# Chemistry course
## ACME Faculty, EHVE course
## B.Sc. Studies, I year, I semester
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# Energy and thermodynamics

## Few words about energy
### (approximate data)

| | |
|---|---|
| Heating a glass of water by 10°C | 10 kJ |
| Lift a car (1.5 t) by a meter | 15 kJ |
| Boil water in 2-liter electric kettle | 668 kJ |
| Average daily diet for a human (2400) | 10 MJ |
| Combustion of a bucket of coal (20 kg) | 440 MJ |
| Warsaw to Gdansk by car, 360km trip (6 L/100 km) | 648 MJ |
| Combustion of 1000m$^3$ of natural gas (ca. 400 $) | 36 GJ |
| Fission of 1kg of Uranium-235 | 85 TJ |
| Annual electricity generation in Poland | 558 PJ |
| Annual electricity generation in the world | 518 EJ |

[J = W·s], 1 Wh = 3600 J, 1 cal = 4.18 J
m – $10^{-3}$, k – $10^3$, M – $10^6$, G – $10^9$, T – $10^{12}$, P – $10^{15}$, E - $10^{18}$

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## Few words about energy
### (sample data)

| | |
|---|---|
| AA battery capacity | 5 kJ |
| Phone battery capacity | 24 kJ |
| Notebook energy consumption / h | 20-80 kJ |
| Refrigerator energy consumption / h | 165 kJ |
| Notebook battery capacity | 220 kJ |
| Desktop computer energy consumption / h | 900 kJ |
| Small EV battery capacity | 72 MJ |

[A·V = W], [W·s = J]
1000 mAh·1.2 V = 1 A·1.2 V·3600 s = 4320 J = 4.32 kJ

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## Forms of energy

- **Total energy** is a sum of <u>kinetic energy</u>, <u>potential energy</u> and <u>inner energy</u>
- **Kinetic energy** is energy of movement – result of object mass and its velocity

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## Forms of energy

- **Potential energy** is energy that due to existence of external field of force (*e.g.* gravity, electric field, *etc.*) can be released, *e.g.* pendulum deviation, stretched spring, rock hanging over ground on a line (that can be cut). It depends on deviation from equilibrium, that can be achieved through potential energy release.

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## Forms of energy

- **Inner energy** is an energy of system contained in heat (particles' movement in a system), in form of chemical bonds, nuclear forces, *etc*. It is a sum of energies of all particles of a system.

  It is energy that system has on microscopic level (*i.e.* contents of a chemical reactor, which is not moved, stirred, *etc.*; given that we omit potential energy of contents, like pouring it out or incorporating electromagnetic field to it).

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## Energy types

- Particles possess following forms of energy: translational, rotational, vibrational, electron, electrostatic, nuclear.
- **Translational energy** is usually kinetic energy of molecule/particle movement (velocity) in space (depends mostly on temperature);
- **Rotational energy** is a kinetic energy of rotational movement of molecule – particles are constantly rotating (randomly in different axes, also their parts independently around bonds);
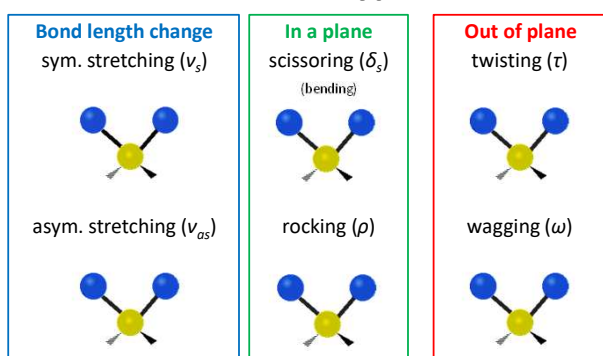
## Forms of energy

**Vibrational energy**
is both kinetic
and potential energy
of atomic vibrations
in a particle (stretching
of bonds, twisting
of whole molecule, *etc*.);

## Vibration types



| Bond length change | In a plane | Out of plane |
|---|---|---|
| sym. stretching ($v_s$) | scissoring ($\delta_s$) (bending) | twisting ($\tau$) |
| asym. stretching ($v_{as}$) | rocking ($\rho$) | wagging ($\omega$) |

## Forms of energy

- **Electron energy** is kinetic and potential energy of electron movement around nucleus (in electric field of nucleus);
- **Electrostatic energy** is potential and kinetic energy of particle movement (always containing some charge, at least locally) in each other's reaction fields;
- **Nuclear energy** is inner energy of forces keeping nucleons together as a nucleus.

## Energy of particles/molecules

| Energy of… | order of magnitude |
|---|---|
| rotational energy in $H_2O$ molecule | $10^{-20}$ J |
| translational energy of $H_2O$ molecule | $10^{-19}$ J |
| interactions between $H_2O$ molecules | $10^{-19}$ J |
| vibrational energy of $H_2O$ molecule | $10^{-18}$ J |
| combustion (oxidation) of one carbon atom | $10^{-18}$ J |
| $H_2O$ molecule electrons | $10^{-17}$ J |
| one U-235 nucleus fission | $10^{-11}$ J |

m – $10^{-3}$, μ – $10^{-6}$, n – $10^{-9}$, p – $10^{-12}$, f – $10^{-15}$

## Energy change

- Energy cannot change in a continuous way, but it can only change through step changes – those step-changes are called **quantum** of energy.
- For instance, electron can change its energy level (change shell/sub-shell) only after receiving or giving up specific amount of energy (quantum). Portions of energy smaller than this specific value cannot be absorbed or given up by electron.

## Energy change

Similarly, translational energy is also <u>quantized</u> – although quants of energies in this case are much smaller (orders of magnitude) than that of electron energy levels. It is still not a continuous change though. Between temperature of absolute zero and room temperature there are billions of billions of energy quanta. In macro scale energy is also quantized, but due to number of particles (each type has its own quantum size) that can receive of give up energy (in a chaotic/random way, not all with the same amount of energy, exchanging the energy between themselves all the time with collisions) it is not possible to measure it.
As a result, those changes <u>seem to be</u> continuous for a human.

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## Energy change

- Within the system, if it is not exchanging energy with surroundings, sum of all types of energy cannot change. **Amount of energy in isolated system is constant!**
- Energy cannot change into anything else and nothing can be transformed into energy.
- In reality, it is impossible to create perfectly isolated system – ideals exist only in books and chemistry lectures;). Even vacuum is not ideal insulator.
- Extreme example: Whole universe is an isolated system: **amount of energy in the universe is constant!**

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## Energy transfer

- By heating up water in electric kettle, we consume inner energy (coal combustion in power plant) and we increase translational energy of water molecules in kettle.
- Crane lifting up a weigh consumes kinetic energy of its engine to increase potential energy (gravity) of a load. Theoretically that energy can be recovered during lowering of weight, *e.g.* with appropriately designed electric motor.

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## Energy transfer

- Above examples show the only known methods of energy transfer: **by means of heat** and through **work**.
- Work, like lifting up a load, is easy to imagine.
- Energy transfer by means of heat consists in transferring energy through collisions between two particles (often through other particles on the way).

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## Mass vs energy

- Each mass has a corresponding energy and vice-versa. *E.g.* atomic nucleus is lighter than sum of nucleons before their merger into nucleus. That difference is consumed on nucleus formation (interactions between nucleons).
- Each mass has its own rest energy, so at the molecular level, mass of elementary particles can be indicated in energy (mass of electron is 510 999 eV/$c^2$).
- For rest mass of matter expression one can use $E = mc^2$ or $m = E/c^2$ formulae.
- In cases where mass conversion to energy can occur (like nuclear transformations), sum of mass and energy is constant as well.

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## Inner energy

- Inner energy is so-called <u>function of state</u>.
- **Function of state** is a quantity defined by current state of a system and not the way it was achieved. So regardless of its history, we can describe function of state. To put it in different way: the same state can be achieved with different methods.
- Change of function of state value depends on initial and final state, not the way between them.

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## Inner energy

- We cannot calculate the absolute value of inner energy (or most of other functions of state), because we do not have knowledge and possibility to precise calculation of some of its components. However, we can precisely determine **change of inner energy** (we can measure delivered energy by means of heat and work) and that's the main **thermodynamics'** subject of interest.

## State parameter

- State parameter, is a parameter needed to calculate function of state (usually change of function of state).
- State parameters are, among others: temperature, pressure, amount of substance and volume.
- State of a system can be described through measuring all its parameters.

## State parameter

- Multicomponent systems require for their unequivocal description determining of: pressure, temperature, volume, what are their components and their amounts.
- Unary systems require determining amount of substance, pressure, temperature and volume.

## Unary system state

- Knowing all state parameters but one allows to unequivocally determine the missing one (in multicomponent systems all components'/phases' amounts in moles is needed).
- For gaseous unary system the missing parameter can be calculated using **ideal gas law**:

$$pV = nRT$$

Where: $p$ – pressure / Pa;
$V$ – volume / m$^3$;
$n$ – amount of gas / mol;
$T$ – temperature / K;
R – gas constant = 8.31 J/(mol·K)

## Ideal gas law

In unary gas system not exchanging heat with surroundings one can calculate volume knowing
$n$ = 1 mol, $T$ = 300 K (ca. 27°C)
and $p$ = 1000 hPa = 100 000 Pa

$pV = nRT$      $V = nRT/p$
$V$ = 1·8.31·300/100000 = 0.02493 m$^3$ = 24.93 dm$^3$

In normal conditions ($T$ = 0°C = 273.15K ;
$p$ = 1013.25 hPa = 101325 Pa) volume of 1 mole of gas is:
$V$ = 1·8.3145·273.15/101325 = 0.0224 m$^3$ = **22.4 dm$^3$**

## Ideal gas law

One can also calculate pressure of 1 mole of gas, knowing $T$ (600°C) and $V$ (20 dm$^3$):
$p$ = 8.31·873 K / 0.02 m$^3$ = 362731 Pa = 3.6 bar

100 000 Pa = 1000 hPa = 1 bar
101 325 Pa = 1013.25 hPa = 1 atm
101 325 Pa = 760 Tr     1 Tr = 133.322 Pa

## Real gas

- Ideal gas law assumes existence of ideal gas. Ideal gas of course does not exist, but a lot of gases (especially elemental gases, including noble ones) have properties so close to ideal, that differences are negligible (1-2% deviation).
- It is worth remembering, that there is a lot of gases with big deviations from ideal gas.

## What is system?

- **System** is an experimental object in a naked-eye visible scale, *e.g.* pure substance, solution, chemical reactor, but also unreal, only potentially existing (so-called perfect), like ideal gas. It can be arbitrarily complex, as long as it can be described.
- **Surroundings of a system** is the rest of the world – outside the system. System is enclosed with **walls** (partitions):
  - perfect – only in books/calculations;
  - real – glass/metal/styrofoam.
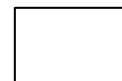
## What is system?

- System can be **closed** (cannot exchange matter with surroundings) or **open** (it can exchange matter). Thermodynamics usually concerns itself with closed systems only.
- System can exchange heat with surroundings (<u>diathermic</u> system) or not (<u>adiabatic</u> system). Perfect diathermic walls are conducting heat perfectly, perfect adiabatic walls are perfect insulators and both do not exist in reality, as it is often the case of perfect things ;).

## What is system?

- Actual approximation of adiabatic wall is styrofoam or vacuum bottle. Approximation of diathermic wall is thin copper wall (it is not coincidence that heat radiators in PC are made of copper).

## Transformation

- **Transformation** is a process that cause at least one state parameter to change.
- No state parameters change for a longer time means, that system is in a state of **thermodynamic equilibrium**.
- Systems and transformations can be **constrained** – can proceed in a way that one or more state parameters is not changing:
  - Isothermal – temperature remains constant ($T = const$);
  - Isobaric – pressure remains constant ($p = const$);
  - Isochoric – volume remains constant ($V = const$).

## Laws of thermodynamic

- If isolated (closed) adiabatic system contains two subsystems separated from each other with diathermic wall (partition), they will exchange energy (slower and slower, asymptotically) until they achieve thermodynamic equilibrium (same temperature).

- If isolated system contains three subsystems, they will achieve equilibrium in pairs, until all will achieve thermodynamic equilibrium – the same temperature.

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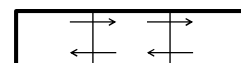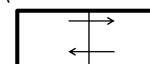
## Laws of thermodynamic

- Inner energy of each phase (component) is a function of its state parameters. Inner energy of the whole system is equal to sum of inner energy of its components.
- Change of inner energy of any system without heat exchange with surroundings is equal to energy exchange by means of work. Example: Movement of a piston in isolated cylinder (constant temperature) – gas expansion pushes piston out of cylinder (pressure drop, volume increase).

(number of moles of matter $n$ is constant – we are not adding or taking away anything, R is a gas constant and temperature is constant – no heat exchange, so from $pV = nRT \rightarrow p \cdot V = const$).

## Laws of thermodynamic

- If inner energy of a system has changed not through work, then it had to change by means of heat transfer.
- Inner energy of a system ($U$) can change by means of the following transformations:
  - heat ($Q$);
  - work ($W$);
  - mixed, in which energy was exchanged by means of both work and heat.

$$\Delta U = \Sigma Q_i + \Sigma W_i$$

## Laws of thermodynamic

- Energy delivered to a system is counted positively (changes are counted from the system's point of view).
- If inner energy has not changed as a result of a sequence of transformations, it means that it was a cyclic process. Sum of both heat and work transformations is then equal to zero:

$$\Sigma Q_i + \Sigma W_i = 0$$

- Two cases can occur in such situation (described on two following pages):

### What results from laws of thermodynamics?

If sum of heat transformations is above zero, than sum of transformations by means of work is below zero ($\Sigma Q_i > 0$; $\Sigma W_i < 0$). It means that system consumed energy by means of heat from the surrounding and gave it up in form of a work – thus, it is a **heat engine** (*e.g.* combustion or steam engine) Heated gas (heat) increase pressure (work) in a cylinder (on a piston) when it expands (volume increases at the expense of pressure).

### What results from laws of thermodynamics?

If sum of all heat transformations is below zero, then sum of transformations by means of work is above zero ($\Sigma Q_i < 0$; $\Sigma W_i > 0$). It means, that system consumed energy from its surroundings by means of work and gave it up to surroundings in form of a heat – thus it is **refrigerator/heat pump**.

Expansion (work) of cooling agent cause its temperature drop and reverse of natural direction of energy flow by means of heat.

## Heat capacity

**Heat capacity ($C_p$)** is a maximum amount of heat exchanged by the system at constant pressure (or constant volume - $C_v$) relative to change (e.g. increase) of temperature.

Heat capacity of a substance is determined experimentally (it is hard to anticipate) and is counted per mole of substance (for engineering purposes, usually converted to quantities per g or kg) per temperature unit (so J/(mol·K) or J/(g·K) ).

## Heat capacity

- When we heat water (or cool it down), we have to deliver (or take away, if cooled) heat equal to heat capacity multiplied by amount of water and temperature difference (in K/°C).
- Example: Heating liter of water ($C_p$ = 4.18 J/(g·°C)) up by 10°C requires energy equal to: $Q$ = 10°C·4.18 J/(g·°C)·1000 g = 41800 J For electric kettle with 2000W power it will take 21 seconds (41800/2000=21).
- Heating up by 90°C (until boiling) will take ca. 190 s (assuming no heat loss of kettle and its 100% efficiency).

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## Spontaneity of reaction

- Energy exchange between systems by means of heat (*e.g.* levelling of temperature between systems);
- Diffusion in solutions and/or dissolving (concentration levelling in whole volume);
- Melting (or other phase transitions);
- Spontaneous chemical reactions (known direction if initial state is known);

are **spontaneous** and **irreversible** processes (in a sense of <u>self-acting</u> reversibility in isolated system – without external influence, *e.g.* without taking heat away, warm water won't freeze).

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## Entropy

- Macroscopic state is a result of averaging states of multiple individual particles often much different from their mean. Velocity (translational energy), rotation and electron energy can be exchanged as a result of intermolecular interactions (or interactions with walls). Those individual changes and energy exchanges are not influencing energy of the whole system, though (which in the equilibrium state does not change [aside from fluctuations], even though state of molecules is changing all the time for each of them).

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## Entropy

- **Entropy ($S$)** is a measure of a number distinguishable quantum states (distribution of energy among particles, sum of translational, rotational, vibrational and electronic energy, *etc.*) which in total make up macroscopic state:

$$S = k_B \ln P$$

(where $P$ is number of states and $k_B$ is Boltzmann constant = $1.38 \cdot 10^{-23}$ J/K)

- Entropy of a system is sum of its components' entropies. Entropy change of a system in a result of spontaneous process is always bigger than exchange heat rate (relative to temperature) that is a result of such process: $dS \geq dQ/T$

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## Entropy

- **In a result of irreversible transition** (actually each one) **entropy is always generated** in the system (reversible process – perfectly slow one, keeping the state of system equilibrium, *e.g.* compression without temperature change – does not generate entropy).
- Entropy of system can change due to entropy transfer between system and its surroundings or through entropy generation (process proceeding).
- In adiabatic system the only process that is allowed is a process that results in entropy increase. Equilibrium of such system is achieved when entropy maximum is achieved (if it is possible in a given system).

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## Entropy

Entropy is a driving force of gas mixing or a diffusion of a substance in a solution. It tends to equilibrium achievement, which occurs as a result of the highest possible disorder. In other words: each system tends towards <u>the biggest diversity of energy division ways among particles and their movement types</u>. Thus, entropy is often called *„<u>measure of disorder</u>"*.

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## Entropy

- Temperature increase is increasing entropy;
- Pressure increase is decreasing degrees of freedom of molecules, so it decreases entropy;

  - Free mixing of gases causes entropy increase – each molecule has bigger space around it, so it has more translational freedom.

## Entropy – last slide ;)!

In a hypothetical temperature of absolute zero (0 K – unattainable in reality) entropy of any pure substance in form of a <u>perfect crystal</u> (ideal – without defects; in a packing minimizing energy) would be equal to zero.

$$T = 0 \text{ K} \qquad \rightarrow \qquad S = 0$$

If there would not be any movement (vibration, rotation due to temperature, translation due to crystal form), or excitation (due to no energy received, all electrons are in ground states), there would be no diversity of energy levels and entropy would be equal to zero. In reality it cannot occur. Entropy always increases in real world.

## Perpetuum Mobile
### (eng. perpetual motion)

- Hypothetical machine generating more energy than it consumes;

OR

- Hypothetical machine, that converts heat into work without losses (100% efficiency) and without entropy increase.

is **against the thermodynamic laws**, so it **cannot exist!**

## Carnot cycle – Carnot engine

Hypothetical machine = ideal engine (lossless)
but the same principle of operation as in every real-world engine!

Consists of:
- heat source (temperature higher than the highest temperature of working gas);
- cylinder with a piston (in ideal case moving without friction) containing gas (working medium, in ideal case – ideal gas);
- cooler (temperature lower than the lowest temperature of working gas).

## Carnot cycle

Cycle consists of (initial gas state - $T_0$, $p_0$, $V_0$):
1. Gas receives from source energy by means of heat, expands isothermally ($T_1$, $p_1$, $V_1$);
2. Gas is further expanded adiabatically (contact with source is broken, *e.g.* cylinder is insulated), temperature drops (performs work at the expense of its own inner energy) ($T_2$, $p_2$, $V_2$).
3. Gas is giving energy up by means of heat to (*e.g.* removed insulation) and is compressed isothermally ($T_3$, $p_3$, $V_3$).
4. Gas is compressed further adiabatically (isolation from cooler), temperature increases (to $T_0$, $p_0$, $V_0$).
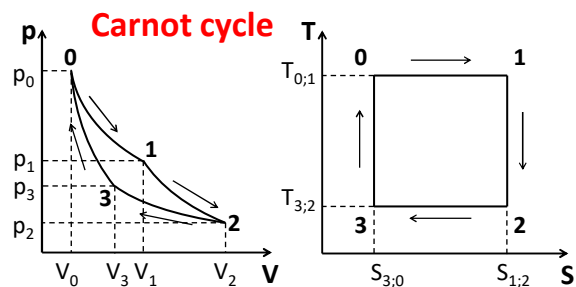
**Carnot cycle**

## Thermodynamic efficiency

- Theoretical efficiency of Carnot engine (ideal heat engine) is the highest possible one for any engine (for a given temperature difference, $T_2$-$T_1$).
- Real-world engines (and their cycles) are analyzed like the Carnot engine analysis before.
- For real engines such analysis is so-called theoretical efficiency of a cycle.
- Real engines have ca. 2 times smaller efficiency than that of Carnot engine (for a given temperature difference, $T_2$-$T_1$).

## Engine efficiency

- **Engine efficiency** is an efficiency with which engine is converting heat energy to work:
  $$\eta = W / Q \quad \text{(always } \eta<1, \text{ usually indicated in \%)}$$
- **Maximal** thermodynamically possible **heat engine efficiency** (ideal one) is:
  $$\eta = (T_s - T_c) / T_s \quad \text{(always } \eta<1\text{)}$$
  (s – heat source, c - cooler)
- **Thermodynamic efficiency** is a difference between work that system could possible perform (if not for heat losses, friction, *etc.*) and real work possible for engine to do:
  $$\eta = W / W_{max} \quad \text{(always } \eta<1, \text{ usually indicated in \%)}$$

## Coolers

- Coolers are working with the same principle of operation as the Carnot engine, just in the opposite direction and in the reverse order of phases (3→2→1→0→3…).
- Coolers' efficiency is analogic to engines' efficiency (although they receive energy by means of work and give it up by means of heat): $\eta = Q/W$

## Coolers

Maximal thermodynamically "efficiency" of a cooler, due to its definition, can be higher than 1 (one).

To heat transferred from the colder towards the warmer medium one should add energy of work performed (*e.g.* compressor). The lower temperature difference between media, the higher (relatively) energy is (by means of work). Due to that, energy given up to the warmer medium is much higher than that received from the colder medium.

Maximal possible thermodynamic efficiency of perfect cooler is:
$$\eta = T_c / (T_s - T_c) \quad \text{(c – cooler, s - source)}$$
That formula also explains why it is impossible to cool down anything to absolute zero temperature.

## Adiabatic process once again

- Adiabatic transitions are theoretical ones, during which no heat exchange with surroundings occur (energy can be transferred only through work).
  In reality, one cannot ideally insulate the system.
- A lot of real-world processes are very close to adiabatic one due to their speed or to the system size (heat is not able to penetrate the surroundings).

## Adiabatic process once again

- Diesel engine – compression is so fast, that gas is not able to exchange heat (so it is possible to combust the fuel);
- Temperature in high mountains – air masses are conducting the heat very poorly and those are enormous volumes – so in case of upward air movement (with the flow) it is not able to give its heat up, so during expansion its temperature is decreasing (by ca. -7˚C every 1000 m). As a result of that, there is a perennial snow in the top of the highest mountains.
- Foehn (and similar winds around the world) – as a result of a temperature drop moisture is condensing (in form of rain/snow). On the other side of mountains the air is going downward dry and warm due to compression (it is not able to transfer a lot of heat).