

Thermodynamics

2018/2019, lecturer: Martin Zápotocký

2 lectures:

1. Thermodynamic processes, heat and work, calorimetry, 1st and 2nd law of thermodynamics
2. Entropy, thermodynamic potentials, nonequilibrium steady states, heat transport, heat balance in human organism

Warning: figures and equations
drawn on the blackboard are not
included in these slides

Thermodynamic system

- Thermodynamics studies processes of energy transformation on the **macroscopic** level (vs. kinetic theory on the molecular level)
- **Thermodynamic system** (containing a macroscopic number of molecules) is in contact with the surroundings (environment, reservoir). The system can be
 - **isolated** if no energy or matter is exchanged (e.g. liquid in perfectly insulating container)
 - **closed** if only energy is exchanged (e.g. gas constrained by piston)
 - in general **open** (e.g. fluid in contact with its vapor; living cell)
- **State variables**: pressure, temperature, volume, composition, ... uniquely determine the **macroscopic state** of the system

Thermodynamic process

- Thermodynamic **process**: a change in the state of the system
- Example: ideal gas constrained by movable piston – can change p, V, T , constrained by equation of state $pV = nRT$
- **Isobaric** process: fixed p ; **isochoric**: fixed V ; **isothermal**: fixed T
- In isochoric process, no mechanical work performed
- In **adiabatic** process, no heat is exchanged with environment
- **Reversible process**: by reversing the process, one can bring **both the system and its environment** back into the initial state
- Whenever energy is dissipated (mechanical into heat, e.g. due to viscosity), the process is **irreversible**

Thermodynamic equilibrium

- A system in **thermodynamic equilibrium** would remain in the same state if we isolate it. There are no net fluxes.
- System is in **thermodynamic equilibrium with environment** if it has same T (thermal eq.), same p (mechanical eq.), same chemical potential (chemical eq.), and there are no unbalanced forces (fluxes).
- After a change in external conditions, the system requires a finite **relaxation time** to achieve the new state of thermodynamic equilibrium
- A reversible process goes through a sequence of equilibrium states; must be sufficiently slow (quasi-static)
- **Living systems: maintained far from thermodynamic equilibrium** (due to non-zero fluxes of matter and energy between system and environment)

Isothermal vs. adiabatic process, thermal reservoir

- Isothermal vs. adiabatic process:
 - example of **isothermal process**: system in contact with reservoir with large heat capacity + **sufficiently slow process** to maintain thermal equilibrium between system and reservoir
 - **a sufficiently fast process will be adiabatic** – not enough time to exchange any heat with environment
- For ideal gas:
 - during isothermal process, $pV = \text{const}$
 - during adiabatic reversible process, $pV^\gamma = \text{const}$, $\gamma = \frac{c_p}{c_v} = 5/3$
- Newton's mistake when calculating the speed of sound

Heat vs. work

- Heat is the **transfer of energy** between two systems, during which no work is performed
- Spontaneous heat transfer from system with higher temperature T_1 to system with lower temperature T_2 (if the systems are in thermal contact).

$$Q_1 < 0, Q_2 > 0 \text{ (system 2 gained heat)}$$

- Basic unit for both heat and work is

$$1\text{Joule} = \text{Newton} \times \text{m} = \text{kg m}^2/\text{s}^2$$

- Reminder:

If under constant force \vec{F} a body is moved by space interval \vec{x} , work done is

$$W = \vec{F} \cdot \vec{x} = F x \cos \alpha$$



James Prescott Joule
1818-1889

Work expressed as integral

- For gas with piston of area A displaced by small interval dx : work done by the gas is

$$dW = \vec{F} \cdot d\vec{x} = p A dx = p dV$$

where $dV = A dx$ is the volume change

- Therefore work done by gas during a process that changes the volume from V_i to V_f is given by the integral

$$W = \int_{V_i}^{V_f} p dV$$

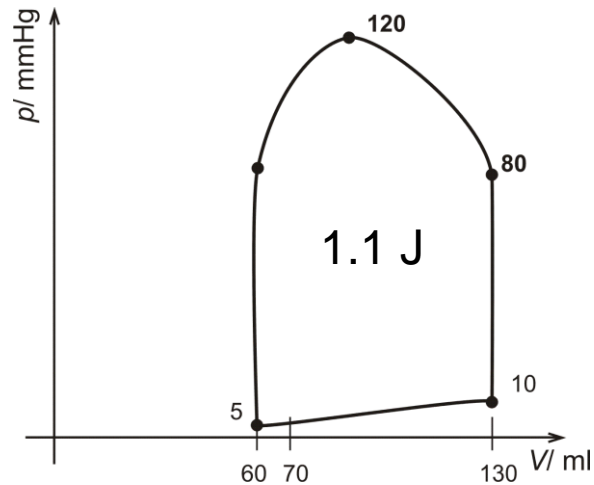
where the pressure $p(V)$ can depend on volume V !

- Meaning of the integral: area under the $p(V)$ curve
- This implies that W depends on the path of the process, i.e. work is not a state variable. E.g. for isothermal process in ideal gas,

$$W = nRT \ln\left(\frac{V_f}{V_i}\right)$$

Example: work loop of the left ventricle

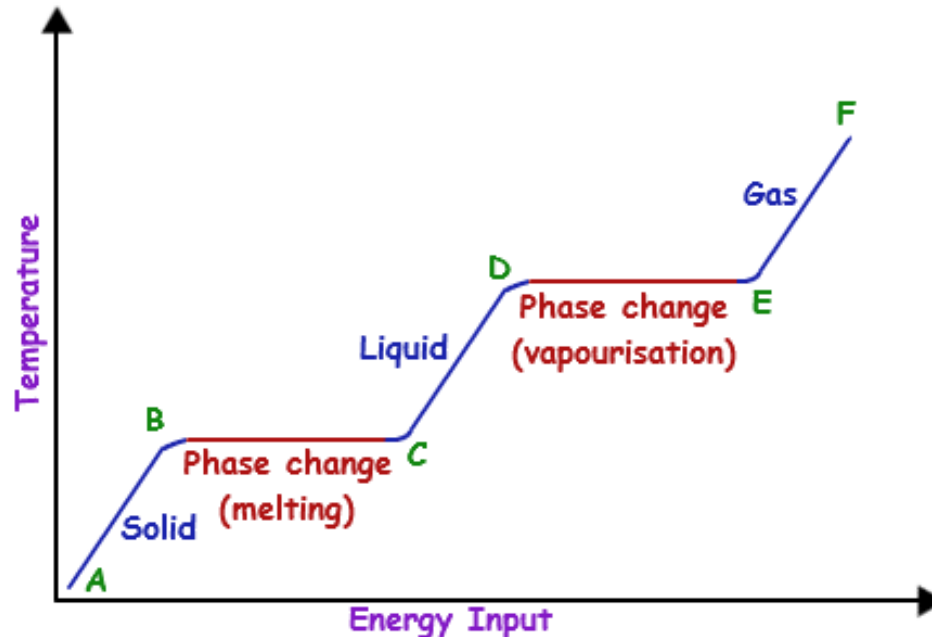
- The amount of work performed by the left ventricle during one cycle of heart contraction: the area within the loop in the diagram of intraventricular blood pressure vs. ventricle volume



- 1 contraction (in resting physical state) performs work of 1.1 J.
- Total power of the heart muscle (work/second): 1.3 W to 8 W, depending on level of physical activity. Regulated by heart rate and stroke volume.

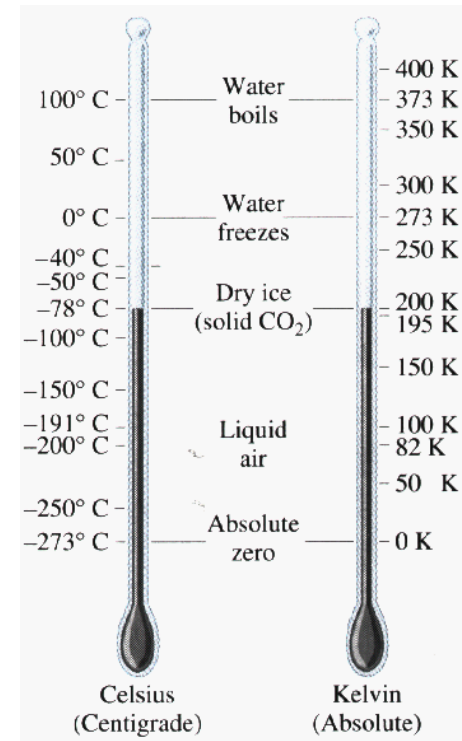
Heat is distinct from temperature!

- **Temperature** quantifies the kinetic energy of microscopic thermal motion (recall the equipartition theorem)
- In a given thermodynamics state, the system has a particular temperature T , but does **not** have a particular heat Q
- Heat is a transfer of energy during a process, and is not a state quantity



Measurement of temperature

- To measure temperature T , we bring the **thermometer** into **thermal equilibrium** with the measured system
- Temperature scales: defined by the zero point and the unit
- **Celsius (centigrade)** scale: zero point is the temperature of water (at standard p), unit = $1\text{ }^{\circ}\text{C}$, water boils at $100\text{ }^{\circ}\text{C}$.
- **Fahrenheit** scale (in $^{\circ}\text{F}$): $32 + \frac{9}{5} t_{\text{Celsius}}$
- **Absolute scale**: zero point is the lowest possible temperature (all thermal motion stops), absolute zero = $0\text{ K} = -273.15\text{ }^{\circ}\text{C}$. Unit is $1\text{ Kelvin} = 1\text{ }^{\circ}\text{C}$.
- Therefore the temperature of human body on the absolute scale: $273.15\text{ }^{\circ}\text{C} + 37\text{ }^{\circ}\text{C} = 310.15\text{ K}$



Types of thermometers

- **Liquid thermometers:**
 - based on liquid volume expansion, $\Delta V/V_0 = \beta\Delta T$
 - the coefficient of expansion for **mercury**: $\beta = 1.8 \cdot 10^{-4} \text{ K}^{-1}$ (vacuum above liquid)
 - mercury thermometer range: -39 °C to +250 °C
- **Bimetallic strip:** difference in volume expansion coefficients of two metals welded together → bending (used in mechanical thermostats)
- Based on changes in **electric resistance**:
 - metal resistance thermometer (e.g. platinum, wide range)
 - **thermistor** (lab No. 3) – strong decrease of resistance with T in a **semiconductor** (mK precision)
- **Thermocouple:** two metals in contact generate **electromotive force** (voltage) with magnitude depending on T. Measure voltage difference between hot and cold junction.
- **Thermography:** record intensity of **thermal radiation** with infrared camera. Helps to localize tumors.

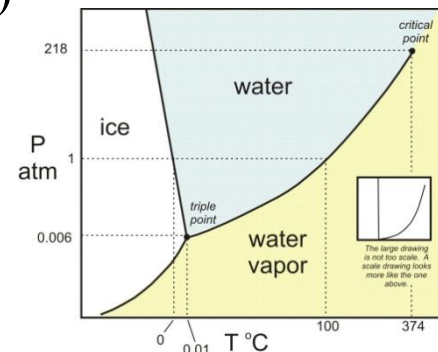
Specific heat, latent heat

- The **specific heat capacity** gives the amount of heat needed to increase temperature by 1 Kelvin (while remaining in the same phase):

$$Q = mc\Delta T = nC\Delta T$$

water: specific heat $c = 4.2 \text{ kJ kg}^{-1}\text{K}^{-1}$, molar specific heat $C = Mc$

- Specific heat at constant p is higher than at constant V :**
 - due to work $p\Delta V$
 - for ideal gas: $C_P = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R$
 - adiabatic index $\gamma = C_P/C_V > 1$ (water vapors ≈ 1.3)
 - for fluids close to 1
- Latent heat** is the heat associated with a phase transition
 - $Q = mL$, $L =$ specific latent heat,
 - e.g. $L = 2.3 \text{ MJ kg}^{-1}$ for evaporation of water at $100 \text{ }^\circ\text{C}$

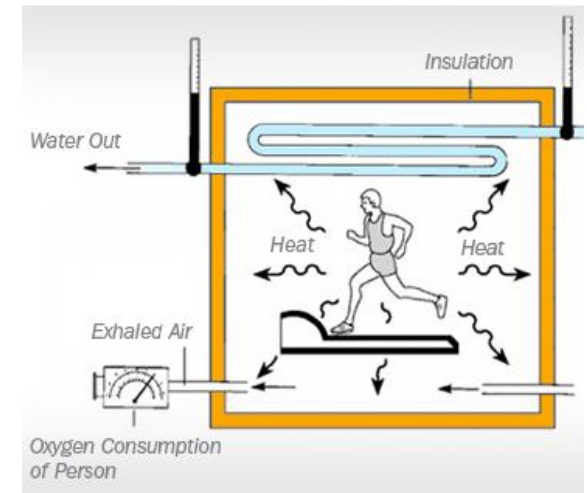
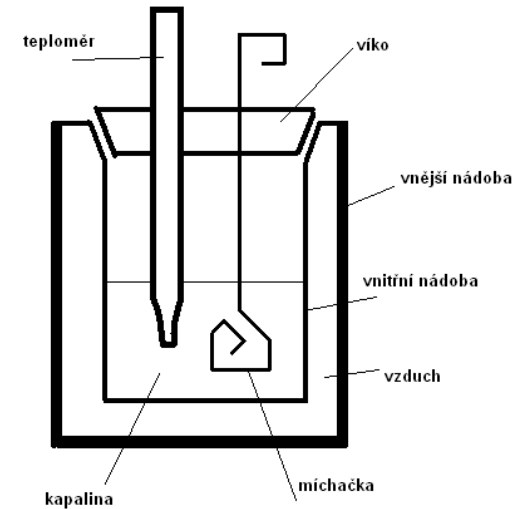


Calorimetry

- Heat can be measured in a **calorimeter**. Based on measurement of temperature change + knowledge of heat capacity.
- Basic calorimeter: water in thermally isolating vessel
- If water temperature increases by ΔT :
 - water absorbed heat $Mc\Delta T$ (M = mass of water, c = specific heat of water)
 - rest of calorimeter absorbed heat $Kc\Delta T$, where K = **water value** of the calorimeter (kg) – calibrated before measurement
 - total heat absorbed (**calorimetric equation**):

$$Q = (M + K) c \Delta T$$

- **Calorimetric units:** 1 cal = heat needed to bring 1 g of water from 14.5 °C to 15.5 °C; 1 cal = 4,187 J
- Direct calorimetry of metabolic rate – whole body calorimeter



Internal energy

- Internal energy of a system:
 internal kinetic energy + potential energy of internal forces
- Internal kinetic energy: sum of kinetic energies of all system parts
 - does not include motion of the whole system (center of mass)
 - includes translational, rotational, and vibrational kinetic energy of molecules
 - average kinetic energy of 1 molecule = $n \frac{1}{2} k_B T$; $v \sim 1$ km/s
(n = number of degrees of freedom
 k_B = Boltzmann const = 1.38×10^{-23} J /K)
- Internal potential energy includes the energy of chemical bonds; does not include energy from external forces (e.g. gravitation)
- Example: internal energy of 1 mole of inert gas (no chemical bonding):
 $N_A \frac{3}{2} k_B T = \frac{3}{2} RT = 3406$ J

First law of thermodynamics

- Law of conservation of energy: **the total energy of a isolated system does not change in time**. Note: the only truly isolated system is the Universe!
- A thermodynamic system in interaction with environment: exchange of energy in the form of work and heat
- **1st law of thermodynamics:**

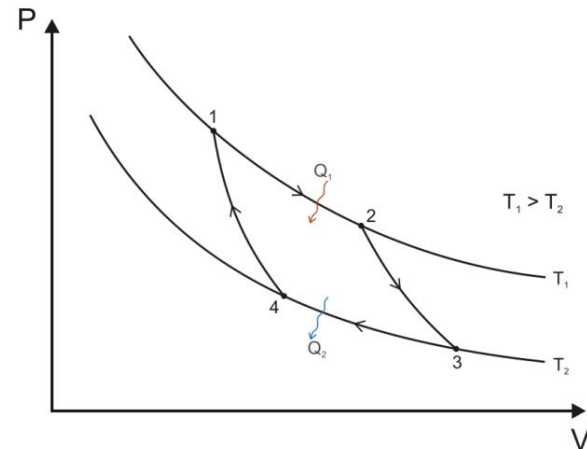
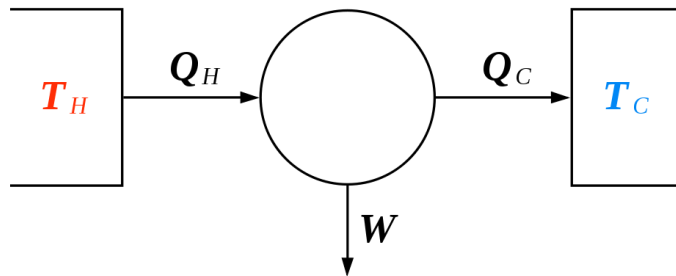
$$\Delta U = Q - W$$

where $\Delta U = U_f - U_i$ is the change in internal energy, Q the heat received and W the work performed during the process

- **Internal energy is a state variable!** ΔU does not depend on the path of the process, even though Q and W are **not** state variables.
- Remember the signs: received heat increases internal energy ($\Delta U > 0$), performed work decreases internal energy ($\Delta U < 0$). For an isolated system, $\Delta U = 0$.

Cyclic process, heat engine

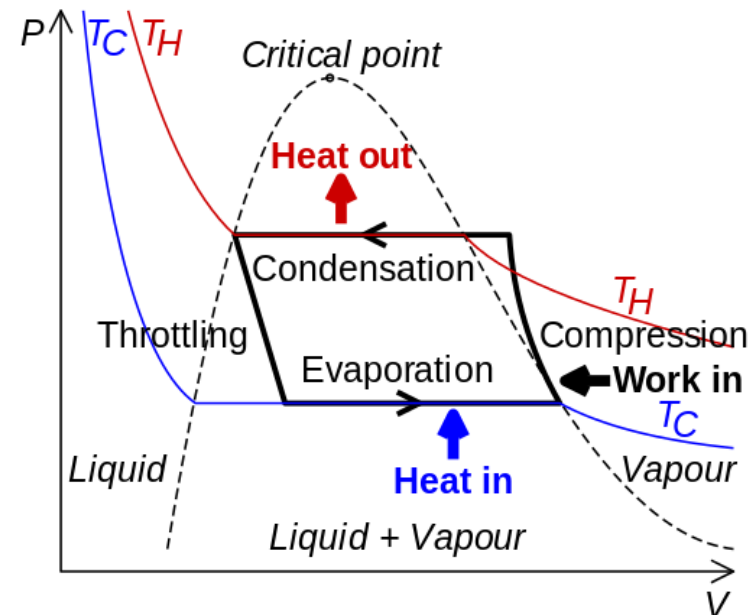
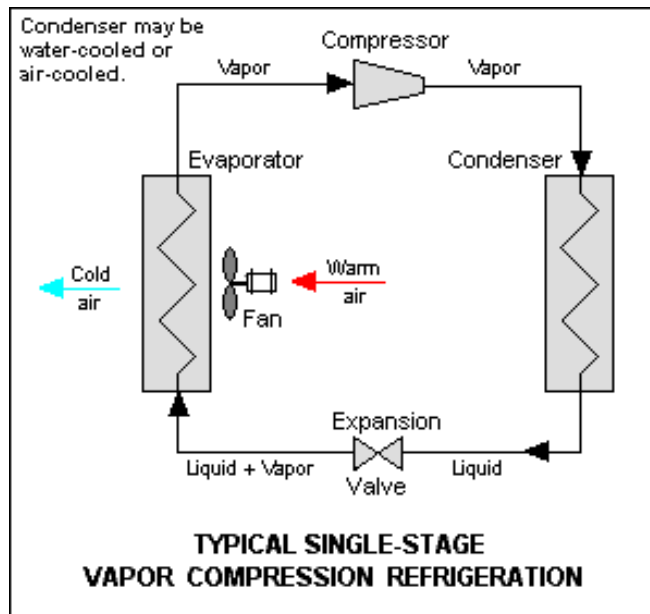
- A **cyclic process** returns to the same state
- Work in cycle is equal to the area enclosed by the process path in the p-V diagram (positive if clockwise)
- A heat engine performs conversion of heat energy to mechanical work. Two segments of the cycle (1-2 and 3-4) operate at temperatures of **hot and cold reservoir**



- E.g. **Carnot cycle**: isothermal expansion (heat intake) → adiabatic expansion (work output) → isothermal compression → adiabatic compression

Heat engine running in reverse: the heat pump

- In a vapor compression refrigerator: the coolant absorbs heat when it is evaporating during expansion



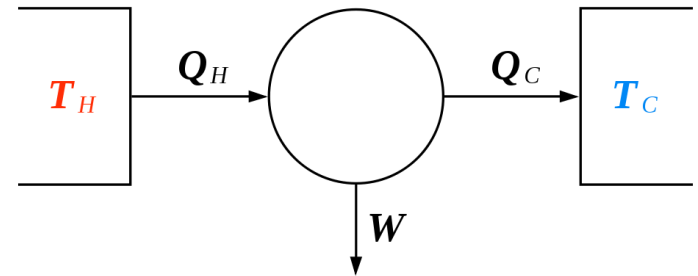
Second law of thermodynamics

- It is impossible to make a heat engine which only takes heat from one reservoir. Part of the heat must be passed to another reservoir with lower temperature. (It is therefore degraded – cannot be put back into hot reservoir without additional energy cost.)

- Efficiency of heat engine:

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

- Efficiency η is always below 1 (100%)



- The maximum possible efficiency of a heat engine is

$$\eta = 1 - \frac{T_C}{T_H}$$

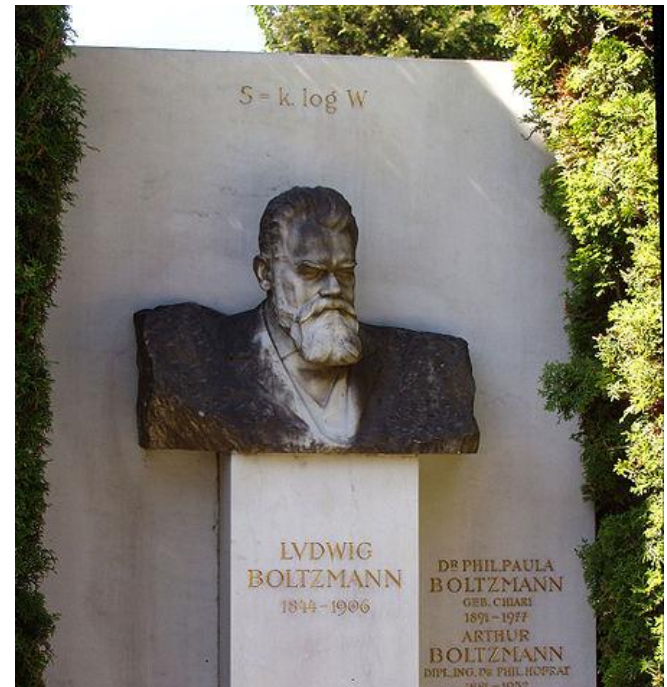
and it is reached only if the engine process is reversible

- Alternative formulation of 2nd law of thermodynamics: using entropy.

History of entropy: macroscopic and microscopic



Rudolf Clausius, 1865:
The energy of the universe is constant.
The entropy of the universe tends to a maximum.



Ludwig Boltzmann, 1877:
entropy measures disorder
$$S = k_B \ln W$$

Entropy

- Entropy expresses the degree of disorder in the system. Given by:

$$S = k_B \ln W$$

$$k_B = \text{Boltzmann const} = 1.38 \times 10^{-23} \text{ J /K}$$

W = thermodynamic likelihood of the state

(number of microscopic ways to obtain the macroscopic state)

- Increase in S means that the new state of the system is less organized.
- Example: melting of the crystal lattice increases entropy.
- Example: 1 mol of ideal gas put in left half of partitioned container. After removal of partition, the gas freely expands into right half, and

$$\Delta S = k_B \ln \frac{W_f}{W_i} = k_B \ln 2^{N_A} = k_B N_A \ln 2 = R \ln 2 = 5,76 \text{ J/K}$$

- 2nd law formulated in terms of entropy:
In an isolated system: entropy can never decrease. It will increase during any irreversible process. The system will spontaneously approach the most probable configuration: the state of thermodynamic equilibrium, with maximal entropy.

Heat and entropy

- During a **reversible isothermal** process, the entropy change is proportional to absorbed heat:

$$\Delta S = S_f - S_i = \frac{Q}{T}$$

- For any **irreversible** process:

$$S_f - S_i > \int_i^f \frac{dQ}{T}$$

therefore for any **irreversible adiabatic** process, $\Delta S > 0$

- Therefore the entropy of an isolated system (the Universe) stays constant or increases. However, **in a non-isolated subsystem, entropy can decrease** (at the expense of the rest of the system).

Dissipation, „lost work“ in irreversible process

- For **reversible** process at temperature T:

$$\Delta U = Q_{\text{rev}} - W_{\text{rev}} = T\Delta S - W_{\text{rev}}$$

- Consider an **irreversible process with the same initial and final states**:

$$Q_{\text{irr}} - W_{\text{irr}} = \Delta U = T\Delta S - W_{\text{rev}}$$

Since $Q_{\text{irr}} < T\Delta S$, we have $W_{\text{irr}} < W_{\text{rev}}$

- Work done in the irreversible process is lower by the „lost work“ amount $W_{\text{lost}} = W_{\text{rev}} - W_{\text{irr}}$. Interpretation: some of the internal energy is **dissipated**, i.e. used to increase entropy rather than to perform work.
- Can write for **any process at temperature T**:

$$\Delta S = \frac{Q}{T} + \frac{W_{\text{lost}}}{T}$$

i.e. entropy of the system can be changed by heat transfer with surroundings (Q) **or** by internal dissipation ($W_{\text{lost}} > 0$)

Thermodynamic potentials

- The 4 thermodynamic potentials express the potential of the system to do work under specific conditions
- Are **minimized in thermodynamic equilibrium**
- Analogous concept in mechanics: potential energy
- **State functions**, do not depend on process path. Extensive quantities, units: Joule.
- **Internal energy U**
 - recall: internal kinetic energy + potential energy of internal forces
 - U = energy needed to create the system (in isolation)
 - $\Delta U = Q - W$, therefore in an adiabatic process, $Q = 0$, $W = \Delta U$
 - for isolated system at fixed volume, U is **minimized in thermodynamic equilibrium**

Enthalpy, free energy, free enthalpy

- Free energy (Helmholtz function) $F = U - TS$
 - energy needed to create the system while in contact with reservoir at T
 - for isothermal, reversible process: $\Delta F = \Delta U - T\Delta S = \Delta U - Q = -W$
 - i.e. decrease in free energy = maximum work that can be done in a process at fixed T and V. Less work done if the process is irreversible.
- Enthalpy $H = U + pV$
 - for isobaric process: $\Delta H = \Delta U + p\Delta V = \Delta U + W = Q$,
 - i.e. change in enthalpy = heat received by system
 - for exothermic reaction at constant pressure, $Q < 0$, enthalpy decreases (and achieves minimum in thermodynamic equilibrium)
 - Law of Hess: reaction heat does not depend on the reaction path (enthalpy is a state function)
- Free enthalpy (Gibbs function) $G = U + pV - TS = H - TS$
 - if $\Delta G < 0$, reaction will be spontaneous (at const T and p)
 - G is the maximum work that can be performed by chemical reaction

Chemical potential

(is not a thermodynamic potential – not minimized in TD equilibrium)

- In an open system, changes in composition lead to changes in energy
- Chemical potential μ_i for chemical substance i: change in energy of the system if 1 mole of substance i is added (and the amount of other substances is not changed)

- At given p, T: change in free enthalpy of the equilibrium state is

$$\Delta G = \mu_1 \Delta n_1 + \mu_2 \Delta n_2 + \dots$$

where $\Delta n_1, \Delta n_2, \dots$ are the changes in number of moles

- Chemical potential is a measure of chemical affinity, but depends on state parameters. For ideal gas

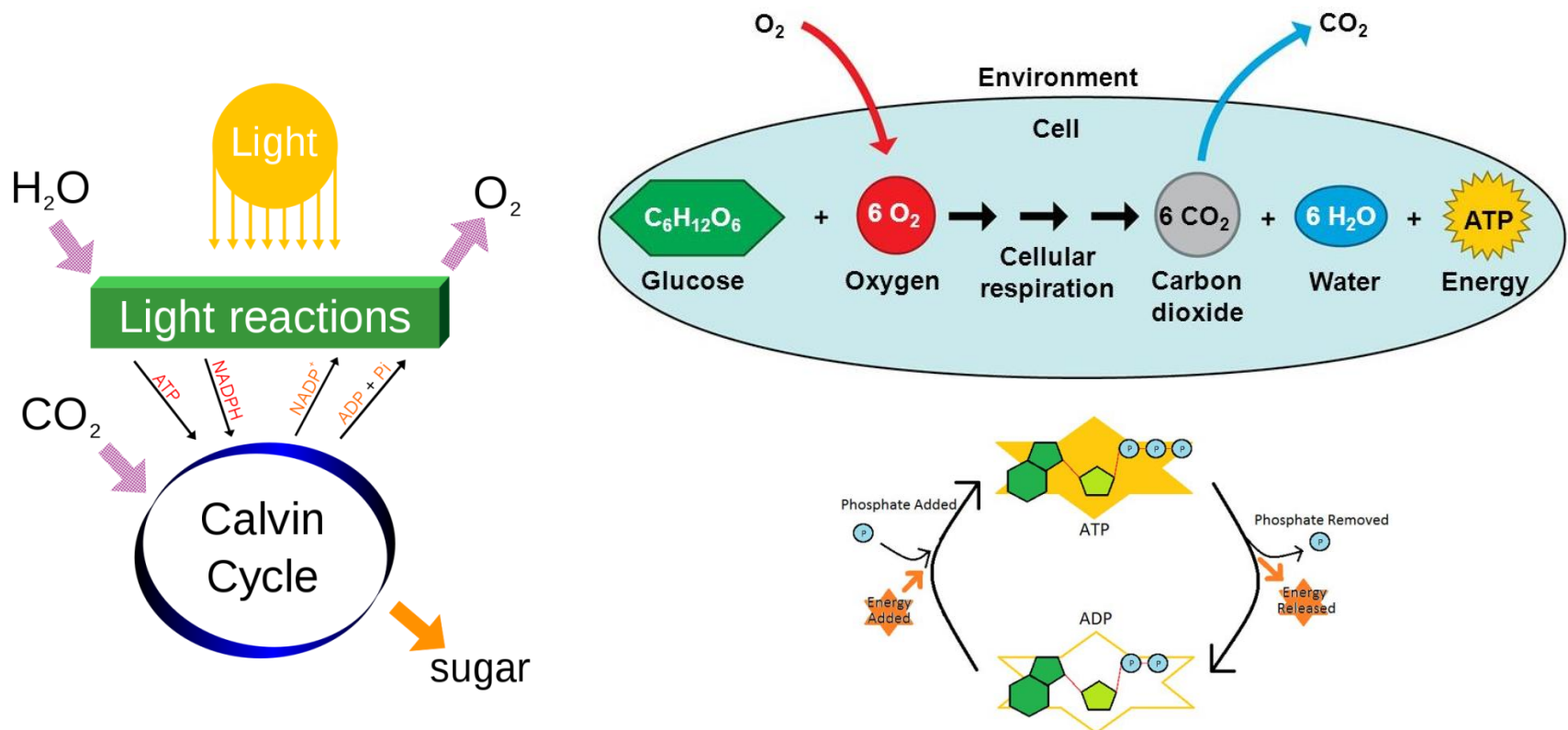
$$\mu(p, T) = \mu_o(T) + k_B T \ln \frac{p}{p_0}$$

Nonequilibrium steady states, principle of minimal entropy production

- **Living systems** operate far from thermodynamic equilibrium and continuously dissipate energy
- ΔS (of system + environment) per unit time = **entropy production rate** > 0
- **Nonequilibrium steady state** examples:
 - steady heat flux in system in contact with two thermal reservoirs
 - combustion engine: steady supply of reactants + steady removal of products
- The thermodynamic potentials are **not** minimized in such noneq. states. Under restricted conditions (not too far from equilibrium), the following principle holds:
- **Principle of minimal entropy production**: a nonequilibrium system tends to **lower its rate σ of production of entropy** (per unit volume), and reaches a minimum σ in the nonequilibrium steady state.

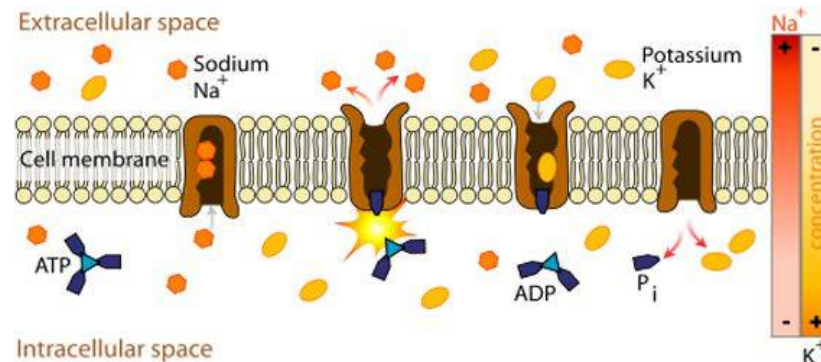
Energy conversions in biological processes

- Remember from biochemistry:
 - Photosynthesis in chloroplasts
 - Cellular respiration: nutrients \rightarrow ATP
 - ATP hydrolysis: intracellular source of energy (7.3 kcal/mol)



Passive and active transport at the cell membrane

- **Passive transport:**
 - down the concentration gradient, or more generally down the electrochemical gradient (see lectures on electric phenomena)
 - **requires no energy** (energy is gained during the transport)
 - examples: diffusion of O_2 into cell; facilitated diffusion of glucose from blood into erythrocytes; ions flowing through an **open ion channel**
- **Active transport:**
 - against diffusion / electrical force. Consumes energy supplied by **ATP hydrolysis**.
 - Example: in each cycle, **the Na^+/K^+ pump** moves 3 Na^+ out and 2 K^+ in (against concentration gradient), hydrolysing 1 ATP



Energetic requirements of human organism

- Most energy is obtained through metabolic reactions (food). ATP used in nonequilibrium (active) processes inside cells. See notes p. 58-60.
- Metabolic energy usage, **per unit area of body surface** (total area 1,7 m²)
 - sleep: 35 kcal/m²/hod
 - reading, sitting: 60 kcal/m²/hod
 - walking 5 km/h: 140 kcal/m²/hod
 - cycling 250 kcal/m²/hod
 - running 600 kcal/m²/hod
- For an active average human, total of 2300 kcal/day = 11 MJ /day
- **Most of the metabolic energy is converted to heat** (e.g. during muscle contraction, less than 40% of energy from ATP hydrolysis is converted to mechanical work).

Mechanisms of heat transport

- **Heat conduction:** thermal energy of molecular motion is transferred by molecular collisions. The rate of heat transfer (amount of heat transferred per unit time) is **proportional to temperature gradient**:

$$\frac{dQ}{dt} = -\kappa A \frac{dT}{dx}$$

A = area of surface perpendicular to \hat{x} , κ = **thermal conductivity**

- For water: $\kappa = 0.6 \text{ Wm}^{-1}\text{K}^{-1}$, air: $0.025 \text{ Wm}^{-1}\text{K}^{-1}$, metal: $100 \text{ Wm}^{-1}\text{K}^{-1}$ (high κ results in cold feeling)
- **Convection:** occurs in fluids. Decreased density in locations with lower $T \rightarrow$ buoyancy forces move fluid, bulk flow transports heat
- **Radiation:** vibrating charged particles emit electromagnetic radiation (act as antenna). Internal energy of the system is transformed into energy of radiation. Radiated energy per unit time, from surface of area A :

$$\frac{dQ}{dt} = e\sigma AT^4$$

σ = Stefan-Boltzmann constant = $5.67 \cdot 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}$

e = **emissivity** of the material ($e \approx 1$ for a black body = perfect absorber)

Thermal balance in human organism

- More than 80% of energy is transformed into heat. Efficient mechanisms for heat removal required to prevent overheating and death.
- Most heat is generated deep in tissues. The coefficient of heat conduction in a tissue is far too low to permit conduction of heat to body surface (would conduct only 20 kcal/hour)
- More efficient mechanism: heat conduction from cells to blood capillaries, then heat convection to body surface
- The skin loses heat:
 - through convection in surrounding air. Depending on air velocity, 65 kcal/hour to several hundred kcal/hour.
 - through radiation. The net heat loss = difference between energy radiated and absorbed = $Ae\sigma(T^4 - T_{ok}^4)$, with skin emissivity $e \approx 1$ (maximum radiation at 10 μm wavelength, i.e. infrared). At 7 °C temperature difference between skin and surroundings, the rate of radiative heat loss is 60 kcal/hour.

Heat loss through evaporation

- This is still not enough... In warm weather (above 31 °C), or even cold weather while exercising, an additional mechanism of heat loss becomes necessary to prevent overheating: **evaporation of sweat**.
- **Latent heat** for sweat vaporization (at 37 °C) is **580 kcal/kg**.
- The human organism can produce up to 4 litres of sweat within 1 hour, and can keep producing 1 litre/hour (assuming rehydration)
- **Only the sweat that evaporates leads to efficient heat loss!** Evaporated portion is highest in hot, dry, windy weather. Cannot vaporize if relative air humidity close to 100% (saturated vapor).