Thermodynamics

2018/2019, lecturer: Martin Zápotocký

2 lectures:

1. Thermodynamic processes, heat and work, calorimetry, 1\textsuperscript{st} and 2\textsuperscript{nd} 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, $pV = const$
  - during adiabatic reversible process, $pV^\gamma = const$, $\gamma = \frac{c_p}{c_v} = 5/3$

- 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).
  \[ Q_1 < 0, \quad Q_2 > 0 \] (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
  \[ W = \vec{F} \cdot \vec{x} = F \times x \cos \alpha \]
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 °C, water boils at 100 °C.
- **Fahrenheit scale** (in °F): \(32 + \frac{9}{5}t_{\text{Celsius}}\)
- **Absolute scale**: zero point is the lowest possible temperature (all thermal motion stops), absolute zero = 0 K = −273.15 °C. Unit is 1 Kelvin = 1 °C.
- Therefore the temperature of human body on the absolute scale: 273.15 °C + 37 °C = 310.15 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 \( \approx 1.3 \))
  - for fluids close to 1

- **Latent heat** is the heat associated with a phase transition
  - \( Q = mL \), \( L = \text{specific latent heat} \),
  - e.g. \( L = 2.3 \text{ MJ kg}^{-1} \) for evaporation of water at 100 °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 $\Delta T$:
  - water absorbed heat $M c \Delta T$ ($M$ = mass of water, $c =$ specific heat of water)
  - rest of calorimeter absorbed heat $K c \Delta T$, 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:
  \[
  \text{internal kinetic energy} + \text{potential energy of internal forces}
  \]

• 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 = \( n \frac{1}{2} k_B T \); \( v \sim 1 \text{ km/s} \)
    (\( n \) = number of degrees of freedom
    \( k_B \) = Boltzmann const = \( 1.38 \times 10^{-23} \text{ J/K} \))

• 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):
  \( N_A \frac{3}{2} k_B T = \frac{3}{2} RT = 3406 \text{ J} \)
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! \( \Delta U \) 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 \( \eta \) 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 2\textsuperscript{nd} 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:
  \[ S = k_B \ln W \]
  
  \( k_B = \) Boltzmann const = \(1.38 \times 10^{-23} \text{ J/K}\)

  \( W = \) thermodynamic likelyhood 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 exothermal 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 $\mu_i$ 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
  \[ \Delta G = \mu_1 \Delta n_1 + \mu_2 \Delta n_2 + \cdots \]
  where $\Delta n_1, \Delta n_2, \ldots$ 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
- $\Delta S$ (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 $\sigma$ of production of entropy (per unit volume), and reaches a minimum $\sigma$ 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\textsubscript{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\textsuperscript{+}/K\textsuperscript{+} pump moves 3 Na\textsuperscript{+} out and 2 K\textsuperscript{+} 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/hour
  - reading, sitting: 60 kcal/m²/hour
  - walking 5 km/h: 140 kcal/m²/hour
  - cycling: 250 kcal/m²/hour
  - running: 600 kcal/m²/hour
- 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 \(x\), \(\kappa\) = thermal conductivity
- For water: \(\kappa = 0.6\) Wm\(^{-1}\)K\(^{-1}\), air: 0.025 Wm\(^{-1}\)K\(^{-1}\), metal: 100 Wm\(^{-1}\)K\(^{-1}\) (high \(\kappa\) results in cold feeling)
- **Convection**: occurs in fluids. Decreased density in locations with lower \(T\) → 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 \(A\):
  \[
  \frac{dQ}{dt} = e\sigma AT^4
  \]
  \(\sigma\) = Stefan-Boltzmann constant = 5.67 ⋅ 10\(^{-8}\)Wm\(^{-2}\)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).