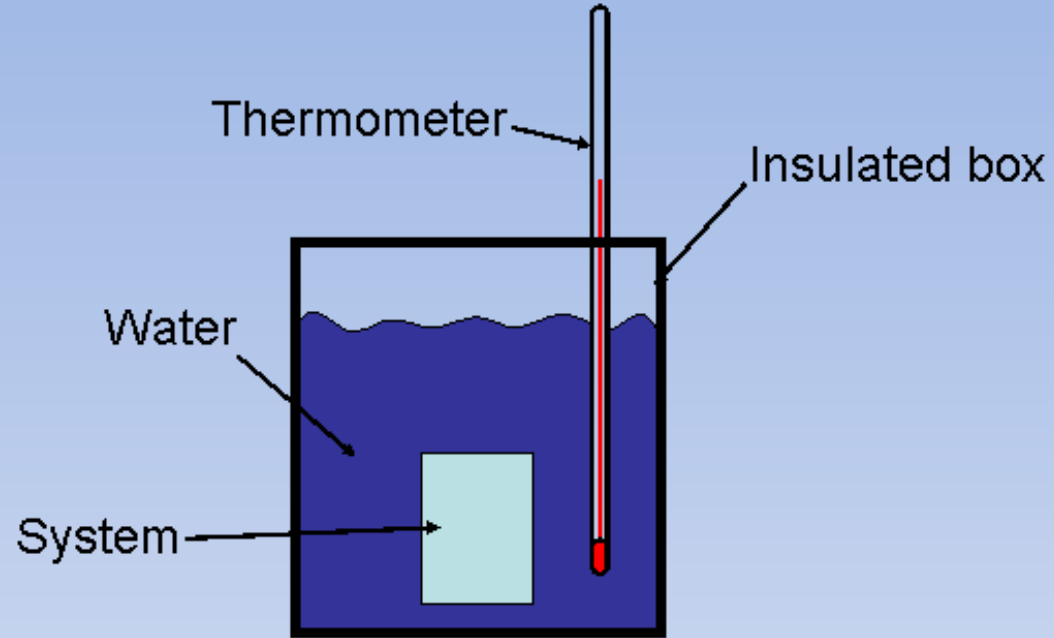
Constant volume or
constant pressure?

How to explain
the differences?

Huge amount of heat can be stored in the seas – it stabilises temperature of Earth surface!!!!

Calorimetry

The „system“
interchanges
heat with the
water bath:



$$\Delta Q_w = \Delta Q_s$$

$$m_w C_w (T_f - T_w) = m_s C_s (T_s - T_f),$$

Where m_w is mass of water, C_w is specific heat capacity of water, T_f is final temperature of water+system, T_w is initial temperature of water, m_s is mass of the „system“, C_s is specific heat capacity of the „system“, T_s is initial temperature of the „system“ .

To obtain *correct* results of calculations we have to consider also the heat capacity of the calorimeter itself!

Thermal conductivity

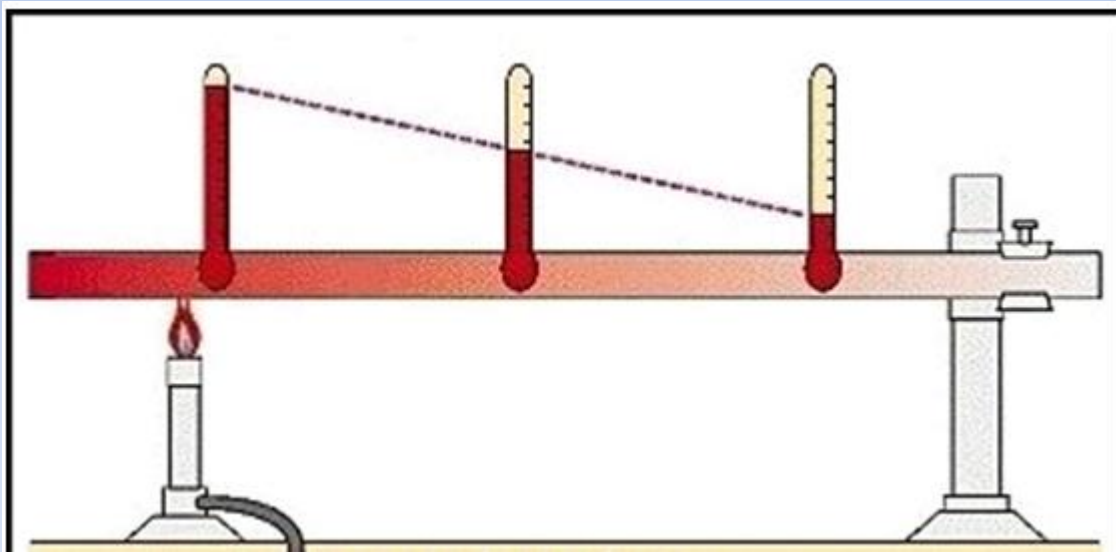
- **Equation of thermal conduction.** A steady heat conduction can be easily illustrated by a rod (cylinder) of a length d one end of which is kept at the temperature t_1 and the second one at the temperature t_2 . The temperature difference $\Delta t = t_2 - t_1$ is constant, the temperature decreases uniformly from the warmer end to the colder one. The fraction $\Delta t/d$ denotes **the temperature gradient**. Amount of heat Q which passes through the rod in an arbitrary (normally oriented) cross-section A during time τ is:

$$Q = \lambda A \frac{t_2 - t_1}{d} \tau$$

- The proportionality constant λ is the **coefficient of thermal conductivity**. By the magnitude of this coefficient we can distinguish good and poor thermal conductors – the second ones are called thermal insulators. Water belongs among relatively good heat conductors, even better are the metals. Typical thermal insulators are e.g. glass, plastics, porous materials, feathers, textile, glass wool etc.

Thermal conductivity

Heat flux in a metallic rod. Is it (could it be) a steady flux?
Discuss the problem. Consider the ambient medium.



Thermal conductivity

- The above equation of heat conduction is the simplest mathematical representation of the problem which otherwise has to be solved by means of integration of differential equations.
- **Thermal resistance** R characterises thermally insulating properties of a material layer of given thickness. If we know the value of the coefficient of thermal conductivity of the material layer, and the heat is transmitted uniformly and normally to the material layer, the thermal resistance is defined as

$$R = d/\lambda,$$

where d is the layer thickness [m] and λ [$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$] is the coefficient of thermal conductivity.

Thermal conductivity

Material	Thermal conductivity (K), (unit : W/m-K)
Diamond	2300
Silver	429
Cooper	401
Aluminum	237
Human skin	0.37
Wood	0.17
Air	0.026

Thermal conductivity table

Substance	$\lambda/W m^{-1} K^{-1}$
Silver	406.0
Copper	385.0
Aluminium	205.0
Brass	109.0
Steel	50.2
Lead	34.7
Mercury	8.3
Glass	1.1
Concrete	0.9
Water	0.56
Cardboard	0.21
Rubber	0.19
Wood	0.12-0.04
Silk	0.09
Fat	0.046
Fibreglass	0.042
Felt	0.04
Cork	0.04
Duck down	0.025
Air	0.024
Polyurethane	0.024

There are some differences / how to explain them?

How to explain apparent difference between the diamond and the air?

Thermal expansion of liquids and solids

Thermal expansion:

Changes in temperature lead to **expansion or contraction** of solids and liquids. In most cases, the dimensions of a body increase with temperature. **Thermal linear expansion** will be explained first:

$$\Delta l = \alpha l_0 \Delta T \quad \text{i.e.} \quad l = l_0 + \alpha l_0 \Delta T \quad [\text{m}],$$

where $\Delta l = l - l_0$ is the linear (longitudinal) expansion [m], ΔT is the temperature increase [K or °C], l_0 is the initial length of the body, and α is the **coefficient of linear expansion** (called also **linear thermal expansivity**).

Thermal expansion of liquids and solids

Material	α coefficient [$^{\circ}\text{C}^{-1}$]	Δl per 1 m and ΔT 100 $^{\circ}\text{C}$	β coefficient [$^{\circ}\text{C}^{-1}$]	ΔV per 1 litre and ΔT 100 $^{\circ}\text{C}$
aluminium	23×10^{-6}	2.3 mm	69×10^{-6}	6,9 ml
Bottle glass	9×10^{-6}	0.9 mm	27×10^{-6}	2,7 ml
Cooking glas	3×10^{-6}	0.3 mm	9×10^{-6}	0,9 ml
Concrete	12×10^{-6}	1.2 mm	36×10^{-6}	3,6 ml
copper	17×10^{-6}	1.7 mm	51×10^{-6}	5,1 ml
methanol	-----	-----	1200×10^{-6}	120 ml
gasoline	-----	-----	950×10^{-6}	95 ml
water	-----	-----	210×10^{-6}	21 ml

Thermal *volume* expansion can be expressed in the following way:

$$\Delta V = \beta V_0 \Delta T \quad \text{i.e.} \quad V = V_0 + \beta V_0 \Delta T$$

β is coefficient of volume expansion. It can be approximated: $V \approx V_0 + 3\alpha V_0 \Delta T$ ($\beta \approx 3\alpha$)

Thermal expansion of liquids and solids

- Applications and examples:



It can happen in very hot days!

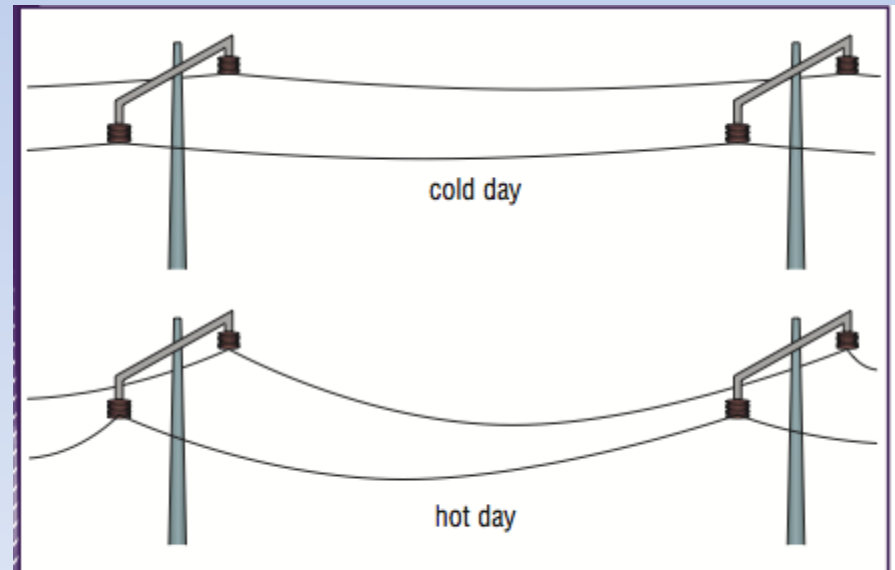


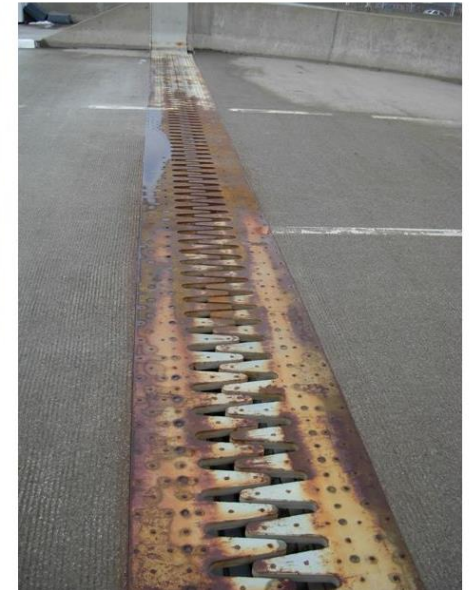
Fig 2.3.3 Power lines sag more on hot days. Heat makes the metal wires expand to become slightly longer.

Thermal expansion of liquids and solids

Expansion loops and joints



Road expansion gaps



The end

