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.

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 [m^3]
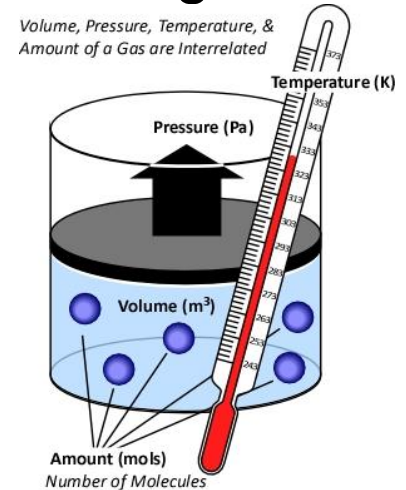
thermodynamic process – all changes of state variables

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 (^{12}C).

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 <u>is set by fixing the numerical value of the Avogadro constant</u> to be equal to exactly $6.02214X \cdot 10^{23}$ 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 <u>a measure of the warmth or coldness</u> of an object or substance with reference to some standard value.
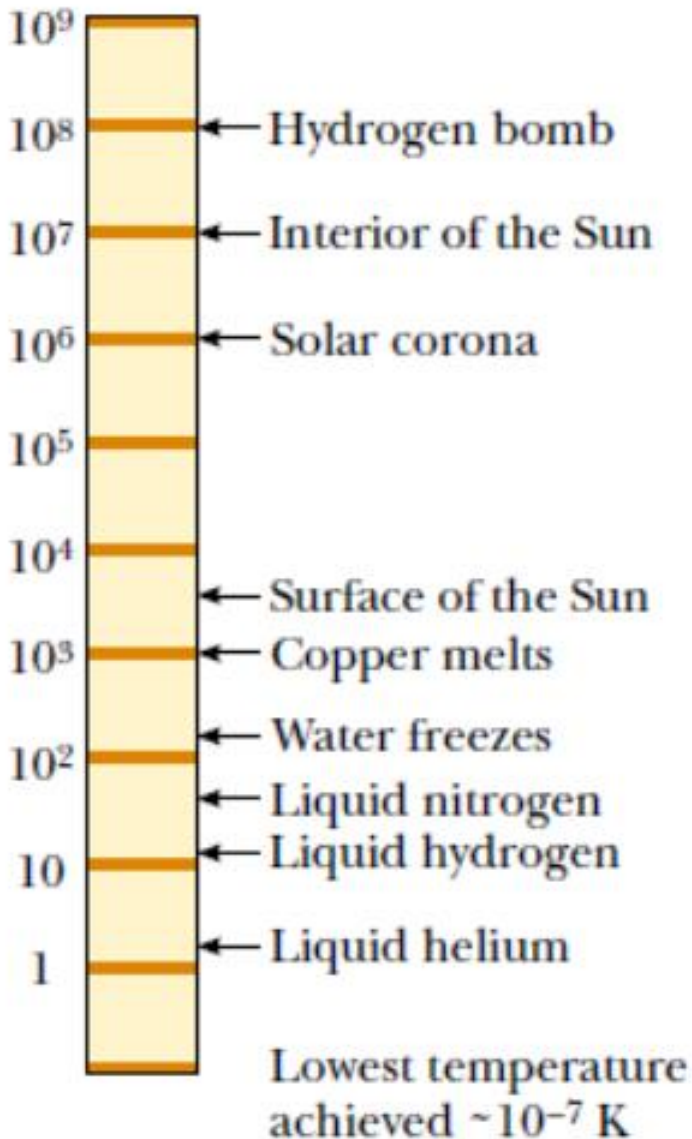
Unit: kelvin

current definition:

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

older definition:

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

thermodynamic temperature

-273,15°C

Temperature (K)

10^9

10^8 ←— Hydrogen bomb

10^7 ←— Interior of the Sun

10^6 ←— Solar corona

10^5

10^4

←— Surface of the Sun

10^3 ←— Copper melts

←— Water freezes

10^2

←— Liquid nitrogen
←— Liquid hydrogen

10

←— Liquid helium

1

Lowest temperature
achieved ~10^{-7} K

500 nK in MIT labs

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.

$$0 \text{ K} = -273.15 \text{ °C}$$

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
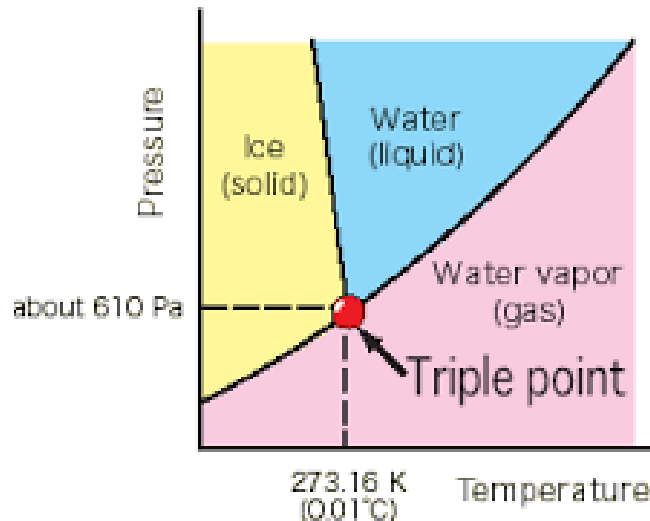
so called pT-diagram (pressure vs temperature)

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.
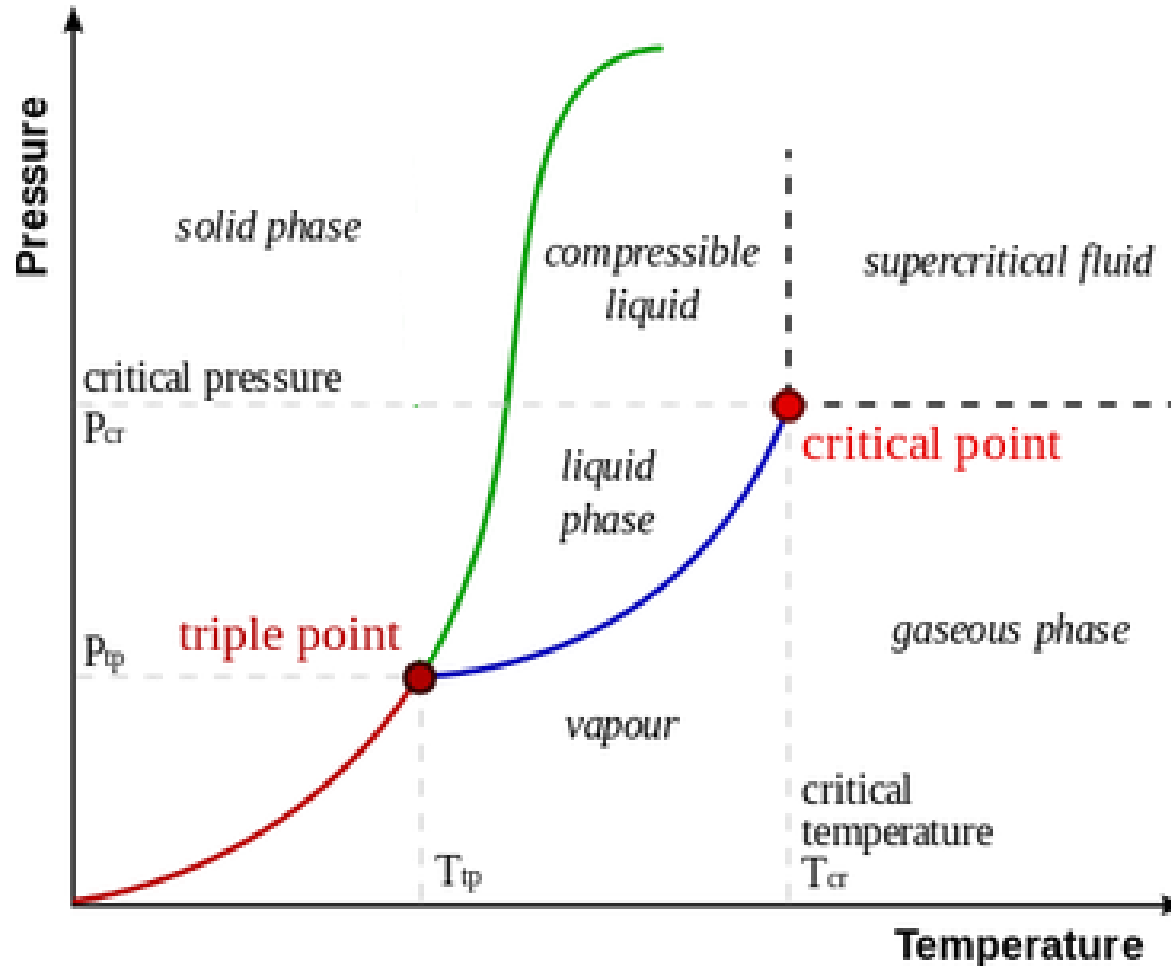
The critical point of water, 647 K at a pressure of 22.064 MPa.
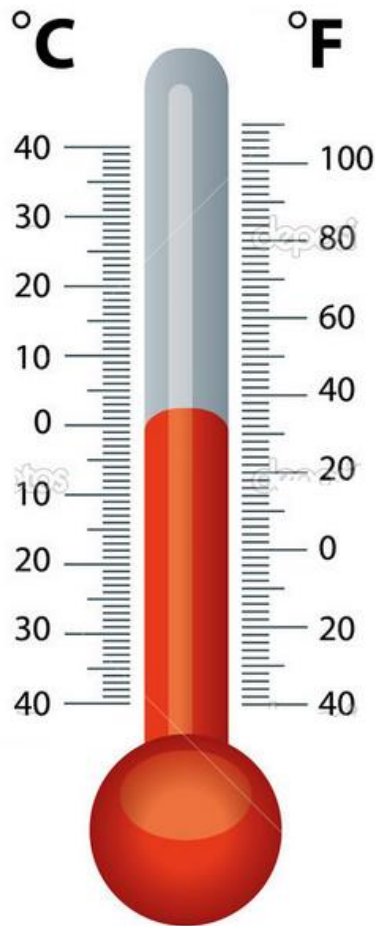
triple point (CO$_2$)

CO$_2$

water
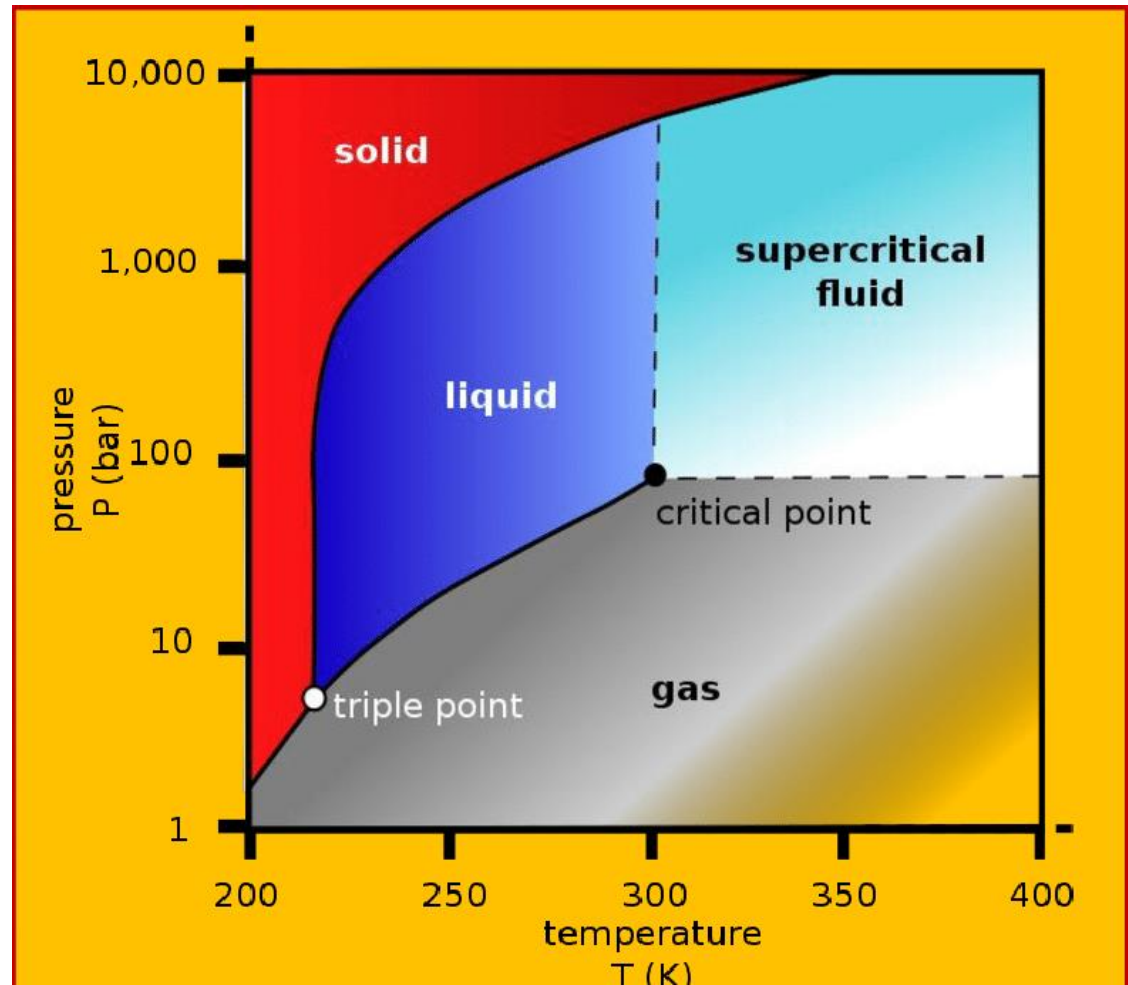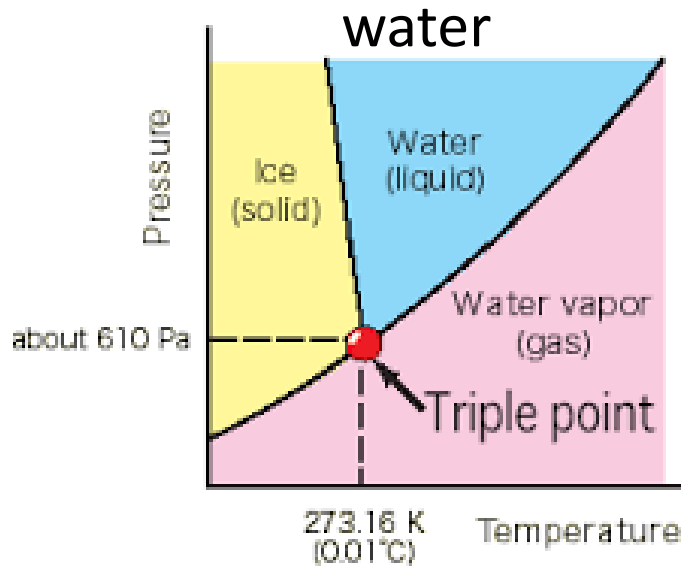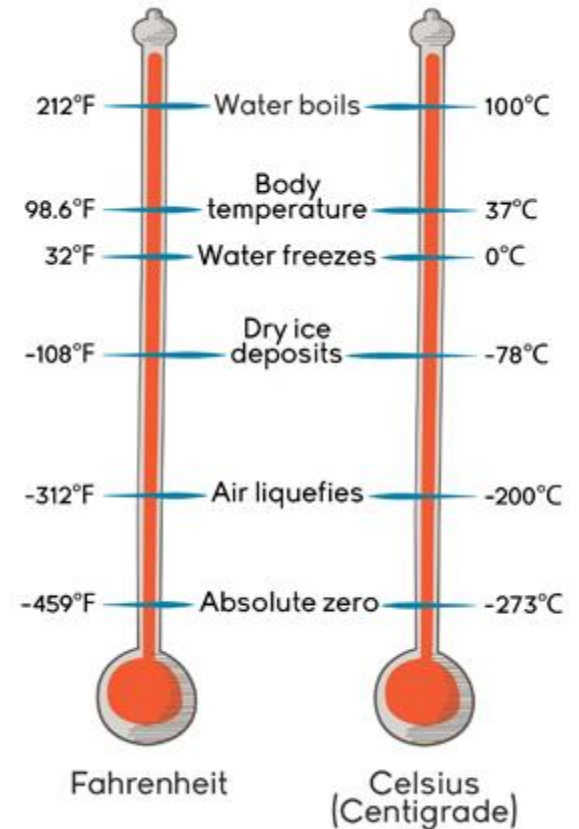

The triple point of CO$_2$: 216.55 K (−56.6 °C) and 517 kPa.

other temperature scales

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

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

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

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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
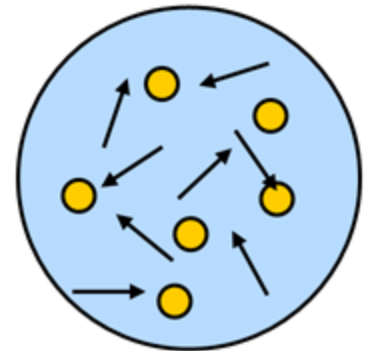
State equation for ideal gas (ideal gas law)

$$pV = NkT$$

p – pressure, *V* – volume, *T* – thermodynamic temperature,
N – total amount of the particles (molecules or atoms),
k – Boltzmann's constant: $k = 1.38064852 \cdot 10^{-23}$ [$s^{-2} \cdot m^2 \cdot kg \cdot K^{-1}$]

or

$$pV = nRT$$

n – amount of substance **(**number of moles),
R – ideal gas constant: $R = 8.3144598$ [$J \cdot K^{-1} \cdot mol^{-1}$],
   (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=lPcEdLNmL8I

State equation for ideal gas (ideal gas law)

What is the relation between the <u>ideal gas constant</u> (R) and the <u>Boltzmann's constant</u> (k)?

$$R = nk$$

R – ideal gas constant: $R = 8.3144598$ [J·K^{-1}·mol^{-1}],
n – amount of substance (number of moles),
k – Boltzmann's constant: $k = 1.38064852 \cdot 10^{-23}$ [s^{-2}·m^2·kg·K^{-1}].

State equation for ideal gas (ideal gas law)

$$pV = NkT$$

p – pressure, V – volume, T – thermodynamic temperature,
N – total amount of the particles (molecules or atoms),
k – Boltzmann's constant: $k = 1.38064852 \cdot 10^{-23}$ [$s^{-2} \cdot m^2 \cdot kg \cdot K^{-1}$]

From this equation follows the definition of kelvin ⬅

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

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

State equation for ideal gas (ideal gas law)

$$pV = NkT$$

N – total amount of the particles (molecules or atoms)
k – Boltzmann's constant: $k = 1.38064852 \cdot 10^{-23}$ [s^{-2}·m^2·kg·K^{-1}]

Little bit from the history:

Ludwig Boltzmann (1844 – 1906)
Austrian physicist,
founder of so called statistical physics
(revolutionary approach at that times).

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) – ratio of the heat added to (or removed from) an object to the resulting temperature change,
unit [J·kg^{-1}·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 (C) –
ratio of the heat added to (or removed from) an object to the
resulting temperature change,
we work in practical application with so called specific heat capacity,
physical unit [J·kg^{-1}·K^{-1}].

Substance	c/J kg^{-1} K^{-1}	Substance	c/J kg^{-1} 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, also in vacuum)
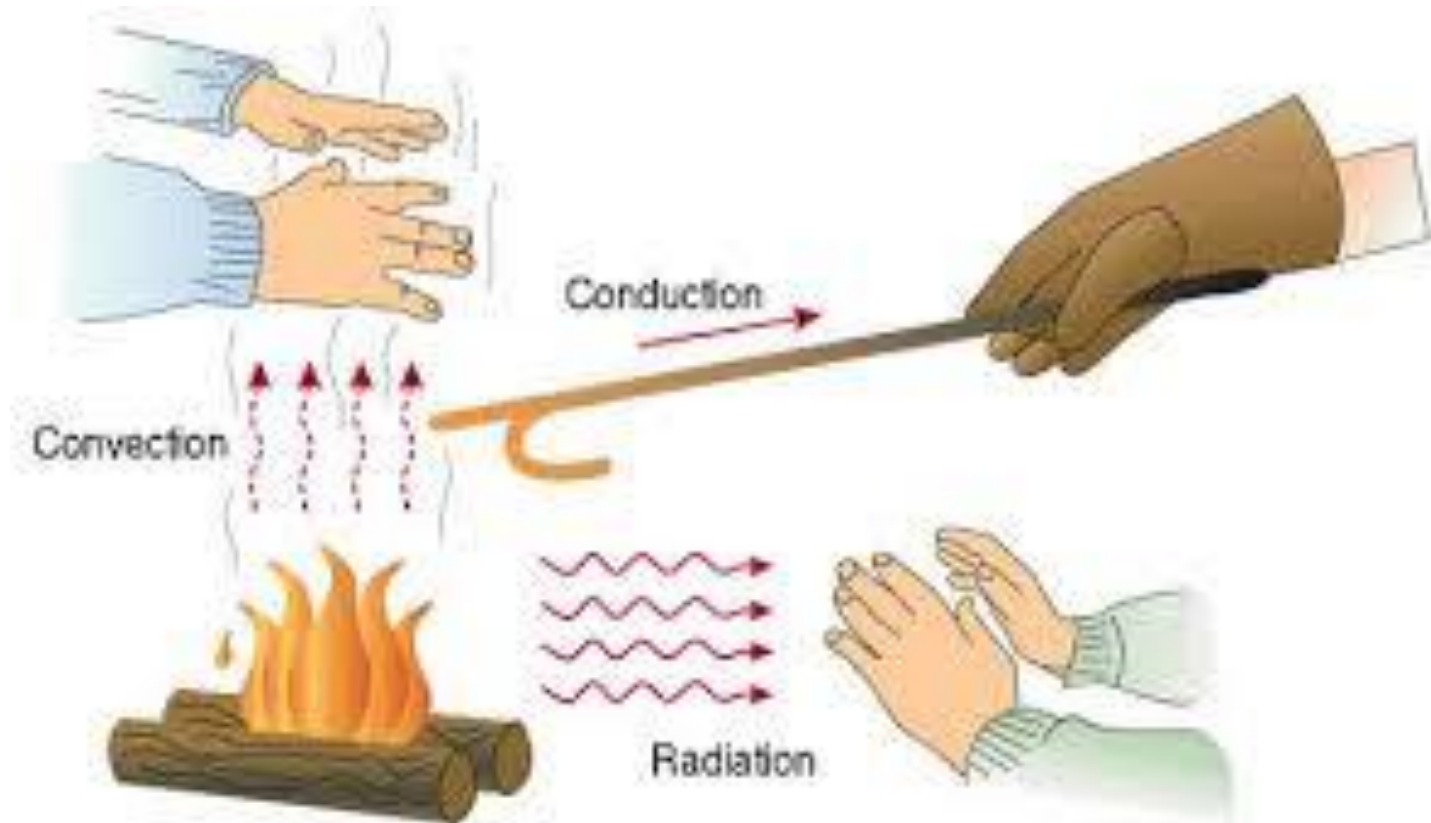
1. conduction

Thermal conduction is the transfer of internal energy by microscopic oscillations of particles and movement of electrons within a body.

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

Physical parameter:

thermal conductivity

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

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

From this reason a cooker is usually made from metal (which has usually high thermal conductivity), but a ladle from wood…

2. convection

Thermal convection is the transfer of heat from one place to another due to the movement of fluid or gas.

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.

Active also in Earth interior.
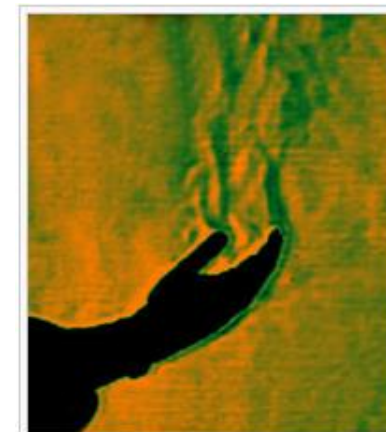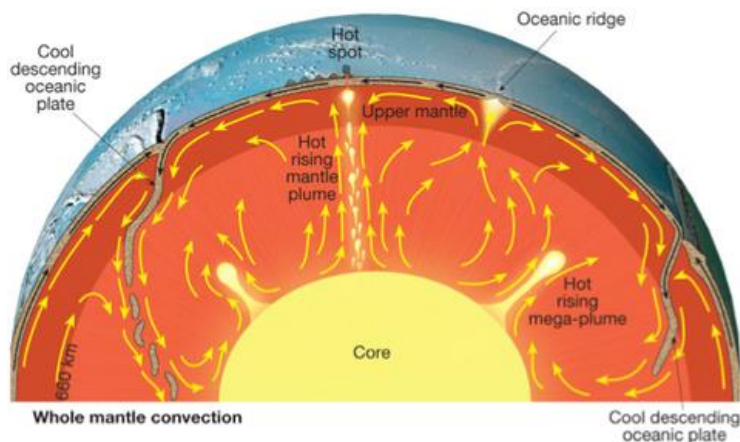
This color schlieren image reveals thermal convection from a human hand (in silhouette) to the surrounding still atmosphere. Photographed using schlieren equipment.

3. radiation

Thermal radiation is electromagnetic radiation generated by the thermal motion of charged particles in matter.
Wavelength interval from the EM spectrum: 0.1 micrometer - 100 micrometer.
Thermal radiation occurs also through a vacuum.
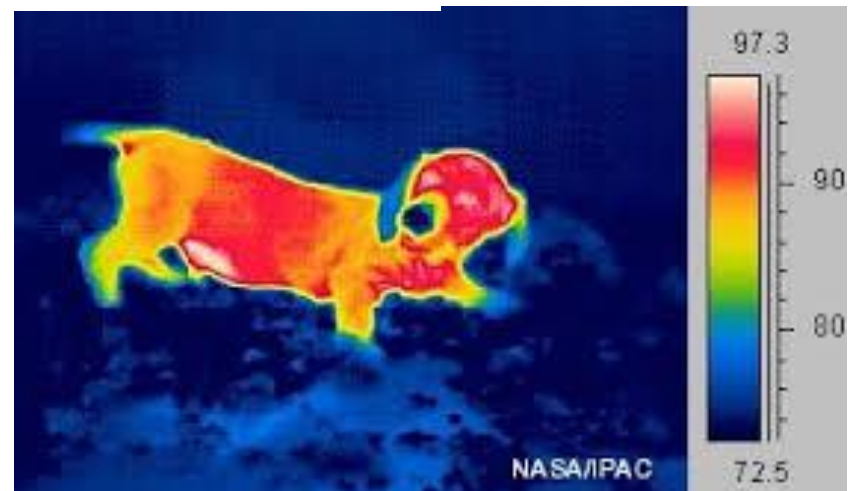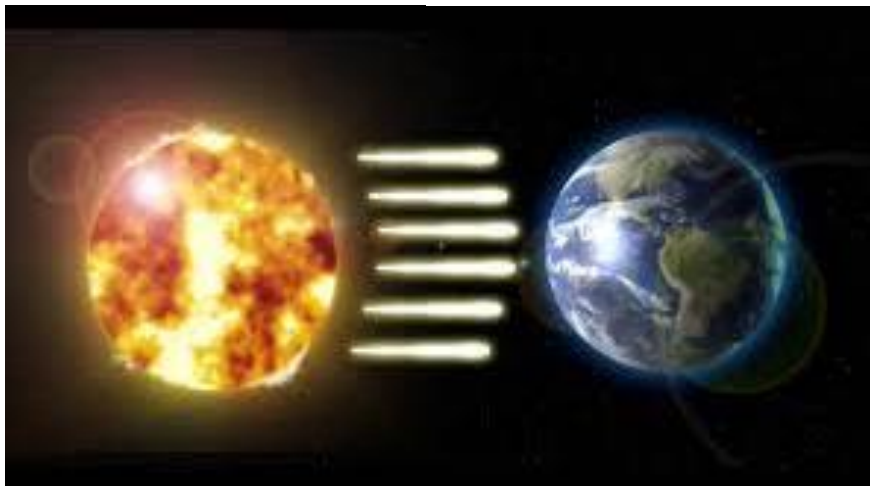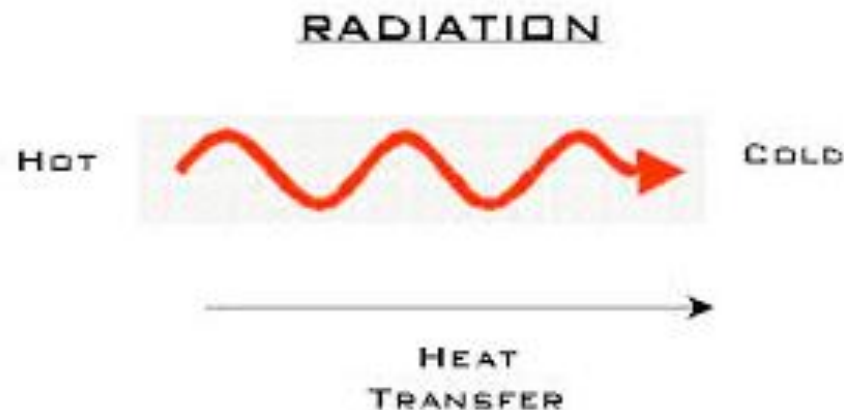
Which of these two snowmans will melt more quickly?

Which of these two snowmans will melt more quickly?

Which of these two snowmans will melt more quickly?

A woman poses by a thermometer, Sunday, July 16, 2023, in Death Valley National Park, Calif.

Will this woman "feel warmer" under the fur coat (Death Valley)?

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Laws of thermodynamics

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

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

Entrophy is the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work. Unit [$J \cdot K^{-1}$]. Because work is obtained from ordered molecular motion, the amount of entropy is also a measure of the molecular disorder, or randomness, of a system.

For an irreversible process in an isolated system (a system not subject to outside influence), entropy is always increasing. In a reversible process, the total entropy of an isolated system *remains constant*.
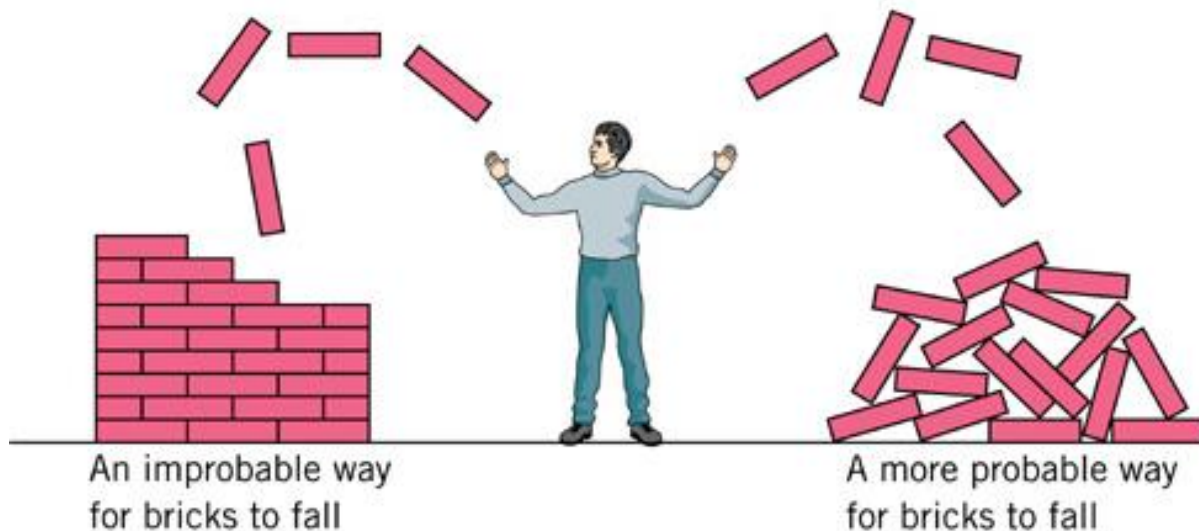
An improbable way
for bricks to fall

A more probable way
for bricks to fall

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

Entrophy is the measure of a system's <u>thermal energy per unit temperature</u> that is unavailable for doing useful work. Unit [J·K⁻¹].
Because work is obtained from ordered molecular motion,
the amount of entropy is also a measure of the molecular disorder, or randomness, of a system.

Austrian physicist **Ludwig Boltzmann** explained entropy as
the measure of the number of possible microscopic arrangements
or states of individual atoms and molecules of a system that comply
with the macroscopic condition of the system.
He has used following formula:

$$S = k \ln(\Omega)$$

where:
k is the Boltzmann's constant,
Ω is the number of configurations of microscopic states
   of a system where all microstates are equiprobable.

Enthalpy and entropy

Enthalpy is the measure of total heat present in the thermodynamic system where the pressure is constant.
It is represented as:
$\Delta H = \Delta E + p \Delta V$, unit [J],
where: E is the internal energy, p is constant pressure, V is the volume

Entropy is the measure of disorder in a thermodynamic system. It describes the system's thermal energy per unit temperature that is unavailable for doing mechanical work. Unit [$J \cdot K^{-1}$].

Entropy increases →

| Solid | Liquid | Gas |

← Enthalpy increases
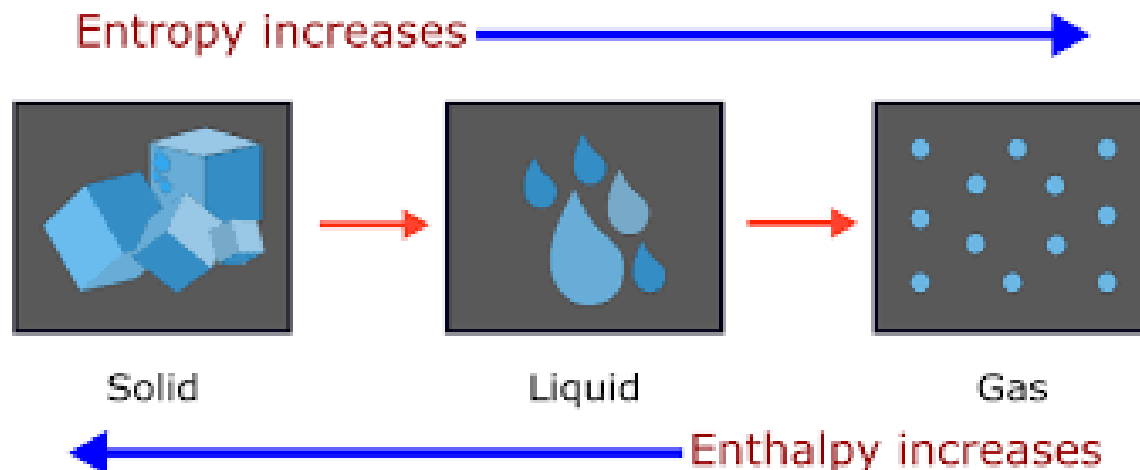
First law of thermodynamics:

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.

In other words: energy can be neither created or destroyed during processes in isolated systems – it can only change forms.

First Law of Thermodynamics Equation

$$\Delta E = Q - W$$

(Net change in total energy)   (Heat added)   (Work done)

First law of thermodynamics:

Consequence of the first law of thermodyamics:
Perpetuum mobile of first order can not be constructed
(perpetuum mobile = perpetual motion machine).

Comment:
A perpetual motion machine of the first kind produces work
without the input of energy.
The second kind would convert all of the heat (it receives) into
work, and the third kind would eliminate all forms of dissipation.
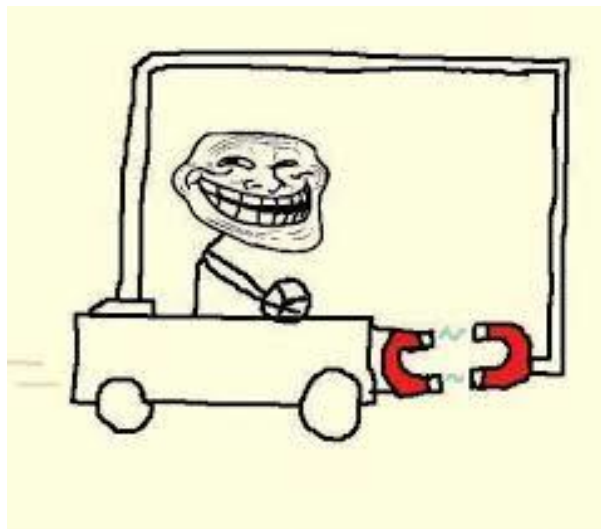
"Oh ye seekers after perpetual motion, how many vain chimeras have you pursued?
Go and take your place with the alchemists."
Leonardo da Vinci, 1494

First law of thermodynamics:

Historical context:

Julius Robert von Mayer was a German physician, chemist, and physicist and one of the founders of thermodynamics.

He was one of the first authors of the idea of the conservation of energy, namely that "energy can be neither created nor destroyed".

His achievements were overlooked and priority for the discovery of the basics of thermo-dynamics was attributed to **James Precott Joule**.

There were also important contributions from and **William Thomson (lord Kelvin)** and **Rudolf Clausius**.

Julius Robert von Mayer

1814 – 1878

James Prescott Joule

1818 – 1889

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.

ΔQ

Heat Transfer

T_1

T_2

(hot)

(cold)

ΔS = Entropy = $\dfrac{\Delta Q}{T}$
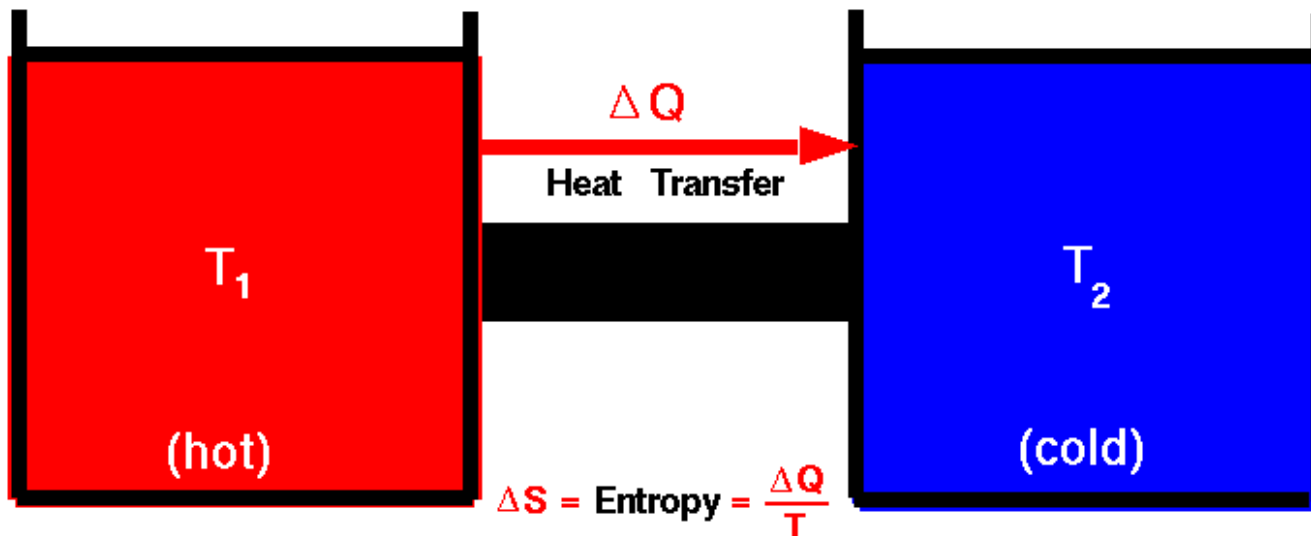
Second law of thermodynamics:

Historical context:

Scottish physicist **William Thomson**, also known as **Lord Kelvin**, and German physicist **Rudolf Clausius** developed the second law of thermodynamics in the mid-19th century. Thomson and Clausius phrased the law in slightly different ways, but the two versions were soon proved equivalent.

Thomson:
"A cyclic transformation whose only final result is to transform heat extracted from a source which is at the same temperature throughout into work is impossible".

Clausius:
"A cyclic transformation whose only final result is to transfer heat from a body at a given temperature to a body at a higher temperature is impossible".

Wiliam Thomson
(lord Kelvin)
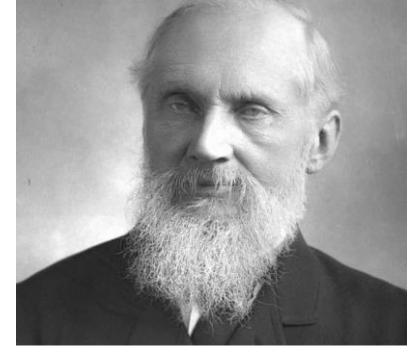
1824 – 1907

Rudolf Clausius

1822 – 1888

Third law of thermodynamics:

The entropy of a system (a perfect crystal) approaches a constant value when its temperature approaches absolute zero.

Third law of thermodynamics:

- "Absolute zero" is a state of zero motion

   - this means absolutely no entropy.
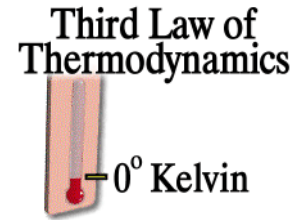
    This constant value cannot depend on any other parameters characterizing the system, such as pressure or applied magnetic field.

    At absolute zero (zero kelvins) the system must be in a state with the minimum possible energy.

A   **B**

Increasing
temperature

T = 0K   T > 0
S = 0   S > 0
W = 1   W > 1

Third law of thermodynamics:

Third Law of
Thermodynamics

-0° Kelvin
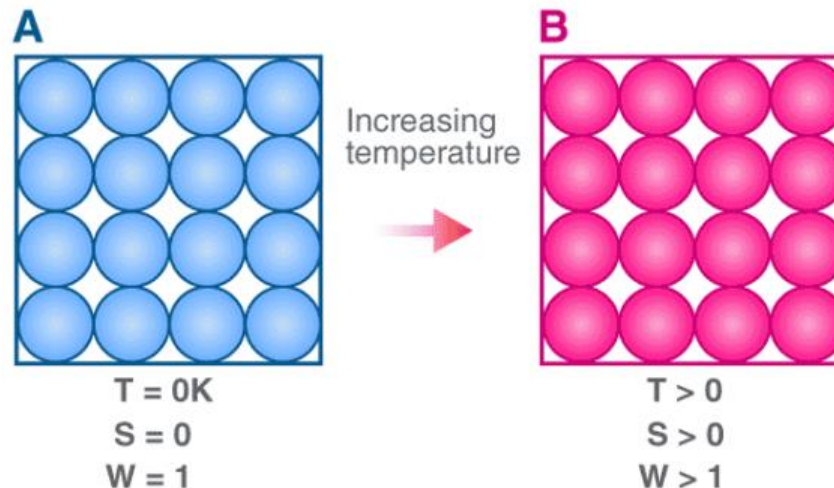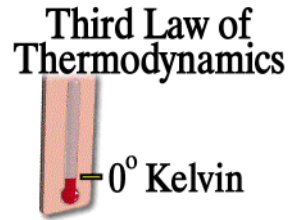
With the Third thermodynamic law the so called **Nernst Theorem** (postulate) is connected:

It is impossible for any process, no matter how idealized, to reduce the entropy of a system to its absolute-zero value in a finite number of operations.

Absolute zero

From the history:

In 1848, Lord Kelvin introduced the idea of absolute zero.
This is the point at which the atoms in an object stop moving entirely and so can't get any colder. By extrapolating from experiments, Kelvin calculated that this point would be reached at -273°C.
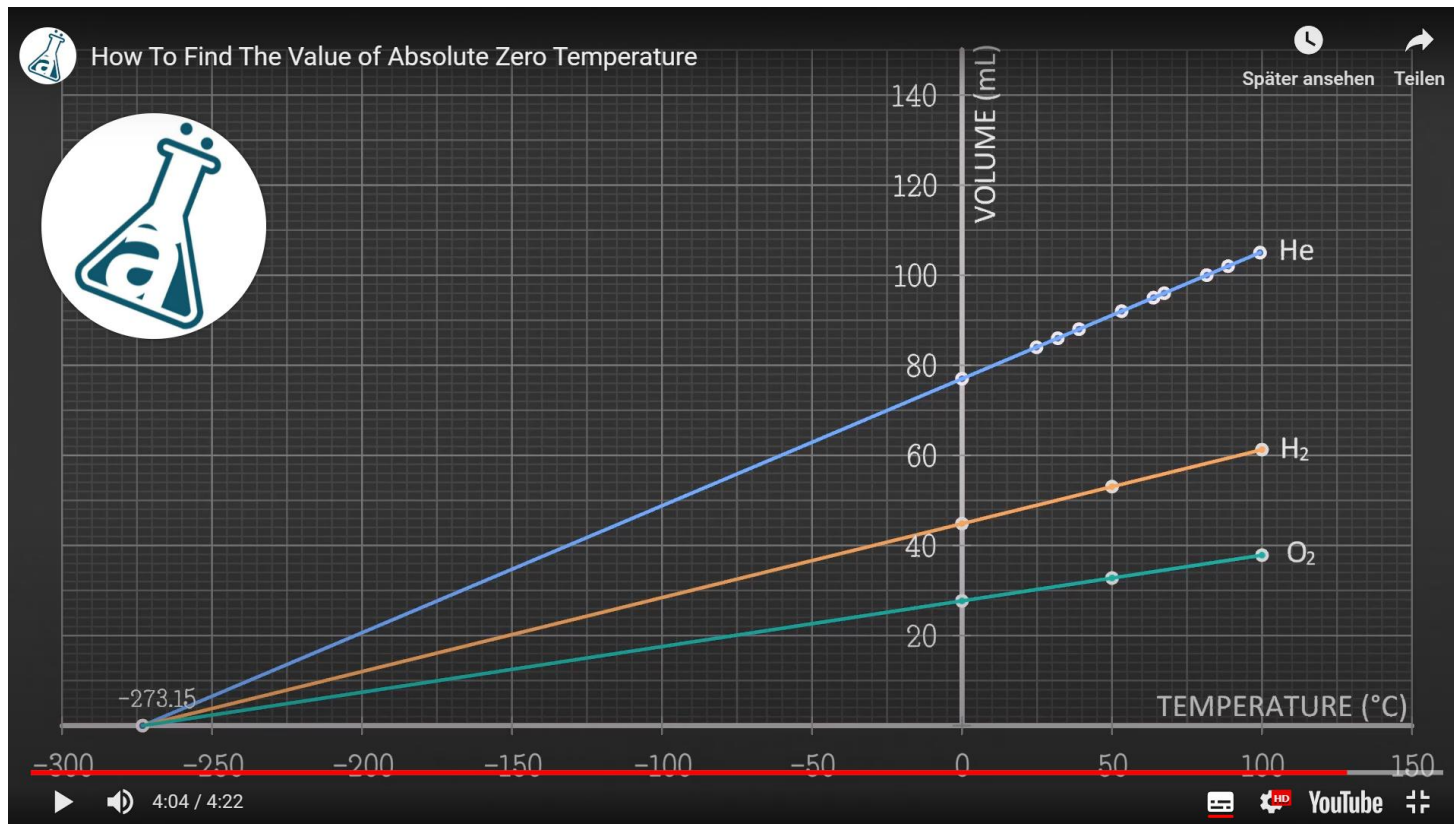
These experiments have been repeated and improved by many other experts and by convention, the value was set to -273.15°C.

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processes in ideal gas

- isobaric process (p = const.),

- isochoric process (V = const.),

- isothermal process (T = const.),

- adiabatic process.

In every process (listed here) we are also interested into the mechanical work, which can be made by the ideal gas.

isobaric process

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

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

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

so called Charles law

The volume occupied by a fixed amount of gas is directly proportional to its temperature (the pressure remains constant).

Charles's Law

Charles's law states that the volume of a gas is directly proportional to its absolute temperature, assuming the quantity of gas and pressure remain constant.

$$V_1 / T_1 = V_2 / T_2$$

Some examples of Charles law in everyday life:
- hot air balloon,
- helium balloon,
- lungs ...

Quantitative experiments establishing the law were first published in 1802 by Gay-Lussac, who credited Jacques Charles with having discovered this law earlier.

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

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

$$\boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2}}$$ so called Charles law

The volume occupied by a fixed amount of gas is directly proportional to its temperature (the pressure remains constant).

The work, done by the gas during an isobaric process is given by:

$$W = p\Delta V = nR\Delta T$$
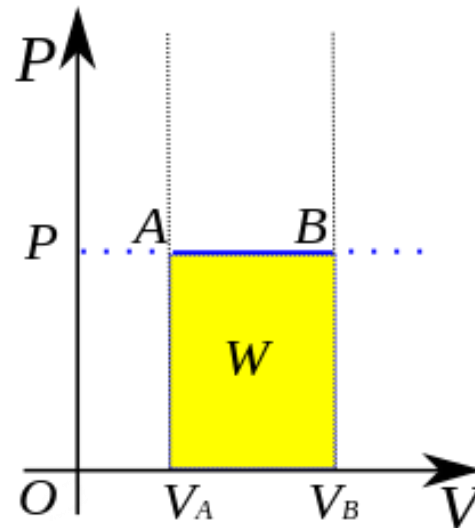
**Isobar**
a line connecting points of equal pressure

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

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

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$ so called Gay - Lussac law

The pressure of a given amount of gas held at constant volume is directly proportional to the Kelvin temperature.

Gay-Lussac's Law

The pressure of a gas increases as its temperature increases, assuming constant mass and volume.

$P_1 / T_1 = P_2 / T_2$

Decreasing Temperature decreases pressure.

Increasing temperature increases pressure.
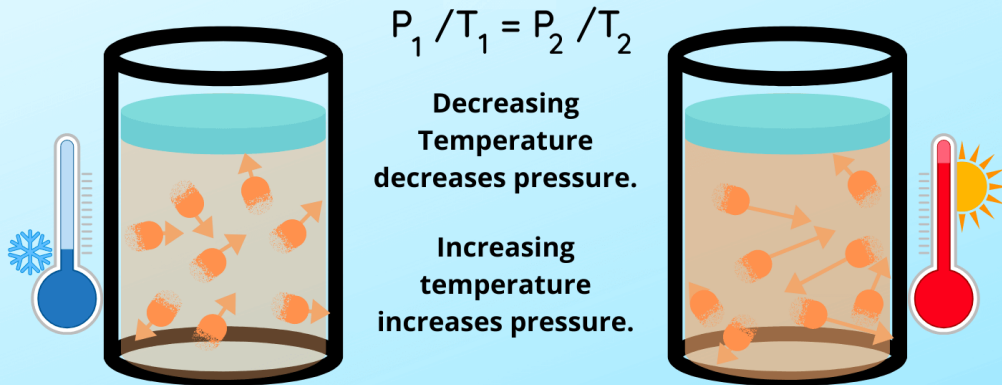
Some examples of Gay-Lussac law in everyday life:
- pressure cooker,
- tyre,
- heater …

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

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

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$ so called Gay - Lussac law

The volume is not changing – so the work made by gas is zero.
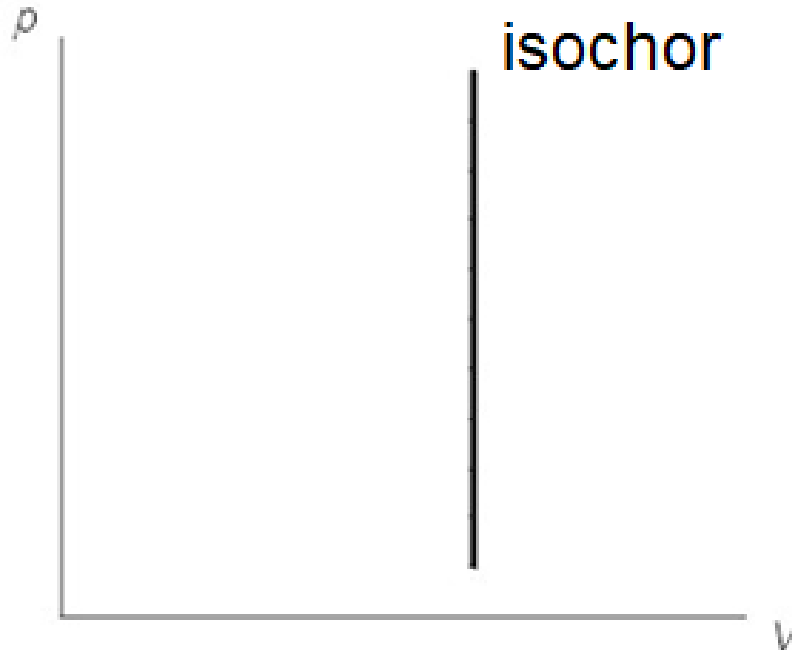
processes in ideal gas

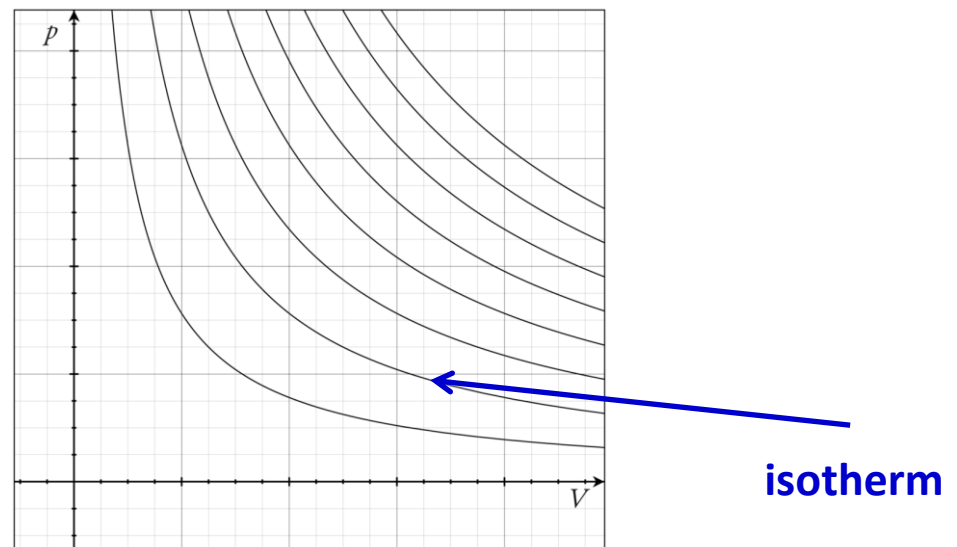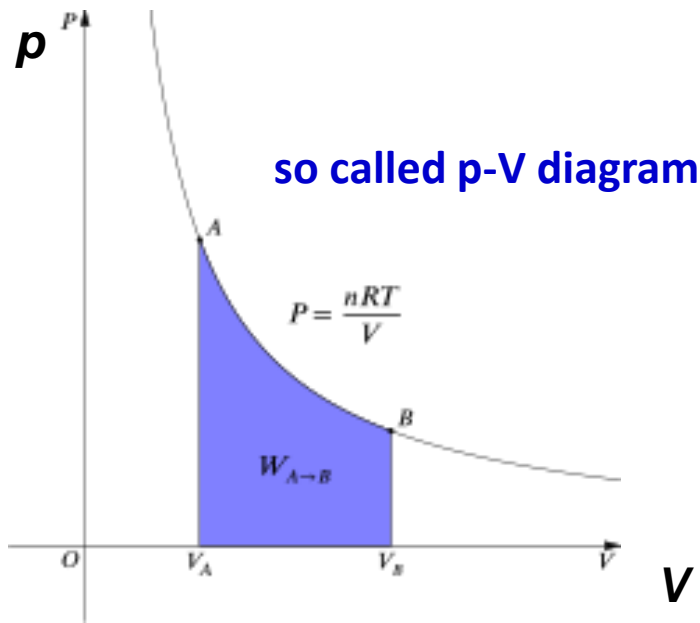**isothermal process**   temperature remains constant: **T = const.**

$$pV = nRT \rightarrow pV = const.$$

$$p_1 V_1 = p_2 V_2$$ so called 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.

so called p-V diagram

$P = \dfrac{nRT}{V}$

$W_{A \rightarrow B}$
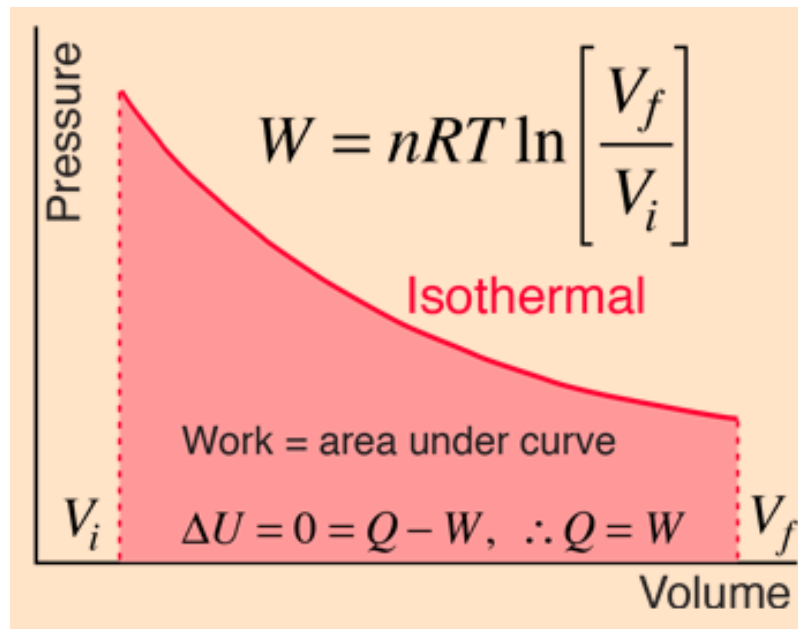
isotherm

processes in ideal gas

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

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

$$p_1 V_1 = p_2 V_2 \qquad \text{so called Boyle - Mariott law}$$

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

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

processes in ideal gas

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

$$pV = nRT \rightarrow pV = const.$$

$$p_1 V_1 = p_2 V_2 \qquad \text{so called Boyle - Mariott law}$$

Some examples of isothermal processes in everyday life:

- the boiling of water at 100°C to steam is an isothermal process because throughout this process the temperature remains constant,
- the heat pump is used to maintain a constant room temperature,
- the refrigerator also maintains a constant temperature, so this comes under the isothermal process.
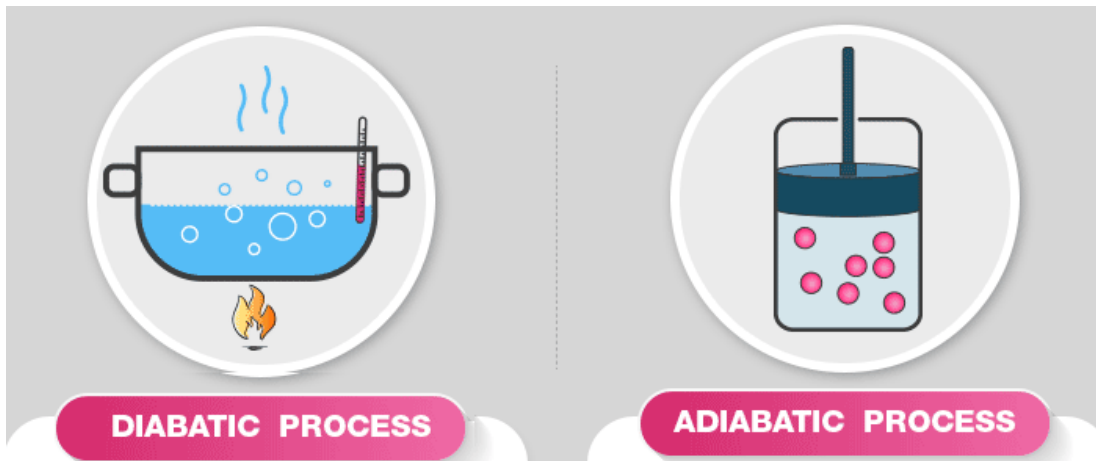
adiabatic process

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

(this does not mean that the temperature is constant, but rather that no heat is transferred into or out from the system)

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

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

Comment: diabatic process is one in which heat is exchanged.

DIABATIC PROCESS

ADIABATIC PROCESS

Examples:
- expansion of steam in steam turbines,

- gas in gas turbines,

- compression of air in compressors.

adiabatic process

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

(this does not mean that the temperature is constant, but rather that no heat is transferred into or out from the system)

$$pV^k = const.$$

k – so called Poisson's constant (5/3 for monoatomic ideal gas, 7/5 for diatomic ideal gas,...)
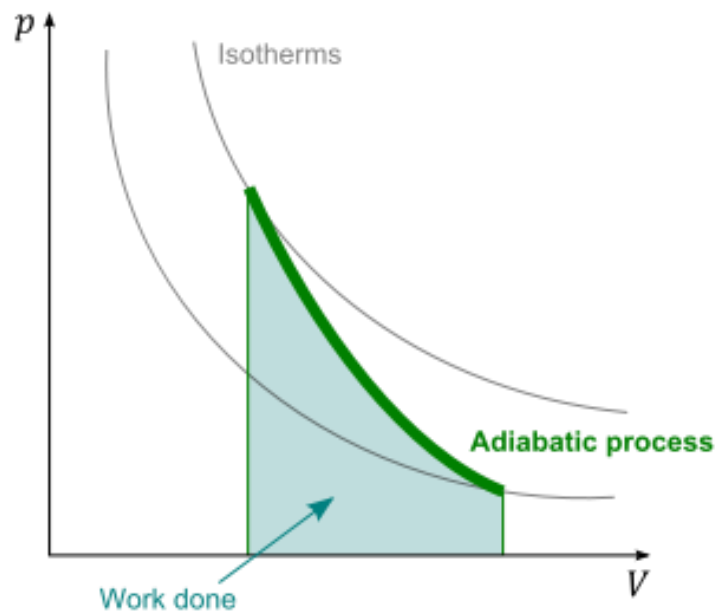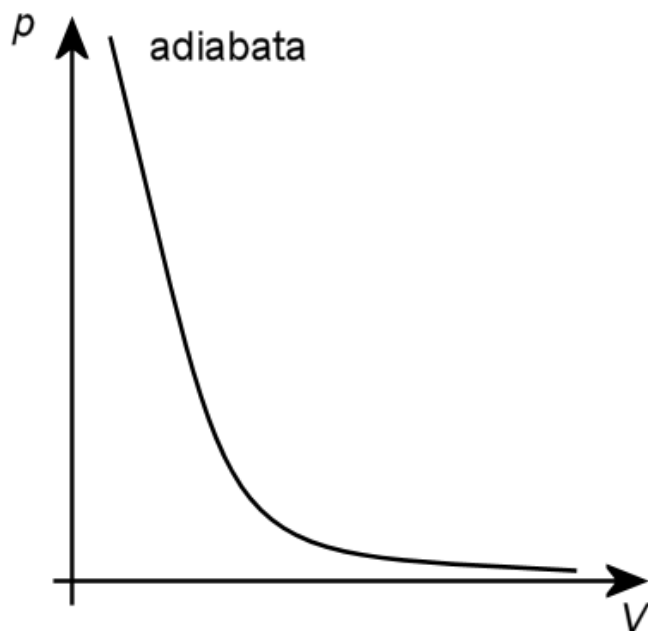
The work is given by:

$$W = \frac{1}{k-1}(p_1V_1 - p_2V_2)$$

Content:

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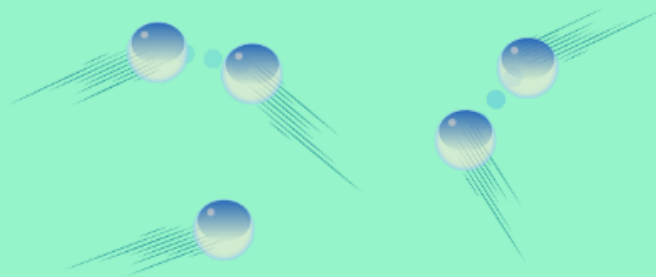- three laws of thermodynamics
- processes in ideal gas
- real gas

kinetic theory (real gas)

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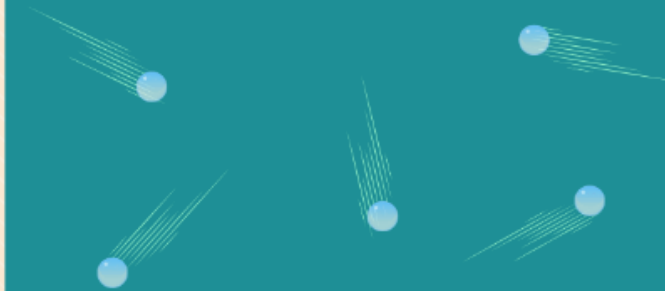

Real Gas vs Ideal Gas

REAL GAS
- Particles have volume
- Energy lost in collisions
- Intermolecular forces

IDEAL GAS
- Particles have no volume
- Collisions are elastic
- No interactions between particles

Real gases behave like ideal gases:
- **At high temperatures**
- **At low pressures**

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.