



The Principles and Concepts of Thermodynamics

The Foundation Course on Physics
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Thermodynamics

Thermodynamics (TMD) is a part of physics which is concerned with transformations of **heat** and other forms of **energy** in TMD systems.

Why to get acquainted with TMD in medicine?

- Heat is produced inside our bodies. To keep ideal body temperature we need some **thermoregulation**.
- **Heat production** accompanies and characterises chemical and biochemical reactions. Enthalpy H and Free enthalpy G are of special importance in *chemistry*.
- **Heat** can be used for different procedures in physiotherapy, we can even speak about thermotherapy (like baths, sauna, diathermy, ultrasound etc.)
- **Intense heating of tissues** is used in surgery to kill e.g. tumours, or to stop some bleedings – we speak about thermal ablation and electrocauterisation. Hyperthermia can kill tissues only by temperature increase by 20 °C!
- **Measurement of temperature** is an important diagnostic method for centuries.
- **Thermography** belongs among imaging methods.

Remember: heat = kind of energy

Example: Activation of body by various thermotherapeutic methods - hydrotherapy



Sauna: hot (80 - 100°C) air of low humidity (10-30%) followed by cooling in cold water. **Steam bath:** about 45°C, up to 100% humidity.

Alternating application of sharp hot and cold water jets – a method with activation effect.



Whirling bath increases blood supply and metabolism.



Baths, paraffin etc.

- Heat can be delivered not only in water bath (which is most common). Quite popular are also **peloids (mud baths)**. →
- Turf can be used as well.
- *Advertisement: Tell your parents about spas in Czechia! 😊*
- For treatment of e.g. an arthritic knee, it can be helpful to use even molten **paraffin** →



Extreme cold – Cryotherapy Chamber



Action of dry and very cold air (up to -160°C !) during some minutes followed by aerobic exercise.



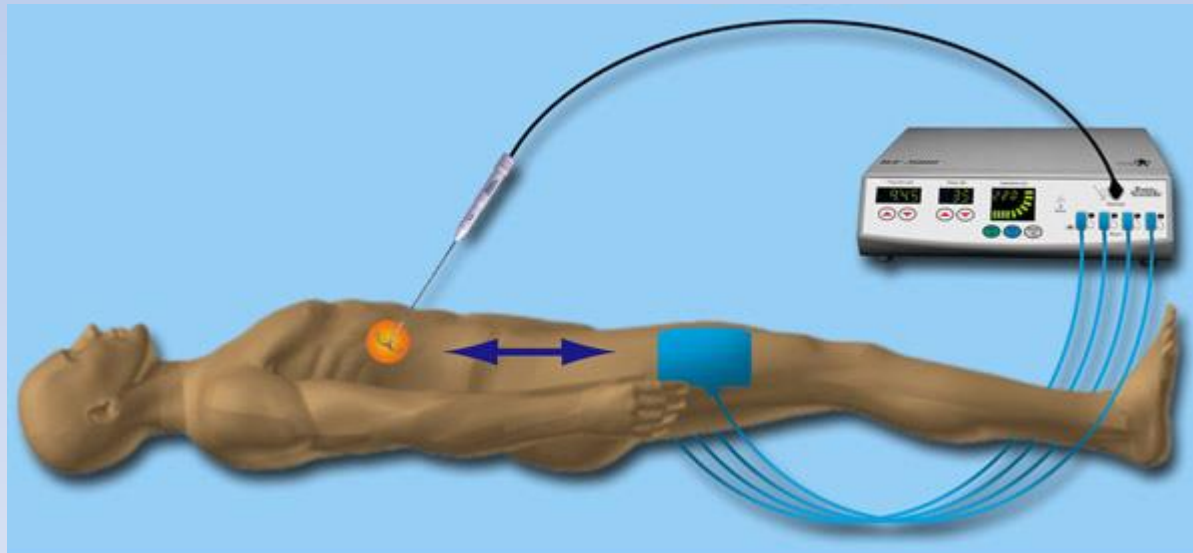
Short-wave **diathermy** – an example of *electric* tissue heating. The disc electrodes are not in direct contact with the skin, there is insulating gap instead.



Heat is produced by an alternating electric field! In this field, the charged molecules are put in motion, heat arises due to friction.

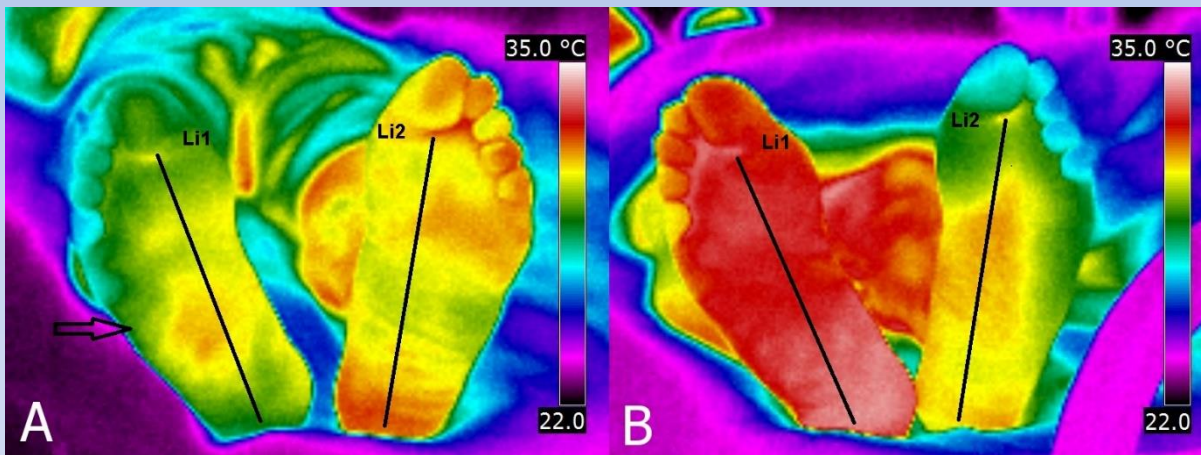
Hyperthermia

- Thermal ablation of a tumor – high frequency currents are used. It is kind of surgery.



Thermography – Infrared cameras

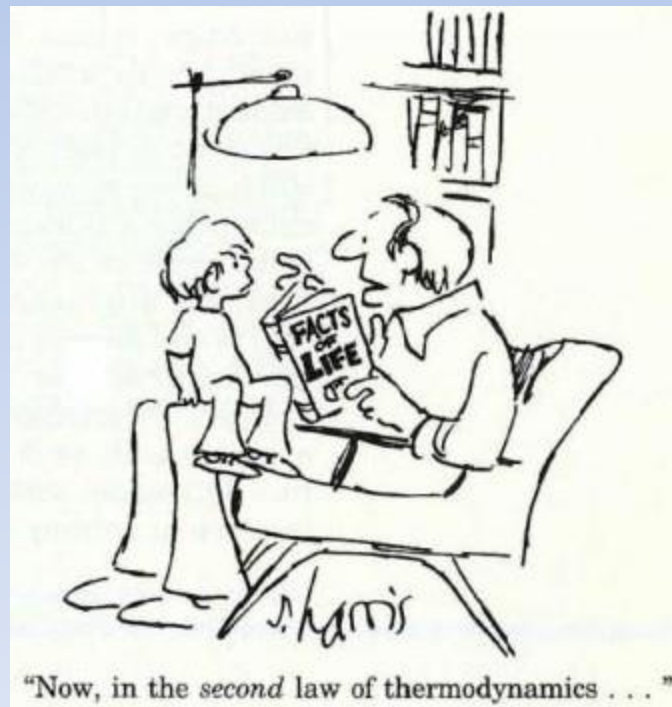
Sophisticated method of temperature measurement – visualisation of temperature maps.



A thermoimage of a patient's feet one day before and one day after „revascularisation“ (renewal of full blood supply). The colours are not real, it is a way how to display different temperatures.

Let us go on!

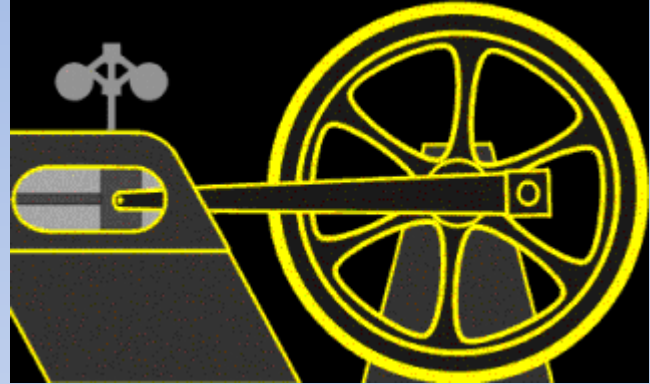
- Thermodynamics is not easy!



Thermodynamics as science



JAMES WATT
19.1.1736 - 19.8.1819



- Development: 19th century – steam engines, combustion engines, turbines.
- At the beginning of 20th century it became solid foundation of Physical chemistry.
- It is the key to understanding uniqueness of life, and answer to questions e.g.:
- *What is the difference between an animated and unanimated matter?*
- This question can be answered in the so-called non-equilibrium thermodynamics.

Milestones

Otto von Guericke (1650) - first vacuum pump and demonstrated a vacuum („Magdeburg hemispheres“).

Robert Boyle with **Robert Hooke** noticed a correlation between pressure, temperature, and volume a little later.

In 1697 **Thomas Savery** built the first engine driven by steam.

At the University of Glasgow **James Watt** (1781) increased steam engine efficiency.

Sadi Carnot, the "father of thermodynamics", published *Reflections on the Motive Power of Fire* (1824), a discourse on heat, power, energy and engine efficiency (Carnot cycle!). It marked the start of thermodynamics as a modern science.

The first thermodynamic textbook was written in 1859 by **William Rankine**.

The first and second laws of thermodynamics emerged simultaneously in the 1850s, primarily out of the works of **W. Rankine**, **R. Clausius**, and **William Thomson** (Lord Kelvin).

The foundations of statistical thermodynamics were set by physicists such as **James Clerk Maxwell**, **Ludwig Boltzmann**, **Max Planck**, **Rudolf Clausius** and **Josiah Willard Gibbs**.

During the years 1873-76 the American physicist **Gibbs** published a paper *On the Equilibrium of Heterogeneous Substances*, in which he showed how thermodynamic processes, including chemical reactions, could be graphically analyzed to determine if a process would *occur spontaneously*.

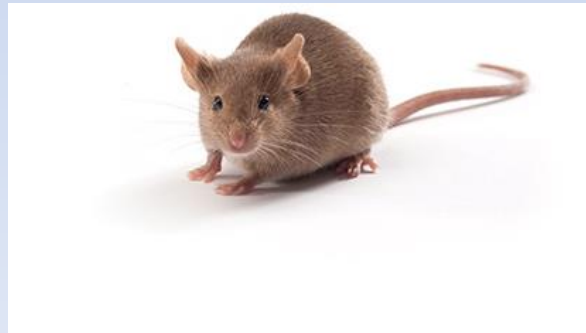
<u>École Polytechnique</u>	<u>Glasgow school</u>	<u>Berlin school</u>	<u>Edinburgh school</u>
			
<u>Sadi Carnot</u> (1796-1832)	<u>William Thomson</u> (1824-1907)	<u>Rudolf Clausius</u> (1822-1888)	<u>James Maxwell</u> (1831-1879)
<u>Vienna school</u>	<u>Gibbsian school</u>	<u>Dresden school</u>	<u>Dutch school</u>
			
<u>Ludwig Boltzmann</u> (1844-1906)	<u>Willard Gibbs</u> (1839-1903)	<u>Gustav Zeuner</u> (1828-1907)	<u>Johannes der Waals</u> (1837-1923)

The Thermodynamic System

- Definition:
 - Thermodynamic system: A region of space bounded by arbitrary surfaces which delineate the portion of the universe we are interested in. In other words: an arbitrary object, a body greater than a molecule.

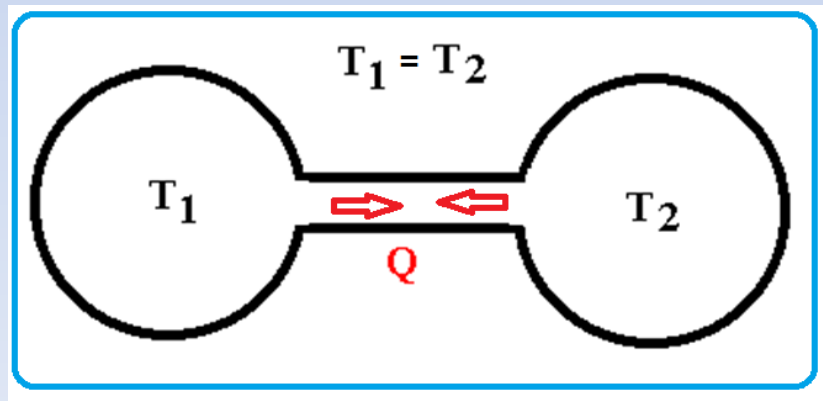
We can distinguish:

- **Isolated system**: one which cannot exchange particles or energy with its environment.
- **Open system**: one which can exchange both particles and energy with its environment.
- **Closed system**: can exchange energy but no particles.



The Equilibrium State

- *An isolated* system always reaches an **equilibrium state** in which it does not macroscopically change. Open systems do not reach the equilibrium state in general.
- **LIVING SYSTEMS ARE OPEN SYSTEMS**
- **Thermal equilibrium** is a special case of an equilibrium state.
- Two systems in thermal equilibrium have the same rate of thermal energy exchange between them. They are at **the same temperature** in any given point.



Thermodynamics – the State Parameters

- Quantities describing a TMD system in equilibrium are called **state parameters**.
- In a case of thermal equilibrium, the **temperature** is a determinant quantity/state parameter. However, it is not sufficient for full description of a thermodynamic system.
- A **defined set** of state parameters is necessary for full description of a TMD system. It can be volume V , pressure p , temperature T , concentration of substance c , internal energy U , enthalpy H
- These parameters are mutually related to each other in the **equations of state**.
- The simplest thermodynamic system is the **ideal (or perfect) gas**.
- Equation of state for ideal gas (you may already know) – it is the **universal gas law**:

$$pV = nRT$$

$$[\text{Pa}, \text{m}^3, \text{mol}, \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}, \text{K}]$$

What is the ideal (perfect) gas?

- A **perfect gas** is a theoretical gas that differs from real gases in a way that makes certain calculations easier. In most cases the perfect gas is the same as an **ideal gas**. In particular, intermolecular forces are neglected, which means that one can neglect many complications that may arise from the **Van der Waals (intermolecular) forces**. The particles of the perfect gas have no volume *of its own* but they can elastically *collide and share their kinetic energy!*
- (Van der Waals forces are, in principle, attraction forces of electric character acting between all molecules.)

Equation of State for a Real Gas (optional)

Van der Waals equation:

$$\left(p + n^2 \cdot \frac{a}{V^2} \right) \cdot (V - n \cdot b) = n \cdot R \cdot T$$

P – pressure, V – volume, n – amount of substance in moles, R – molar gas constant, a, b – semi-empirical constants. In the real gas the molecules are attracted (thus lowering the gas pressure) and have their own volumes (real gas cannot be compressed to infinitely small volume).

Reversible and Irreversible Thermodynamic Process

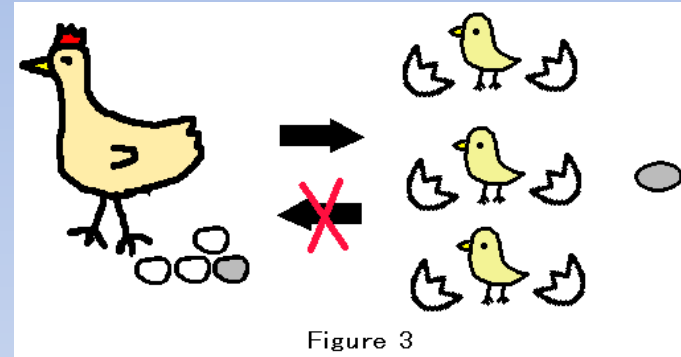
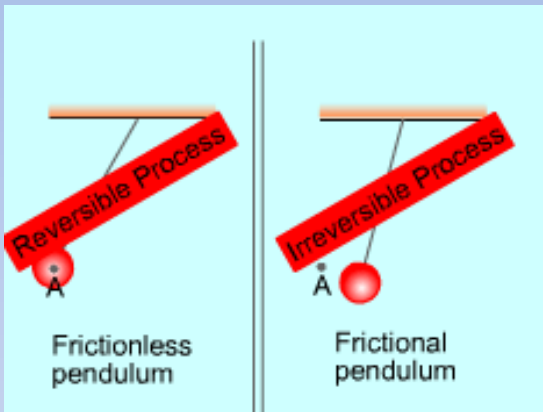
- **Reversible TMD processes** are represented by a sequence (series, train) of very close equilibrium states which differ only slightly in values of some thermodynamic state quantities. This sequence could be “reversed”, and then the same process would proceed backwards. The reversible processes are only approximations of real ones. They do not take place in nature.
- In other words, the reversible process is the one after which a second process could be performed so that the *system and surroundings* can be restored to their initial states with no change in the system or surroundings.
- **Irreversible processes** are sequences of non-equilibrium states, and they cannot be “reversed”.

Reversible and Irreversible Thermodynamic Process

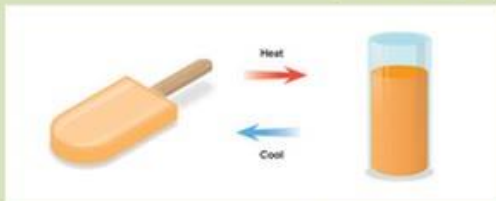
- **Cyclic process:** the initial and final states of the system are identical (but not necessarily the state of surroundings)
- **Sign convention:** energy given to a system and work done by an external force on the system are considered to be positive. Energy transferred from the system to its surroundings and work done by the system on its surroundings are considered to be negative.

Most of the formulas/equations in this presentation are fully valid only for reversible processes. Mathematical approach to irreversible processes is much more complex.

Irreversible Processes



Reversible and Irreversible Changes



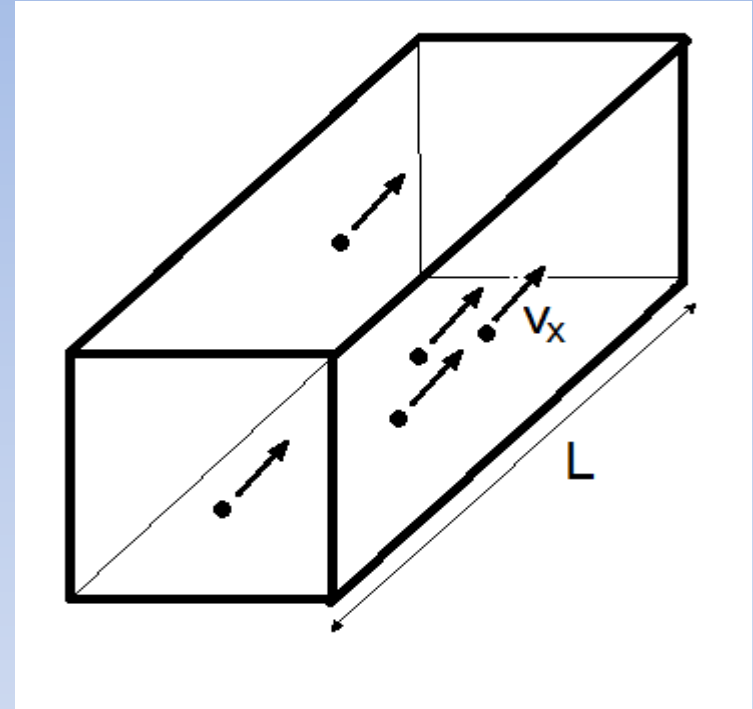
Back to Kinetic Theory

Before we will deal with thermodynamic processes and laws we should finish the explanation of the two fundamental thermodynamic quantities – the pressure and temperature.

The following explanation is based on the description of the movement of individual molecules in a *perfect gas* enclosed in a vessel. We also need to *average* physical properties of these molecules.

Pressure of a gas

- First, we assume constant amount of a gas in an thermally insulated vessel.
- For maximum simplification, the particles will move *only* along the x-axis.
- The particles collide sometimes with the perfectly elastic walls, and have to change their momentum (Δp) because they *reverse* their movement.
- The whole „round trip“ between the opposite walls takes Δt for each particle.
- The $\overline{F_x}$ bar and $\overline{v_x}$ bar symbols denote *average* values of respective quantities (force and velocity).



Impulse – Force theorem:

$$\overline{F_x} \Delta t = \Delta p = 2m\overline{v_x}$$

(Total change of velocity of the particle colliding with the wall is $2v_x$ because the particle has to stop and then gain an opposite velocity.)

Pressure of a gas

We can derive the time for the whole „round trip“ of a particle:

$$\Delta t = \frac{2L}{v_x} \quad \text{because} \quad v_x = \frac{2L}{\Delta t}$$

Thus, after substitution, the average force exerted by one particle on the wall is:

$$\overline{F}_x = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{\frac{2L}{v_x}} = \frac{mv_x^2}{L}$$

For N molecules with the same mass m we can write:

$$\overline{F}_x = \frac{m(v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + \dots v_{Nx}^2)}{L}$$

And also:

$$\overline{v_x^2} = \frac{v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + \dots v_{Nx}^2}{N}$$

Pressure of a gas

Hence the average force of all molecules exerted on the wall is:

$$\overline{F}_x = \frac{mN \overline{v_x^2}}{L}$$

We have considered movement of the molecules only along the x-axis which would be possible only in a „one-dimensional“ gas. In 3D space the kinetic energy of particles is equally distributed in individual dimensions. We can say the same about the force acting on the walls. So the total force F has to be one third of the F_x .

$$\overline{F} = \frac{1}{3} \overline{F}_x = \frac{1}{3} \frac{mN \overline{v^2}}{L}$$

Pressure p is defined as F/A , where A is the force action area. In our case it is the area of the wall.

$A \times L$ is the volume V of the gas. Thus (bars are omitted):

$$p = \frac{F}{A} = \frac{mN \overline{v^2}}{3LA} = \frac{mN \overline{v^2}}{3V}$$

Pressure and the Universal Gas Law

Transferred from previous slide:

$$p = \frac{F}{A} = \frac{mNv^2}{3LA} = \frac{mNv^2}{3V}$$

The velocity v in above formula is called **mean quadratic velocity**. It can be shown that the same velocity can be expressed also:

$$v = \sqrt{\frac{3kT}{m}}$$

where k is the Boltzmann constant ($1.38064852 \cdot 10^{-23} \text{ m}^2 \cdot \text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1}$ i.e. $\text{J} \cdot \text{K}^{-1}$) and T is the Kelvin temperature.

Now we can substitute in the formula for pressure where $N = nN_A$ (n is the number of moles, N_A is the Avogadro constant).

$$p = \frac{mnN_A}{3V} \frac{3kT}{m} = \frac{nN_A kT}{V} \Rightarrow pV = nN_A kT \quad \begin{array}{l} N_A k = R \\ R \text{ is molar gas constant!} \end{array}$$

So we have: **$pV = nRT$** - **the Universal Gas Law!**

Tired?

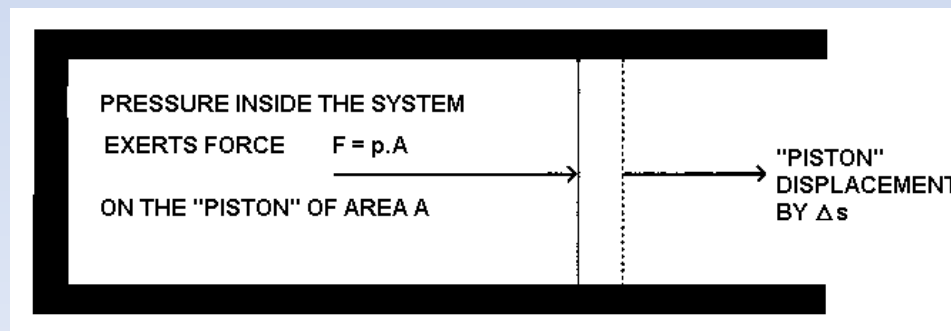


Work done by / on thermodynamic systems

Gas and piston system (heat engines)- *This kind of work can be called mechanic or volumetric*

- In thermodynamic systems doing mechanical work the acting force can be expressed as the product of pressure p and surface area A , on which the pressure is exerted, that is $F = p.A$. Let us imagine that the piston face area A moves along a very short trajectory Δs , thus increasing gas volume (see Fig). The volume change ΔV is calculated as $\Delta V = A.\Delta s$. If the gas volume increases against external forces mechanical work is done, which is equal to the product of force and the displacement along which the force is exerted, hence:

$$W = F.\Delta s = p.A.\Delta s = p.\Delta V.$$



**Work is not
a state
parameter!!**

Work done by / on thermodynamic systems

a) electric work (done by galvanic cell or nerve cell membrane)

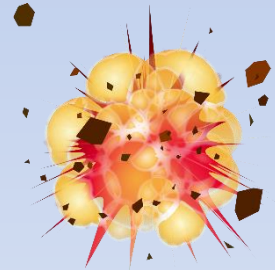
$$W = Q.U ,$$



where W is the work necessary to transfer an electric charge Q between places with potential difference U^*

b) chemical work (crucial for chemistry or biochemistry)

$$W = \mu.\Delta n,$$



where W is the work necessary to increase or decrease amount of a chemical compound Δn in a chemical reaction. μ is **chemical potential**.

*Potential difference = voltage (denoted as U , V or E)

Other important quantities:

Kelvin temperature is a quantity which indicates the average kinetic energy W_{KS} of the particles in a system e.g., *for an ideal monatomic gas* (k is the Boltzmann constant):

$$T = \frac{2}{3k} \cdot W_{KS}$$

Internal energy of the system is the sum of all kinetic and potential energies of all particles forming the system.

Heat (thermal energy) is the part of internal energy of the system which can be *exchanged* between systems as a result of their different temperatures.

Heat is not a state parameter!!



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