

Lecture 4: Molecular physics and thermodynamics

Content:

- introduction to thermodynamics
- state variables (pressure, temperature, volume)
- temperature scales
- triple point of water
- state equation for ideal gas
- heat
- heat transfer mechanisms
- three laws of thermodynamics
- processes in ideal gas
- real gas

Introduction to the molecular physics and thermodynamics

Molecular physics is the study of the **physical properties** of **molecules**, the chemical bonds between **atoms** as well as the molecular dynamics. The field is closely related to atomic physics and overlaps greatly with theoretical chemistry, physical chemistry and chemical physics.

Thermodynamics is a branch of physics concerned with **heat and temperature** and their **relation to energy and work**. It defines macroscopic variables, such as internal energy, entropy, and pressure, that partly describe a body of matter or radiation. It states that the behavior of those variables is subject to general constraints, that are common to all materials, beyond the peculiar properties of particular materials.

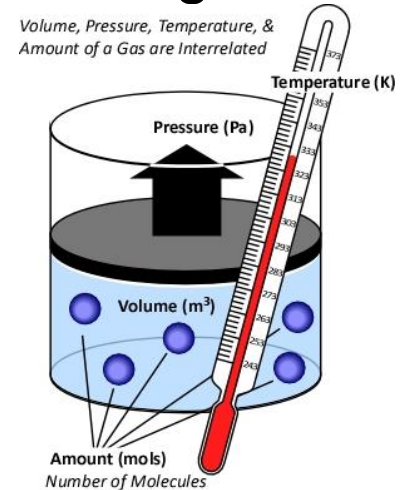
Introduction to the molecular physics and thermodynamics

Basics methods of study of the mechanical and thermal properties of substances:

- **statistic method**: application of probability theory and statistic in searching for new properties and relationships, based on so called **kinetic theory**
- **thermodynamic method**: based on measurements of the physical properties and their relationships (looking for the reasons and mechanisms).

state variables – describe the physical state of ideal gas:

- pressure p [Pa] (is explained by the kinetic theory as arising from the force exerted by molecules or atoms when they hit the walls of the volume)
- temperature T [K] (measure of average kinetic energy of the particles)
- volume V [m³]



thermodynamic process – all changes of state variables

other important variables, units and constants:

- **amount of substance** (amount of elementary entities, such as atoms, molecules, electrons and other particles) N [mol]

Older definition: 1 mole is equal to the amount of substance of a system, which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12 (¹²C).

This number is expressed by the **Avogadro constant** N_A [mol⁻¹], which has a value of $N_A = 6.022140857 \cdot 10^{23}$ [mol⁻¹].

Mole:

current definition:

1 mole is the unit of amount of substance of a specified elementary entity, which may be an atom, molecule, ion, electron, any other particle or a specified group of such particles; its magnitude is set by fixing the numerical value of the Avogadro constant to be equal to exactly 6.02214×10^{23} when it is expressed in the unit mol^{-1} .

older definition:

1 mole is equal to the amount of substance of a system, which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12 (^{12}C).

The problem was the unit kilogram, which was redefined.

Thermodynamic temperature

Thermodynamic temperature is the absolute measure of temperature and is one of the principal parameters of thermodynamics.

It is a measure of the warmth or coldness of an object or substance with reference to some standard value.

Unit: kelvin

current definition:

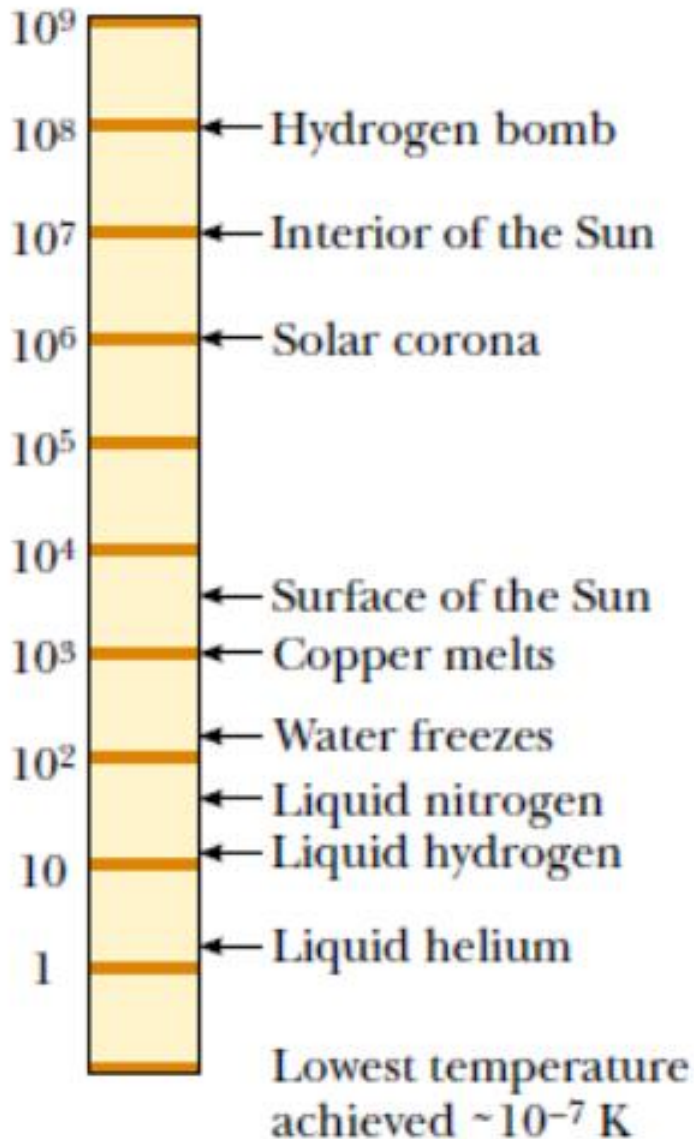
The kelvin, K, is the unit of thermodynamic temperature; its magnitude is set by fixing the numerical value of the Boltzmann constant to be equal to exactly 1.38065×10^{-23} when it is expressed in the unit $\text{s}^{-2} \cdot \text{m}^2 \cdot \text{kg} \cdot \text{K}^{-1}$.

older definition:

1 kelvin is the fraction $1/273.16$ of the thermodynamic temperature of the triple point of water.

thermodynamic temperature

Temperature (K)



500 nK in MIT labs

$-273,15^{\circ}\text{C}$

Absolute zero is the point at which the fundamental particles of nature have minimal vibrational motion, retaining only quantum mechanical, zero-point energy-induced particle motion.

Absolute zero is the lowest possible temperature, where nothing could be colder and no heat energy remains in a substance.

$$0 \text{ K} = -273.15^{\circ}\text{C}$$

thermodynamic temperature

How cold is the space?

The surface temperature of Pluto can get as low as -240 Celsius, just 33 degrees above absolute zero.

Clouds of gas and dust between the stars within our galaxy are only 10 to 20 degrees above absolute zero.

And if you travel out far away from everything in the universe, you can never get lower than a minimum of just **2.7 kelvin** or -270.45 Celsius. This is influenced by cosmic microwave background radiation, which permeates the entire universe.



absolute zero: - 273.15 C

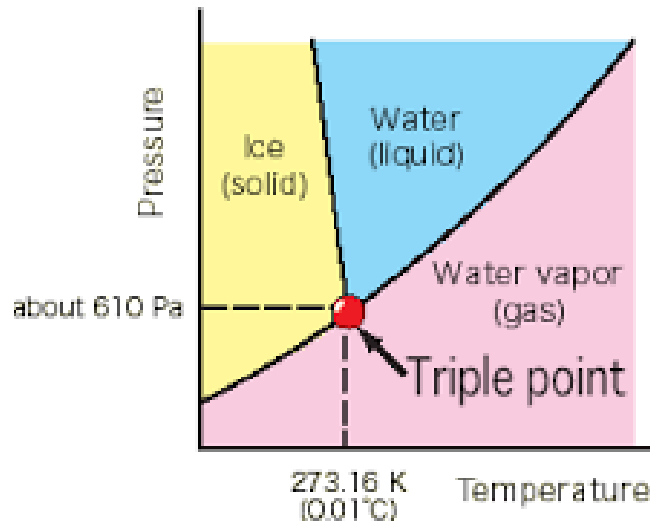
triple point (of water)

In thermodynamics, the triple point of a substance is the temperature and pressure at which the **three phases** (gas, liquid, and solid) of that substance

coexist in a thermodynamic equilibrium.

The triple point of water: 273.16 K at a pressure of 611.2 Pa, it was the basis of the older definition of the kelvin.

	Absolute zero	Freezing point of water	Triple point of water	Boiling point of water
Kelvin	0.00 K	273.15 K	273.16 K	373.15 K
Celsius	-273.15°C	0.00°C	0.01°C	100.00 °C



so called **pT-diagram**
(pressure vs temperature)

triple point values

Triple Point Data

Substance	Temperature K	Pressure 10^5Pa
Helium-4 (l-point)	2.17	0.0507
Hydrogen	13.84	0.0704
Deuterium	18.63	0.171
Neon	24.57	0.432
Oxygen	54.36	0.00152
Nitrogen	63.18	0.125
Ammonia	195.40	0.0607
Sulfur dioxide	197.68	0.00167
Carbon dioxide	216.55	5.17
Water	273.16	0.00610

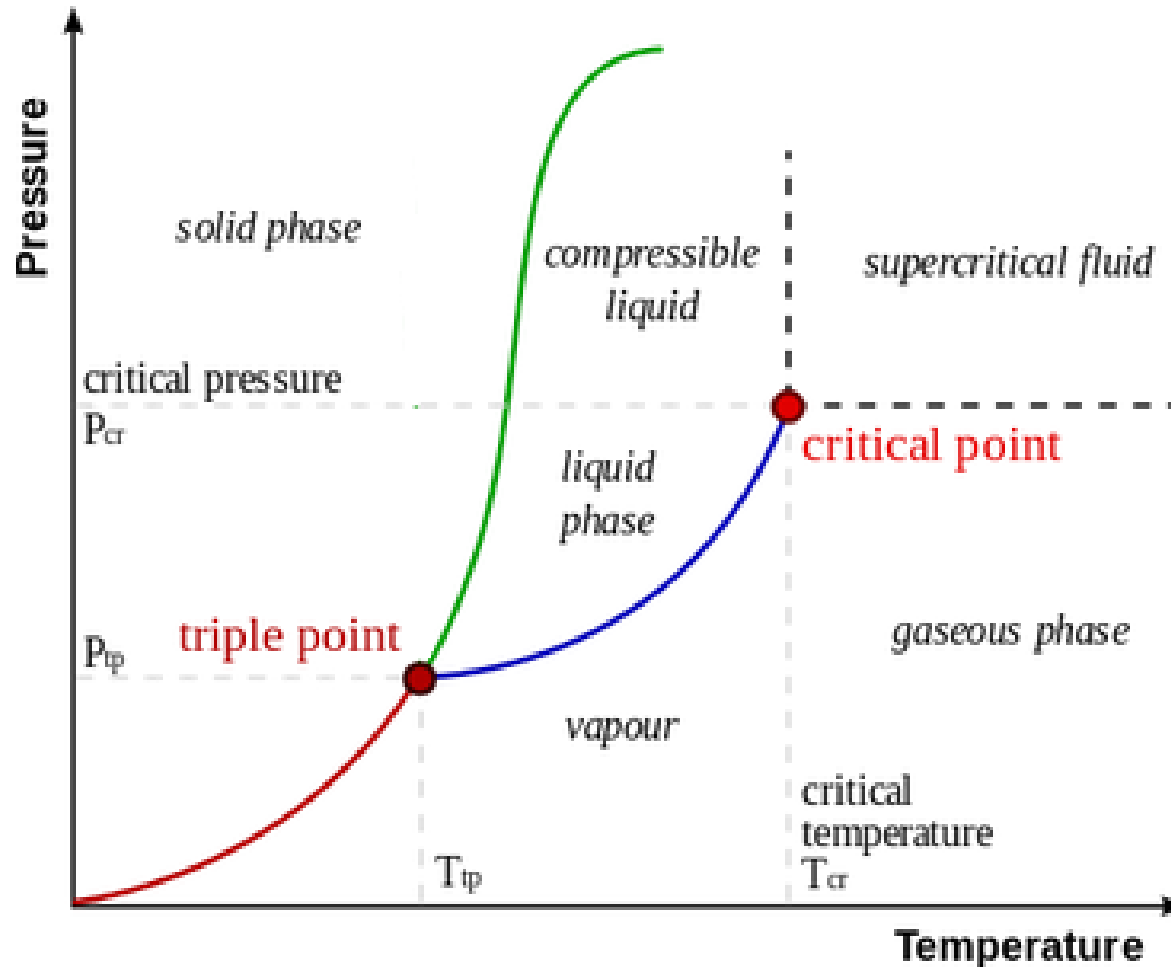
good table is given in Wikipedia...:
https://en.wikipedia.org/wiki/Triple_point

Table of triple points

Substance	T [K] (°C)	p [kPa]* (atm)
Acetylene	192.4 K (−80.7 °C)	120 kPa (1.2 atm)
Ammonia	195.40 K (−77.75 °C)	6.076 kPa (0.05997 atm)
Argon	83.81 K (−189.34 °C)	68.9 kPa (0.680 atm)
Arsenic	1,090 K (820 °C)	3,628 kPa (35.81 atm)
Butane ^[8]	134.6 K (−138.6 °C)	7×10^{-4} kPa
Carbon (graphite)	4,765 K (4,492 °C)	10,132 kPa (100.00 atm)
Carbon dioxide	216.55 K (−56.60 °C)	517 kPa (5.10 atm)
Carbon monoxide	68.10 K (−205.05 °C)	15.37 kPa (0.1517 atm)
Chloroform ^[9]	175.43 K (−97.72 °C)	0.870 kPa (0.00859 atm)
Deuterium	18.63 K (−254.52 °C)	17.1 kPa (0.169 atm)

critical point (of water)

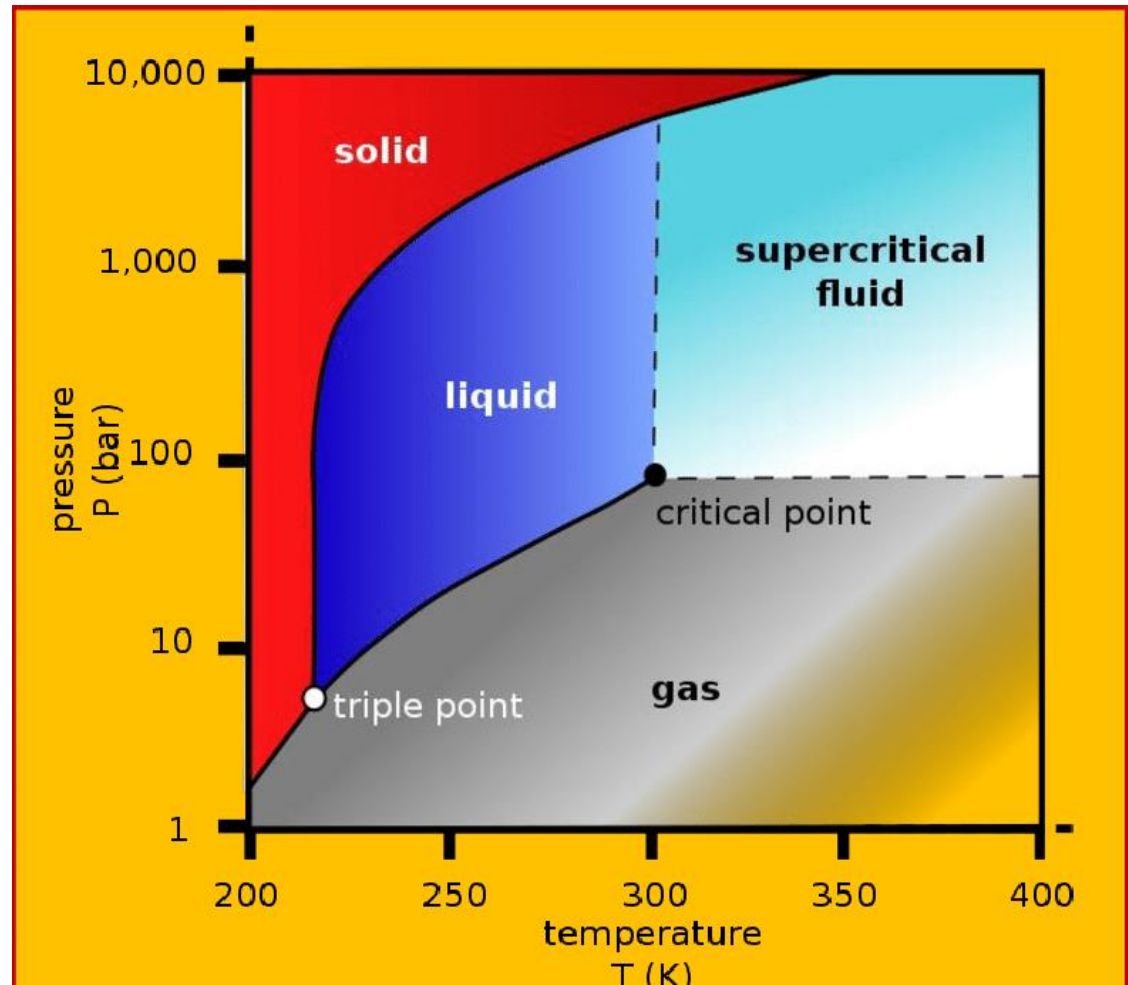
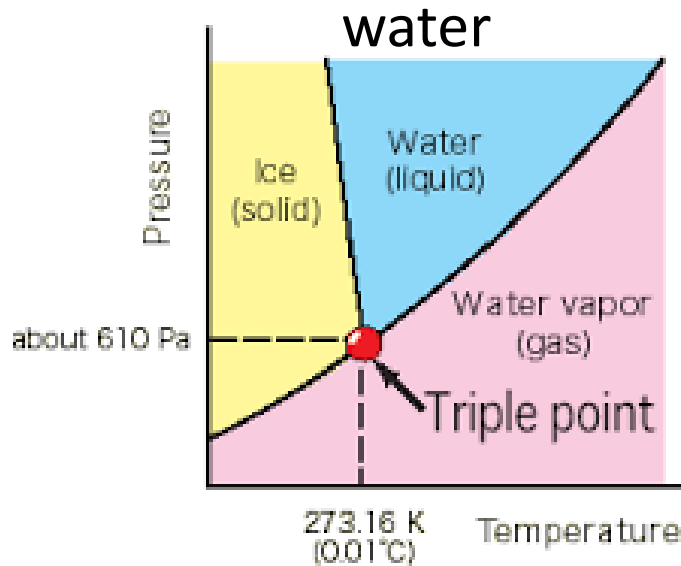
The liquid-vapor boundary terminates in an endpoint at some critical temperature and critical pressure. At the critical point, only one phase exists - so called **supercritical fluid**.



The critical point of water, 647 K at a pressure of 22.064 MPa.

triple point (CO₂)

CO₂

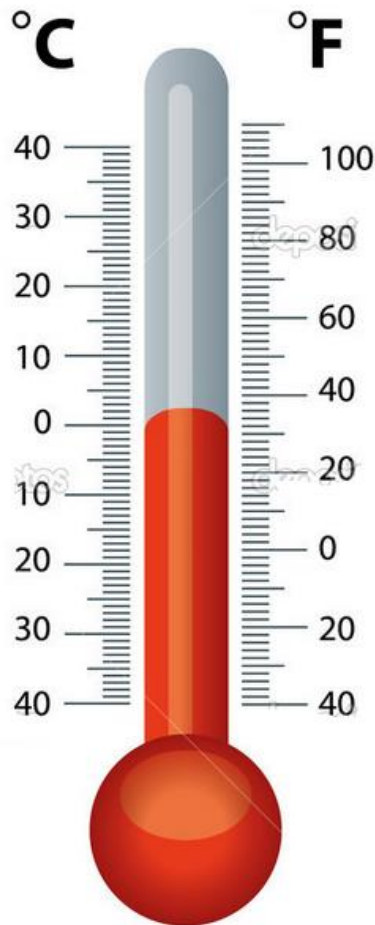


The triple point of CO₂: 216.55 K (−56.6 °C) and 517 kPa.

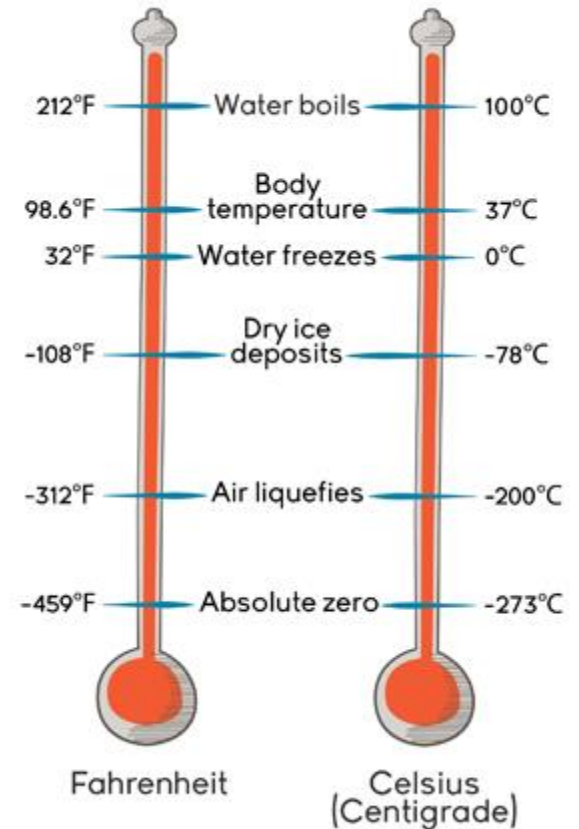
other temperature scales

most important: Celsius T_C and Fahrenheit T_F
(but also Rankine, Roerner, Newton, Delisle, Réaumur, ...)

conversion: $T_F = 9/5 T_C + 32$ (approx. change for 9°F is 5°C)



Celsius	Fahrenheit
0	32
5	41
10	50
15	59
20	68
25	77
30	86
35	95
40	104

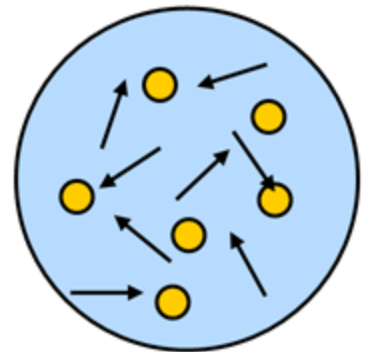


kinetic theory (ideal gas)

- well developed for the so called **ideal gas** –
kinetic theory of gases

Assumptions (**ideal gas**):

- the gas consist of small particles (molecules) distances between particles are large compared to their size,
- particles have the same mass,
- particles are in constant chaotic motion (thermal motion),
- all collisions are perfectly elastic,
- the interactions among molecules are negligible
- all trajectories of molecules motion are linear



State equation for ideal gas (ideal gas law)

$$pV = NkT$$

N – total amount of the particles (molecules or atoms)

k – Boltzmann's constant: $k = 1.38064852 \cdot 10^{-23} [\text{s}^{-2} \cdot \text{m}^2 \cdot \text{kg} \cdot \text{K}^{-1}]$

or

$$pV = nRT$$

n – amount of substance (number of moles)

R – ideal gas constant: $R = 8.3144598 [\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}]$

(valid for any gas or mixture of gases), it is a **product of Boltzmann constant k and Avogadro constant N_A** ,

exact derivation: <http://quantumfreak.com/derivation-of-pvnrt-the-equation-of-ideal-gas/>
or as a video: <https://www.youtube.com/watch?v=IPcEdLNmL8I>

State equation for ideal gas (ideal gas law)

$$pV = NkT$$

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and the definition of kelvin

$$\frac{pV}{NT} = k$$

The kelvin, K, is the unit of thermodynamic temperature; its magnitude is set by fixing the numerical value of the Boltzmann constant to be equal to exactly 1.38065×10^{-23} when it is expressed in the unit $\text{s}^{-2} \cdot \text{m}^2 \cdot \text{kg} \cdot \text{K}^{-1}$.

State equation for ideal gas (ideal gas law)



Simple exercise:

In a car tire at the temperature of 10 °C, the pressure of 200 kPa was measured. How it will change when the temperature will grow (after driving the car) to 27 °C?

We can try to evaluate the ratio of the two stages p_1V_1 and p_2V_2 (using the state equation):

$$\frac{p_1 V_1}{p_2 V_2} = \frac{n_1 R T_1}{n_2 R T_2} \Rightarrow p_2 = \frac{T_2 p_1}{T_1}$$

After entering the actual values, we get: $p_2 = 212$ kPa.

State equation for ideal gas (ideal gas law)

$$pV = NkT$$

N – total amount of the particles (molecules or atoms)

k – Boltzmann's constant: $k = 1.38064852 \cdot 10^{-23} [\text{s}^{-2} \cdot \text{m}^2 \cdot \text{kg} \cdot \text{K}^{-1}]$



Ludwig Boltzmann (1844 – 1906)

Austrian physicist
founder of so called
statistical physics

Heat

Heat (Q) is energy as it spontaneously passes between a system and its surroundings, other than as work or with the transfer of matter.
unit: joule [J].

heat exchange (ΔQ) – exchange of energy between systems with different temperature,

heat is always transferred from warmer to colder system.

heat capacity (C) – equal to the ratio of the heat added to (or removed from) an object to the resulting temperature change [J· K⁻¹]

internal energy – the system has internal energy U_1 at the beginning of thermodynamic process and U_2 at the end of the process. The thermodynamic process is described by changes of internal energy: $\Delta U = U_2 - U_1$

work (W) – it can be **received** by the system: $W > 0$
or **done** by system: $W < 0$ $\Delta U = W + Q$

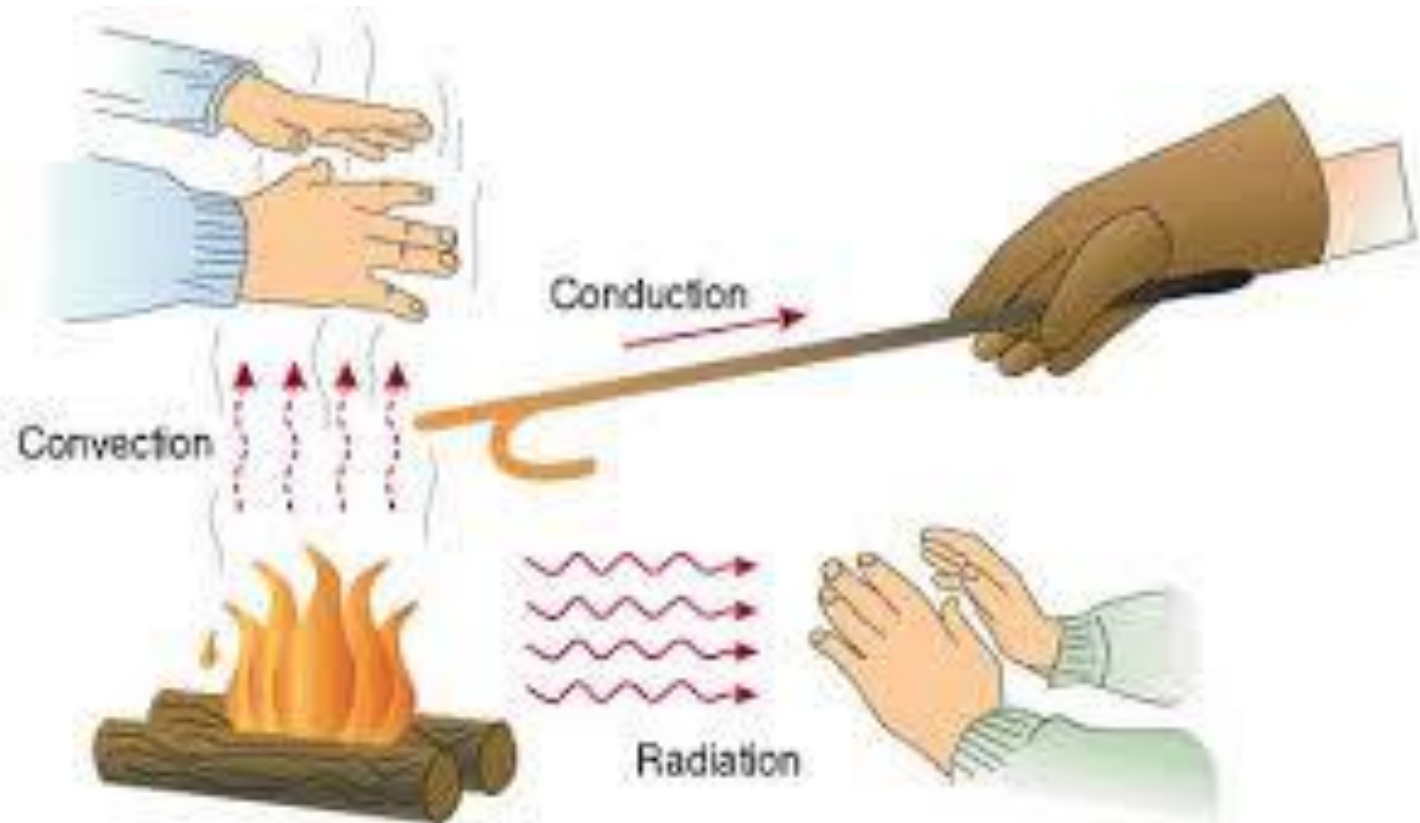
heat capacity – we work in practical application with so called specific heat capacity, unit $[J \cdot kg^{-1} \cdot K^{-1}]$.

Substance	$c/J \text{ kg}^{-1} \text{ K}^{-1}$	Substance	$c/J \text{ kg}^{-1} \text{ K}^{-1}$
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

transfer of heat

Mechanisms of heat transfer:

1. conduction (solid phase)
2. convection (liquid and gas phases)
3. radiation (electromagnetic transfer)



1. conduction

TABLE 17.5 Thermal conductivities

Material	k (W/m K)
Diamond	2000
Silver	430
Copper	400
Aluminum	240
Iron	80
Stainless steel	14
Ice	1.7
Concrete	0.8
Glass	0.8
Styrofoam	0.035
Air (20°C, 1 atm)	0.023

thermal conductivity –

property of a matter to conduct heat
(from warmer parts to colder ones).

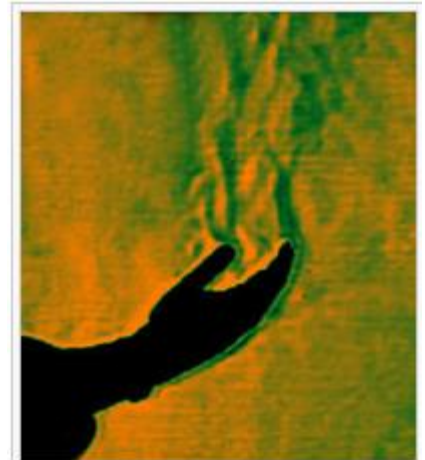
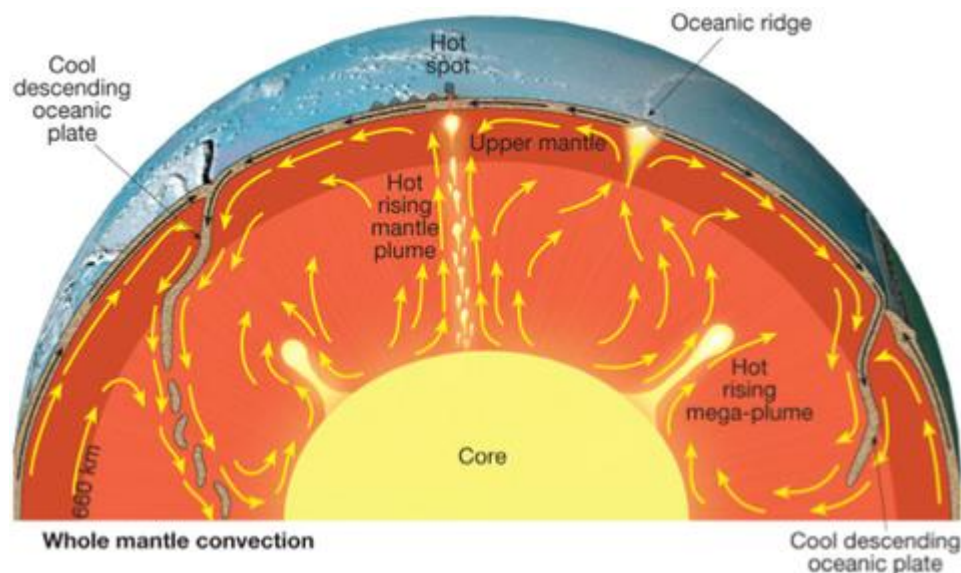
unit: $[\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}]$

2. convection



It is a much more effective way for heat transfer in gases and liquids, because these have a very low thermal conductivity.

Active also in heating and cooling of parts of the human body by blood circulation.

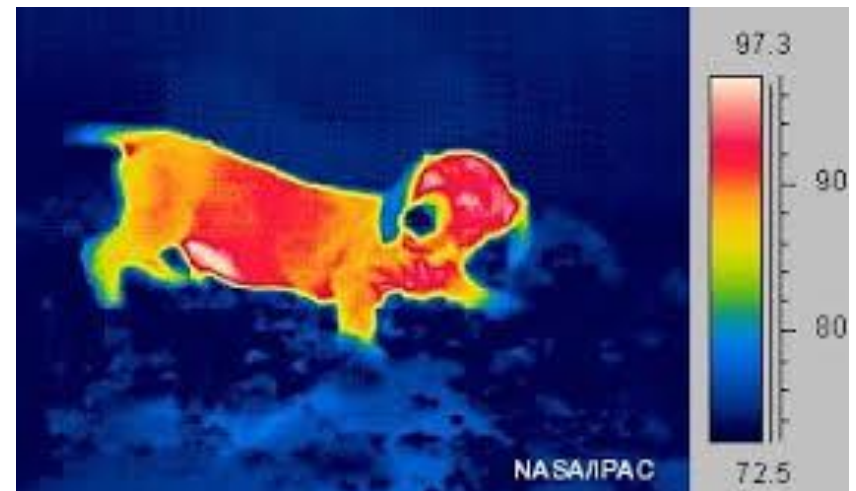
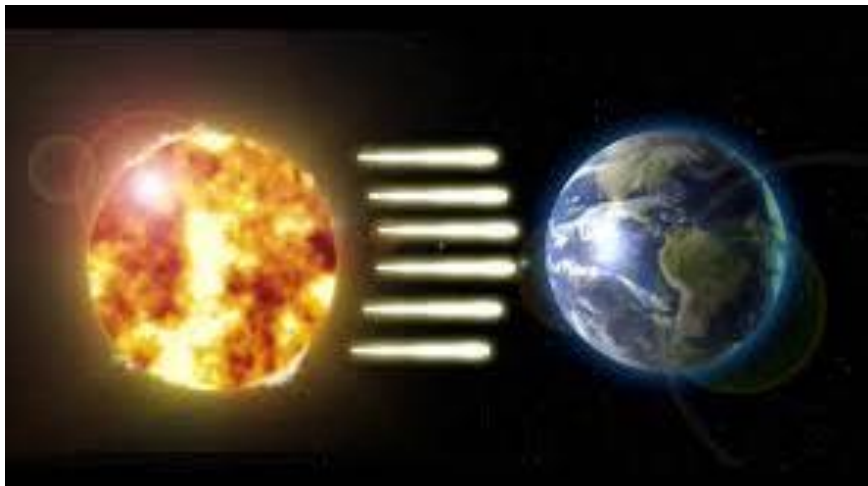
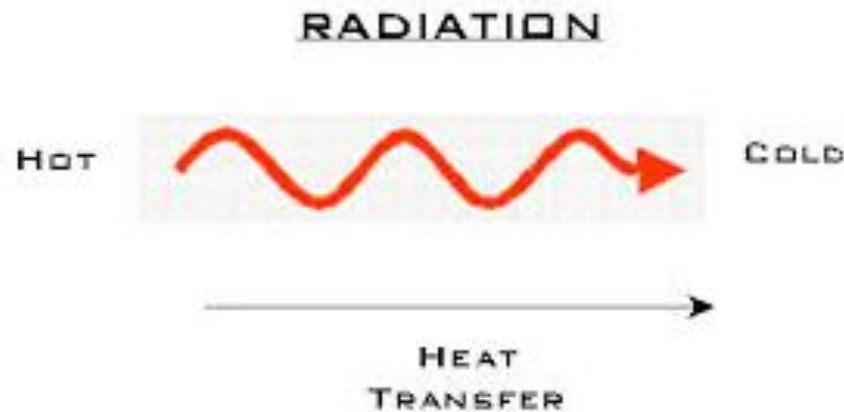


This color [schlieren](#) image reveals [thermal convection](#) from a human hand (in silhouette) to the surrounding still atmosphere. Photographed using schlieren equipment.

3. radiation

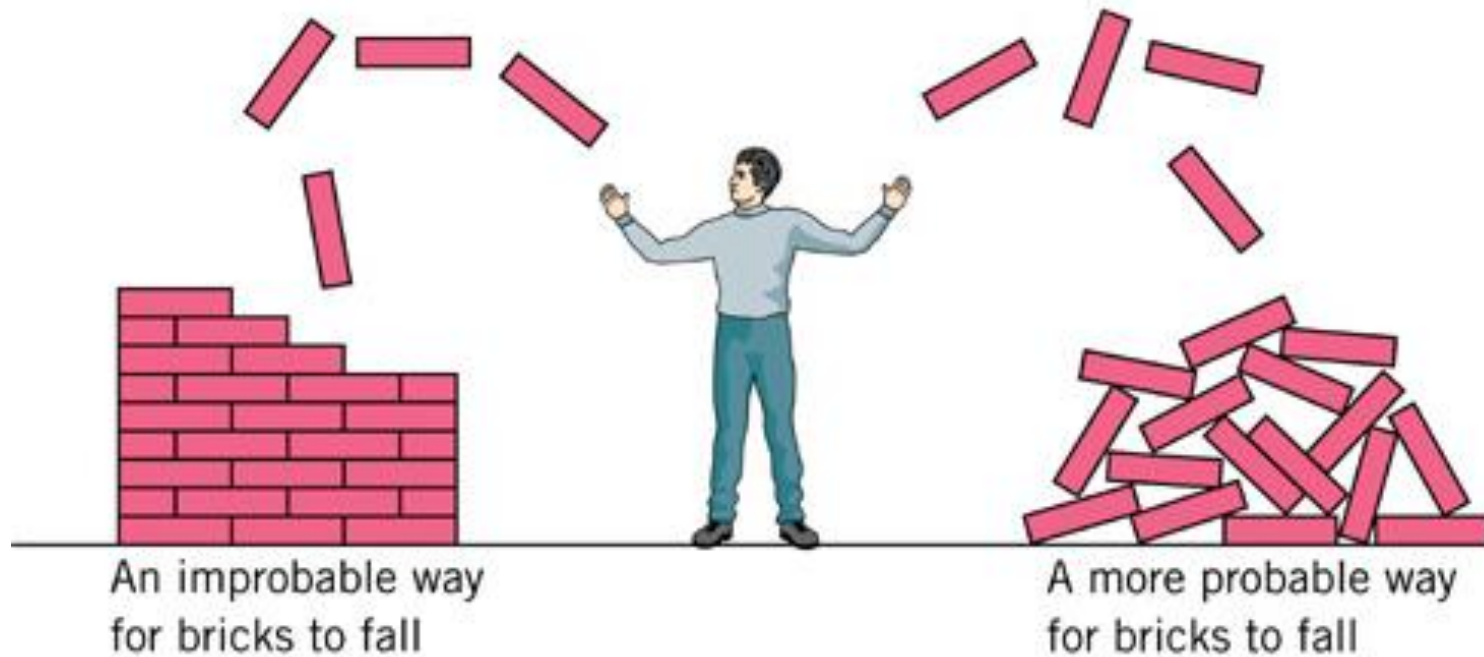
Thermal radiation is electromagnetic radiation generated by the thermal motion of charged particles in matter.

Thermal radiation occurs also through a vacuum.



Entropy (S) – is a measure of the disorder of a system.

For an irreversible process in an isolated system (a system not subject to outside influence), entropy is always increasing.



In thermodynamics, the change in entropy dS of a system, which goes from one state to another one can be expressed:

$$dS = dQ_{\text{rev}}/T ,$$

where dQ_{rev} is the heat absorbed by the system in a reversible process and T is absolute temperature.

laws of thermodynamics

#	LAW [condensed form]
1 st	The ENERGY Principle
2 nd	The ENTROPY Principle
3 rd	The TEMPERATURE Principle

First law of thermodynamics:

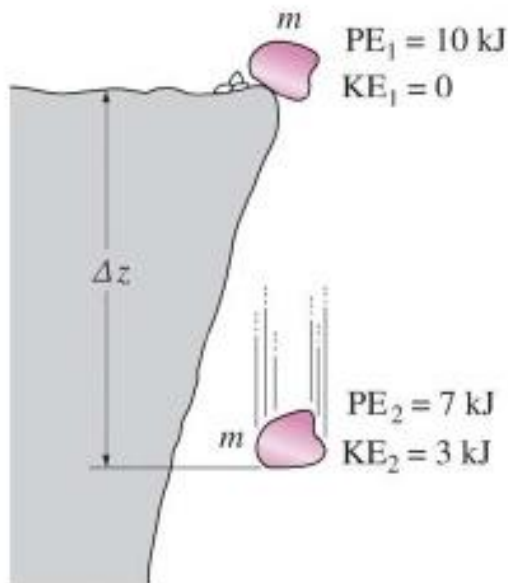
The change of internal energy of a system is equal to heat added to the system minus the work done by the system.

First law of thermodynamics:

When energy passes (work, heat, or matter change), into or out from a system, its internal energy changes in accord with the law of conservation of energy.

Conservation of energy means that the total energy of an isolated system is constant. Equivalently, perpetual motion machines of the first kind are impossible.

- The first law states that *energy can be neither created nor destroyed during a process; it can only change forms.*



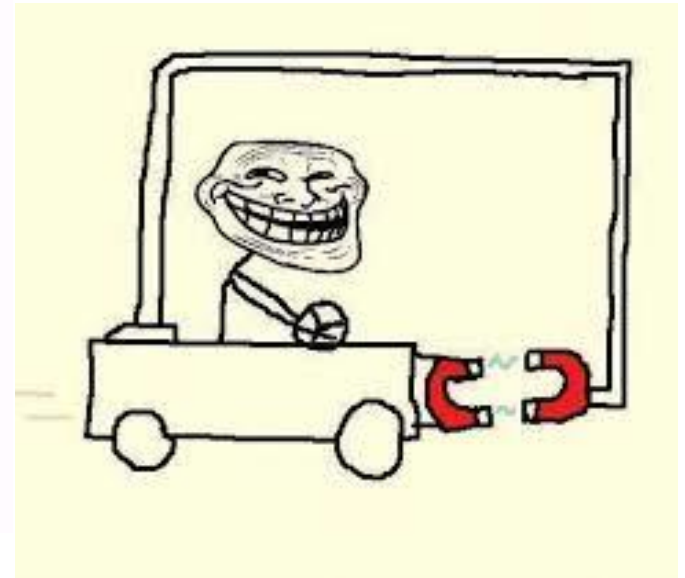
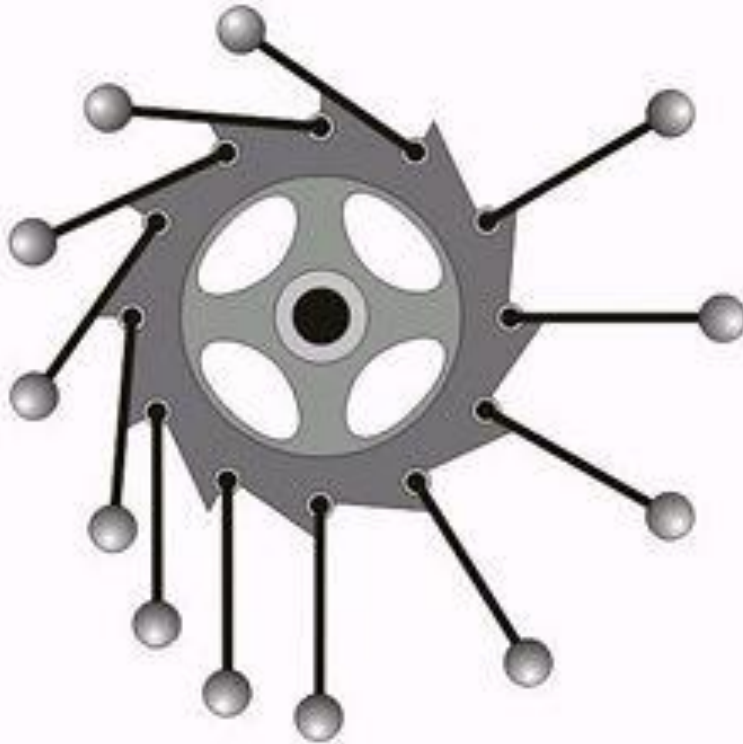
Energy cannot be created or destroyed; it can only change forms.



The increase in the energy of a potato in an oven is equal to the amount of heat transferred to it.

First law of thermodynamics:

Consequence of the first law of thermodynamics:
Perpetum mobile of 1. order can not be constructed.



Second law of thermodynamics:

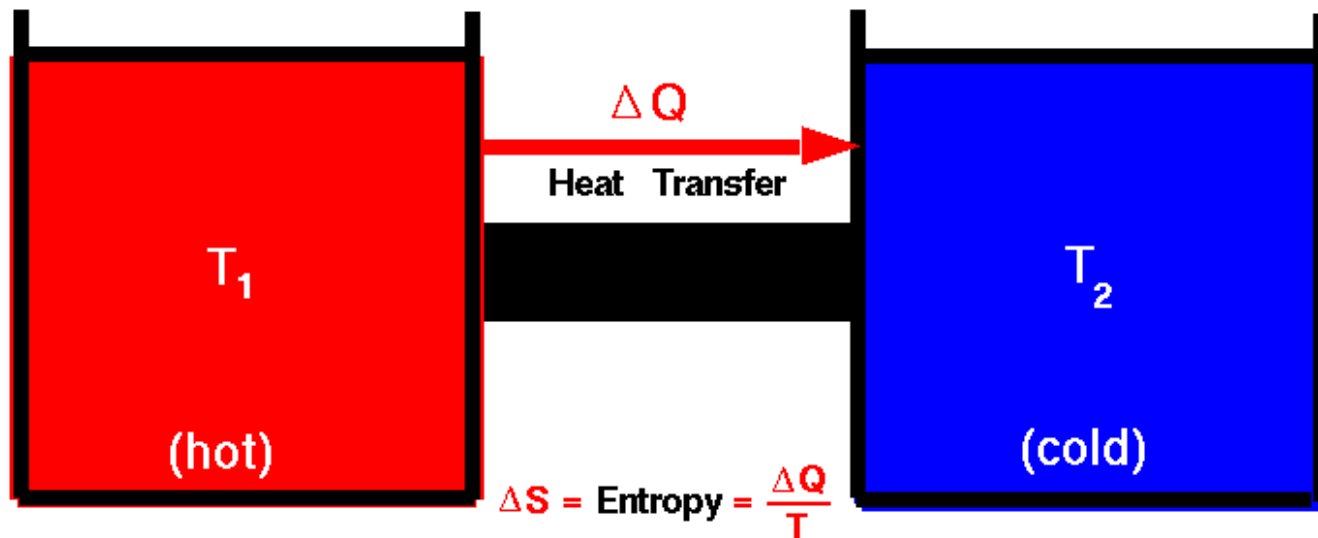
The total entropy of an isolated system always increases over time, or remains constant in ideal cases where the system is in a steady state or undergoing a reversible process.

Second law of thermodynamics:

Entropy must increase (unless controlled by an intelligence).

Consequence of this law: If two objects are *not* the same temperature then: heat will always flow from high to low temperatures.

Hot object will decrease in temperature and cold object will increase in temperature until they are both the same temperature.



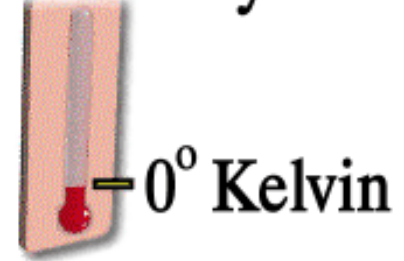
Third law of thermodynamics:

The entropy of a perfect crystal at absolute zero is exactly equal to zero.

Third law of thermodynamics:

- “Absolute zero” is a state of zero motion.
 - this means absolutely no entropy.
 - so it can’t be reached.

Third Law of Thermodynamics



Walther Nernst

Nernst Postulate

No finite sequence of cyclic processes can succeed in cooling a body to Absolute Zero.

Consequence

The entropy of every pure substance, in its lowest energy state, must have the same value.

processes in ideal gas

- isothermal process,
- isochoric process,
- isobaric process,
- adiabatic process.

In every situation we are interested into the mechanical work, which can be made by the ideal gas.

processes in ideal gas

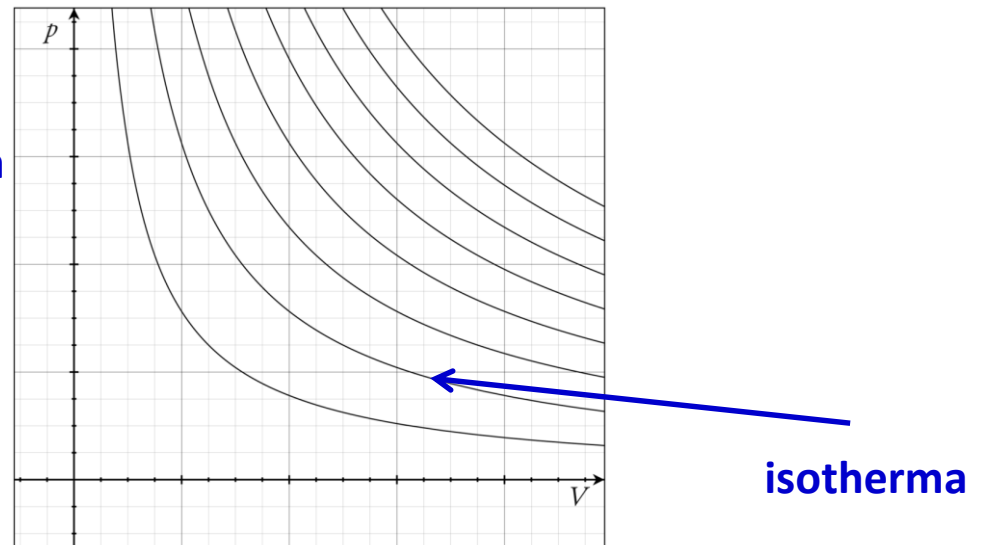
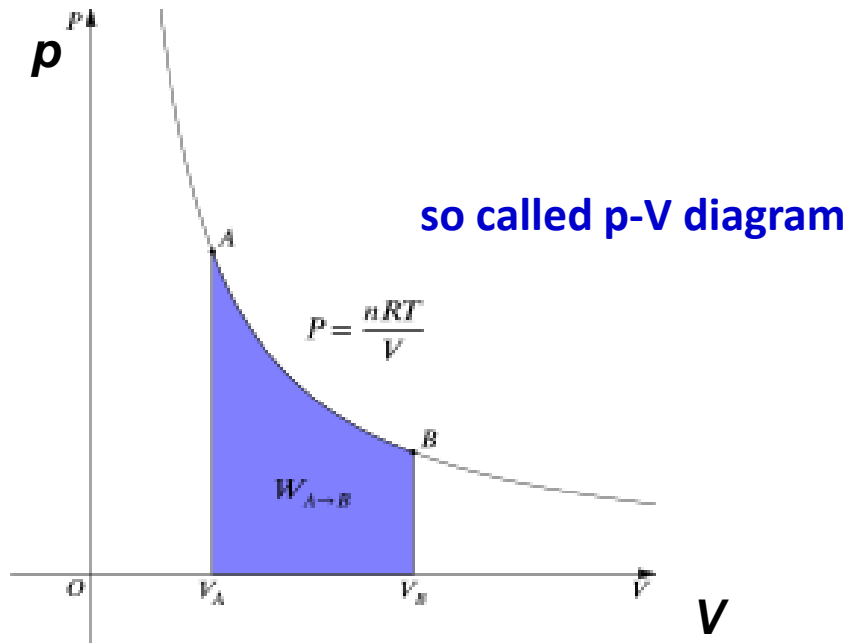
isothermal process temperature remains constant: **T = const.**

$$pV = nRT \rightarrow pV = \text{const.}$$

$$p_1 V_1 = p_2 V_2 \quad \text{Boyle – Mariott law}$$

while the temperature is not changing, the internal energy of the gas is not changing, too: $\Delta U = W + Q = 0 \Rightarrow W = -Q$

The heat received by the system in isothermal process is equal to the work produced by the system.



processes in ideal gas

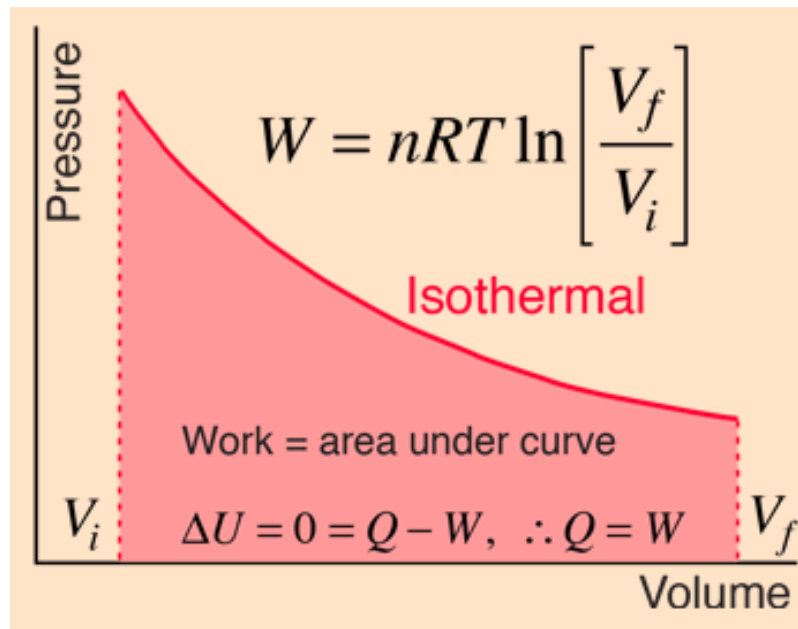
isothermal process temperature remains constant: **T = const.**

$$pV = nRT \rightarrow pV = \text{const.}$$

$$p_1 V_1 = p_2 V_2 \quad \text{Boyle – Mariott law}$$

The work done by ideal gas during an isothermal process is given by:

$$W_{A \rightarrow B} = \int_{V_A}^{V_B} p dV = \int_{V_A}^{V_B} \frac{nRT}{V} dV = -nRT \ln \frac{V_B}{V_A}$$



isochoric process

volume remains constant: **V = const.**

$$pV = nRT \rightarrow \frac{p}{T} = \text{const.}$$

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

Charles law

While the volume is not changing, the work made by gas is zero.

$$\Delta U = Q_V, \quad Q_V = m \cdot c \cdot \Delta T \quad c - \text{specific heat capacity}$$



isobaric process

Pressure remains constant: **p = const.**

$$pV = nRT \rightarrow \frac{V}{T} = \text{const.}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

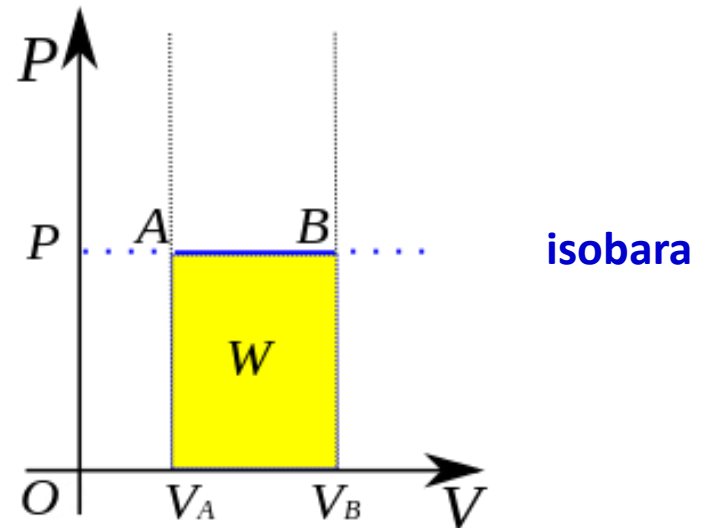
Gay – Lussac law

If the temperature of ideal gas is increased it received the heat

$$\Delta U = Q_p - W, \quad Q_p = m \cdot c_p \cdot \Delta T \quad c_p - \text{specific heat capacity in constant pressure}$$

The work is given by: $W = -nR\Delta T$

Try to think about the integral solution in this case (?)
How the expression for work W can be derived?



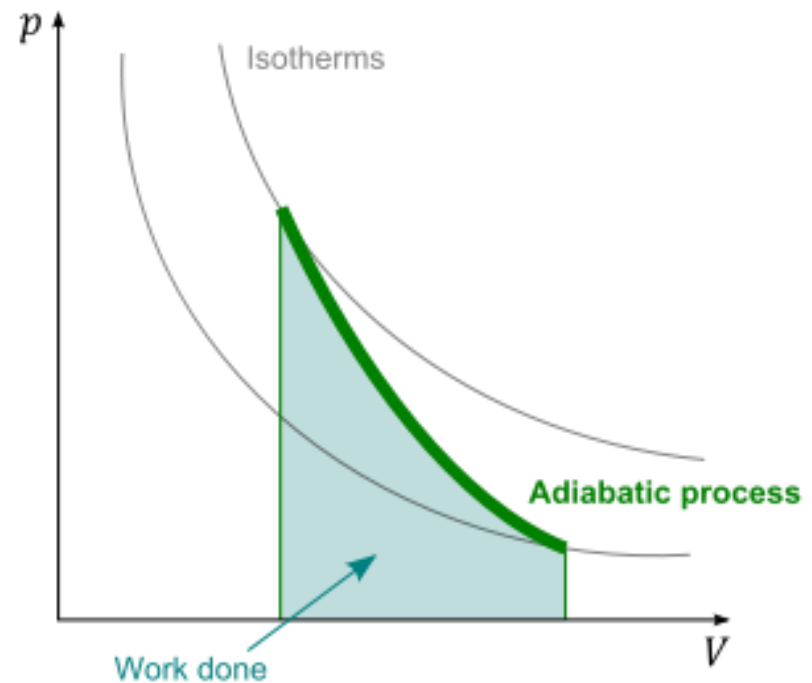
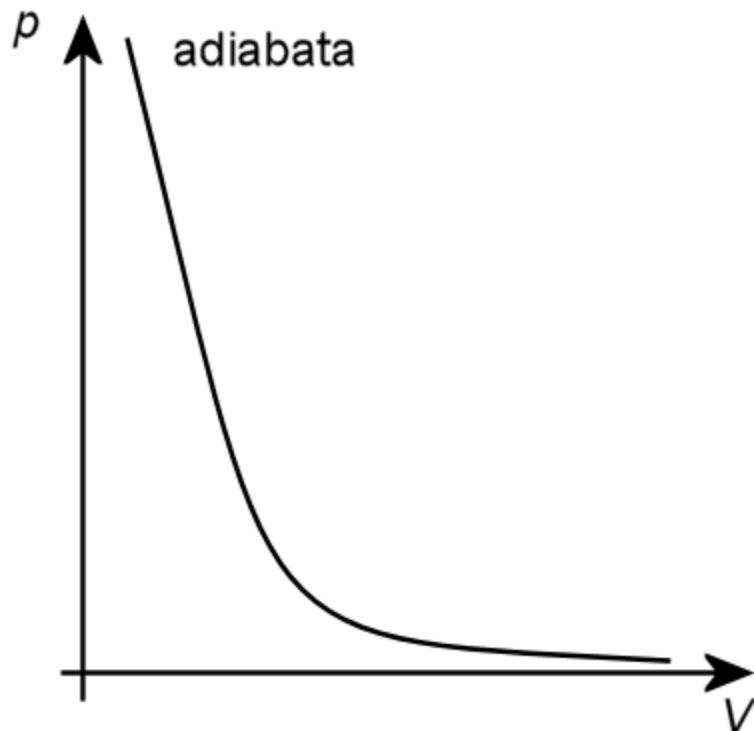
adiabatic process

- **no** transfer of heat or matter between a thermodynamic system and its surroundings

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

The work is given by: $W = \frac{1}{k-1}(p_1 V_1 - p_2 V_2)$

k – so called Poisson's constant
($5/3$ for monoatomic ideal gas,
 $7/5$ for diatomic ideal gas,...)



kinetic theory (real gas)

A real gas is a gas that does not behave as an ideal gas due to **interactions between gas molecules**.

Example: While **cool air** at ordinary pressure behaves like an ideal gas, **increasing its pressure or temperature increases the interactions between molecules**, resulting in real gas behavior that cannot be predicted reliably using the ideal gas law.

