Heat, entropy. Heat conduction.

First, second and third law of thermodynamics. Temperature and internal energy. Statistical interpretation of entropy. Heat conductivity, equation of heat conduction, contact temperature.

Thermal properties

- First law of thermodynamics
- Reversible and irreversible processes
- Entropy
- Heat engines
- Second law of thermodynamics
- Carnot cycle
- Third law of thermodynamics
- Statistical physics – entropy and probability

Thermal properties of matter

Related to the internal energy, i.e. energy of particles

Internal energy is a sum of energies

- Kinetic E_K
- Potential E_P

Temperature T[K] is equivalent to the mean internal energy per particle

Internal energy

- Solids – localized particles

$$E_K \ll E_P$$

- Liquids – particle limited by the vessel volume

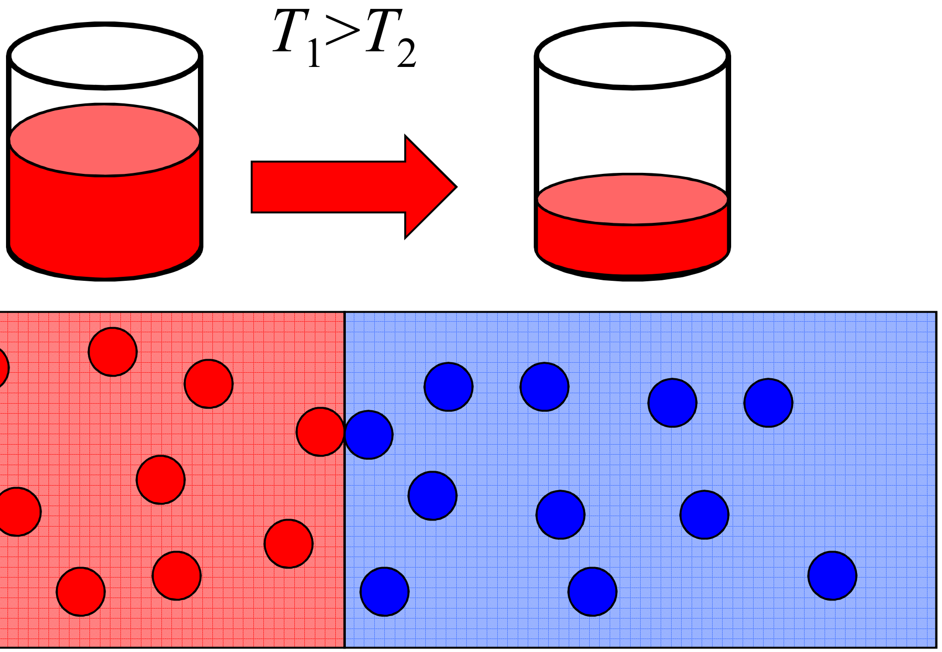
$$E_K \approx E_P$$

- Gasses – particles not localized at all

$$E_K \gg E_P$$

Thermal equilibrium

Equilibrium in the mean internal energy per particle



Zeroth law of thermodynamics

If two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other

Equilibrium is characterized by space and time stable quantitites

– possibility to measure temperature by reaching thermal equilibrium of thermometer and system!

Thermodynamic temperature

Internal energy of single atomic gas (per 1 atom)

$$u = \frac{3}{2} k_B T$$

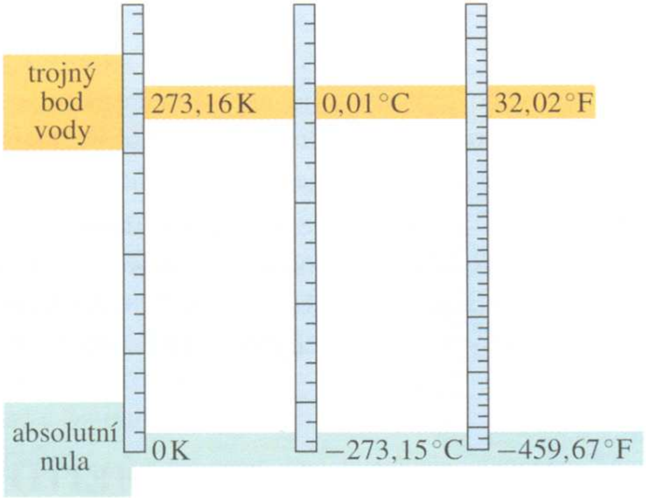
Boltzmann's constant $k_\mathrm{B}=1.38 \cdot 10^{-23}\,\mathrm{JK}^{-1}$

Thermodynamic temperature T [K]

$$\{T\}=\{t\}+273.15$$

Temperature scales

- Celsius (centigrade)
- Fahrenheit
- Kelvin
- …



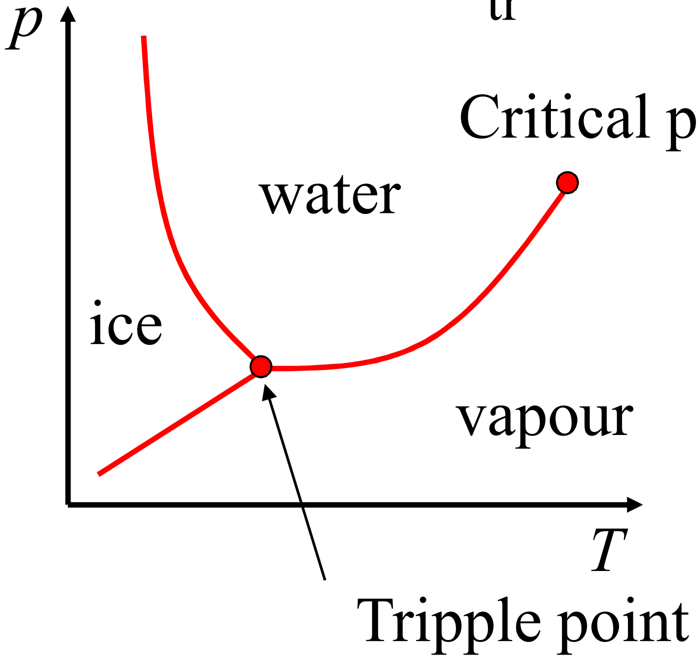
Obr. 19.7 Srovnání stupnice Kelvinovy, Celsiovy a Fahrenheitovy

Definition of temperature scale by phase transition temperatures of matter (tripple points in phase diagrams)

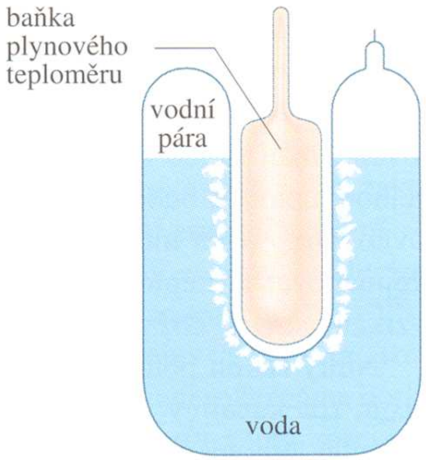
Temperature scale – tripple point

Temperatures of phase transitions depend on pressure – water tripple point

$$T_{tr}=0.01^{o}\mathrm{C},\ p_{tr}=610.6\ \mathrm{Pa}$$



Obr. 19.4 Buňka pro trojný bod vody, v níž jsou v tepelné rovnováze led, kapalná voda a vodní pára. Podle mezinárodní dohody je stanovena teplota této směsi jako 273,16 K. Baňka plynového teploměru je na obrázku vsunuta do dutiny buňky.



Measurement of temperature

- Temperature dependence of material properties (thermal expansion)
- Ideal gas heat engine – gas processes
- Carnot cycle

Thermometer

First law of thermodynamics

Energy conservation law

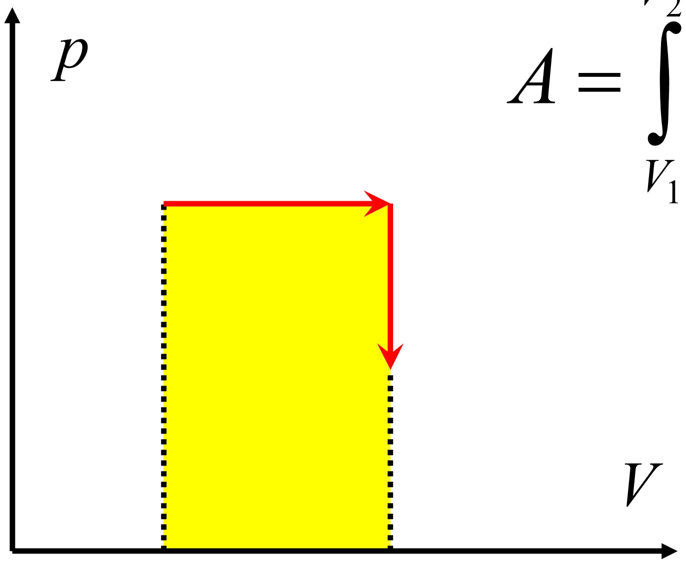
$$\Delta U = Q - A$$

Work A – macroscopic changes of body dimensions, e.g. gas $A = p\Delta V$

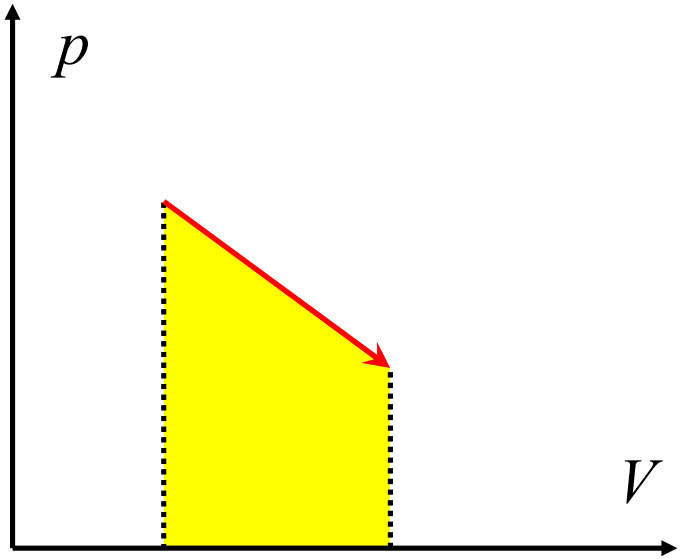
Heat Q – without apparent changes of body dimensions

Work and heat

Work and heat are not state quantities, they depend on the path of system process



$$A = \int_{V_1}^{V_2} pdV$$



Heat capacity

Heat capacity $K = \frac{\Delta Q}{\Delta T} \quad [JK^{-1}]$

Specific heat capacity $c = \frac{\Delta Q}{m\Delta T} \quad [Jkg^{-1}K^{-1}]$

Molar heat capacity $C = \frac{\Delta Q}{n\Delta T} \quad [Jmol^{-1}K^{-1}]$

Heat capacity differ for different gas processes e.g. isovolumetric and isobaric – C_V, C_p, etc.

Specific heat capacity $[\mathrm{Jkg^{-1}K^{-1}}]$

Fe	450	Water	4182	Air	1006
Cu	383	Ice	2090	O_2	917
Al	896	Vapour	1952	H_2	14320
				methane CH_4	2219

Adiabatic process (dQ=0)

All state variables change - p, V, T

First law of thermodynamics

$$dU = dQ - pdV$$

$$C_V ndT = -pdV$$

$$pV = nRT$$

$$Vdp + pdV = nRdT$$

$$\frac{dp}{p} + \frac{C_p}{C_V}\frac{dV}{V} = 0$$

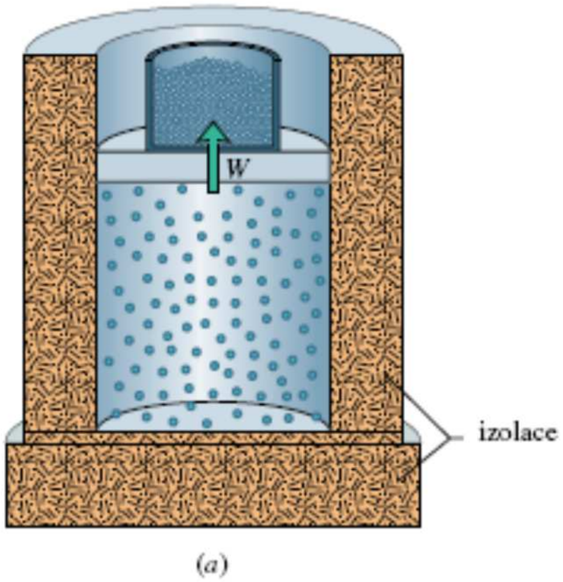
$$pV^\kappa = konst.$$

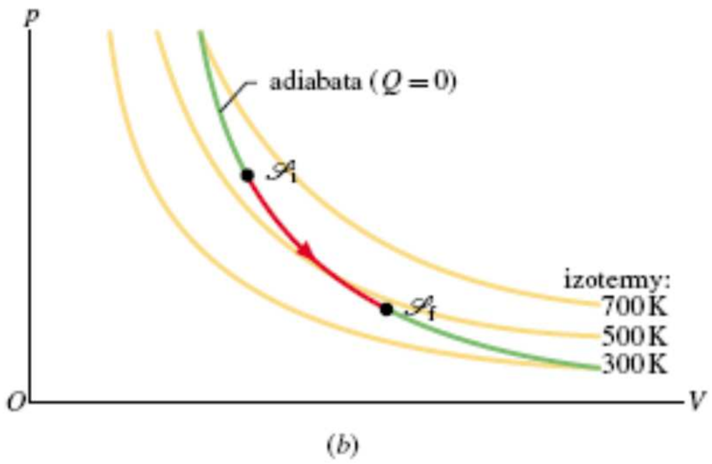
$$\kappa = \frac{C_p}{C_V}$$

Heat capacity is zero for adiabatic process

State variable for an adiabatic process?

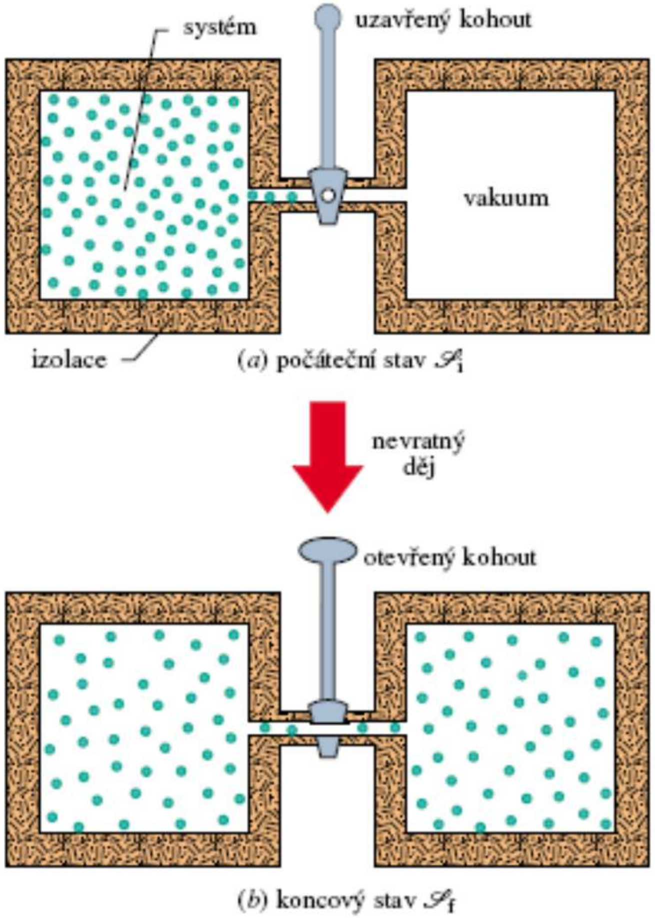
It is not heat! However, system in an isolated vessel changes its state to another equilibrium.





Obr. 20.13 (a) Odebíráme-li závaží z pístu, zvětšuje se objem ideálního plynu. Děj je adiabatický, neboť $Q = 0$. (b) Děj probíhá z počátečního stavu $\mathscr{S}_i$ do koncového stavu $\mathscr{S}_f$ podél adiabaty znázorněné v p-V diagramu.

Reversible and irreversible processes



Gas expansion from vessel into vacuum is irreversible – it is adiabatic process

Reversible adiabatic process

Without change of energy in an isolated system!

Reversible and irreversible processes

- Reversible processes – points and lines in state diagram p, V, T
- Irreversible processes – no possibility to display, while system is not characterized by the same state variable p, V, T within the whole volume!

Entropy

Reversible processes – no guiding force to show „direction“ of the process

Irreversible processes - „direction“ of the process is given by the change of entropy

Entropy always increases for the irreversible process in an isolated system!

Entropy is not conserved during the process.

Entropy

- Definition by heat and temperature
- Statistical definition

Entropy change $\Delta S = S_2 - S_1 = \int_1^2 \frac{dQ}{T}$

Change in entropy is zero for the reversible adiabatic process

Entropy change for reversible and irreversible process

The same initial and final equilibrium state for the reversible and irreversible process

Entropy change for reversible process is given by the heat Q and temperature T

$$\Delta S_n = \Delta S_v$$

Entropy change for an irreversible process is the same as for the reversible process with the same initial and final equilibrium states

Entropy change for isothermal process

Heat

$$Q = nRT\ln\left(\frac{V_2}{V_1}\right)$$

Entropy

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$$

Entropy change for the reversible process

Heat is a function of state variables

$$dQ = pdV + nC_V dT$$

$$pV = nRT$$

$$\frac{dQ}{T} = nR\frac{dV}{V} + nC_V\frac{dT}{T}$$

Entropy for reversible process

$$\Delta S = S_2 - S_1 = nR\ln\frac{V_2}{V_1} + nC_V\ln\frac{T_2}{T_1}$$

Second law of thermodynamics

Gas exchanges its entropy with surrounding medium

Entropy increases in an isolated system for the irreversible processes.

$$\Delta S \geq 0$$

Entropy of isolated system grows for irreversible processes and it is constant for the reversible ones.

Heat engine

Machine using heat from environment and producing mechanical work

Working in cycles

Working system – vapour, water, gasoline vapour, air, etc.

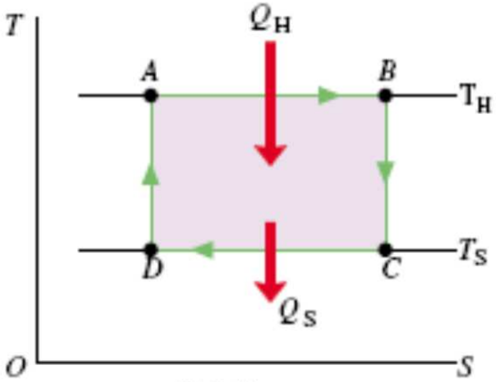
How much work can we get?

Ideal engine – reversible processes with an ideal gas, friction and energy losses negligible etc.

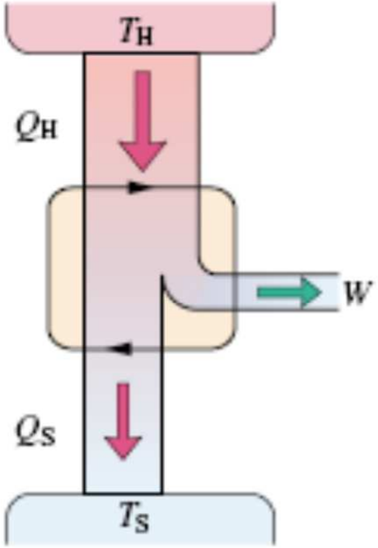
Carnot engine

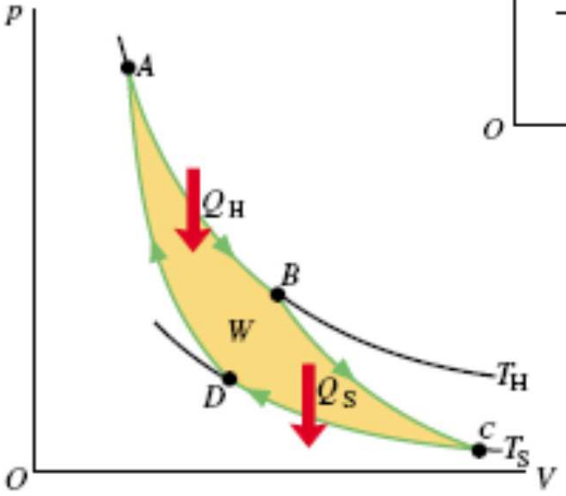
Carnot cycle (Sadi Carnot, 1824)

No losses, all processes reversible



T -S diagram





Efficiency of Carnot cycle

Internal energy change for one cycle

$$\Delta U = 0 = \Delta Q - W$$

Work done

$$W = |Q_H| - |Q_S|$$

Cycle efficiency

$$\eta_C = \frac{|W|}{|Q_H|} = 1 - \frac{|Q_S|}{|Q_H|}$$

Change of entropy

Entropy change for the reversible process

$$\Delta S = \Delta S_H + \Delta S_S = \frac{|Q_H|}{T_H} - \frac{|Q_S|}{T_S} = 0$$

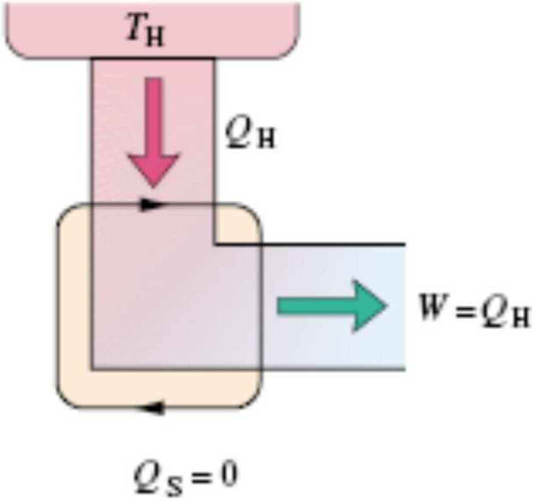
Efficiency of Carnot cycle

$$\eta_C = 1 - \frac{T_S}{T_H} \leq 1$$

Carnot cycle has maximum efficiency for all engines working between the same working temperatures

Carnot engine efficiency

- Increase the temperature $T_H \rightarrow \infty$
- Decrease the temperature $T_S \rightarrow 0$



Is 100% efficiency possible?

perpetum mobile of 2nd kind?

Second law of thermodynamics

Perfect heat engine is not possible.

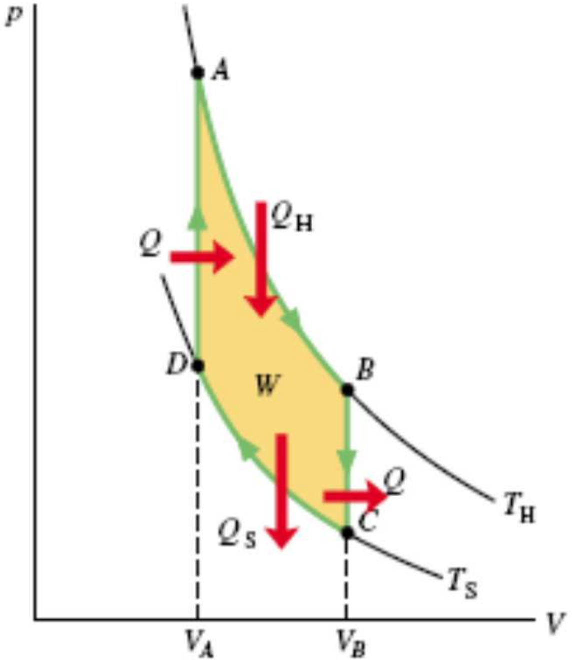
Perpetuum mobile of 2nd kind is not possible.

No device is possible whose sole effect is to transform a given amount of heat completely into work.

Stirling engine

Robert Stirling, 1816

The same efficiency as Carnot engine

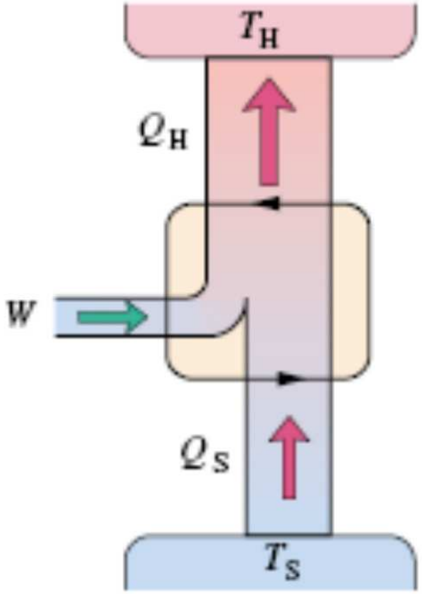


isothermal processes

isovolumetric processes

Refrigerator

Reversed Carnot heat engine – work input results in heat transfer from cold environment to hot environment – refrigerators, air-conditioning



Cooling rate

$$K = \frac{|Q_S|}{|W|} = \frac{|Q_S|}{|Q_H| - |Q_S|}$$

2.5 (air-conditioning) –

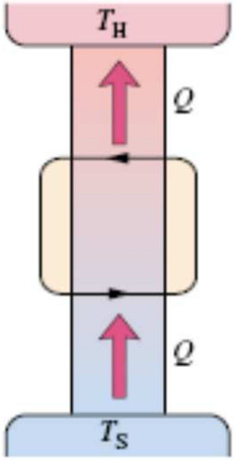
5 (refrigerator)

Perfect refrigerator

Is the transfer of heat from cold to hot body possible without work addition?

Entropy change for the reversible periodic process must be zero

$$\Delta S = -\frac{|Q|}{T_S} + \frac{|Q|}{T_H} < 0, \quad T_H > T_S$$



Impossible by the second law of thermodynamics. Perfect (100%) refrigerator does not exist!

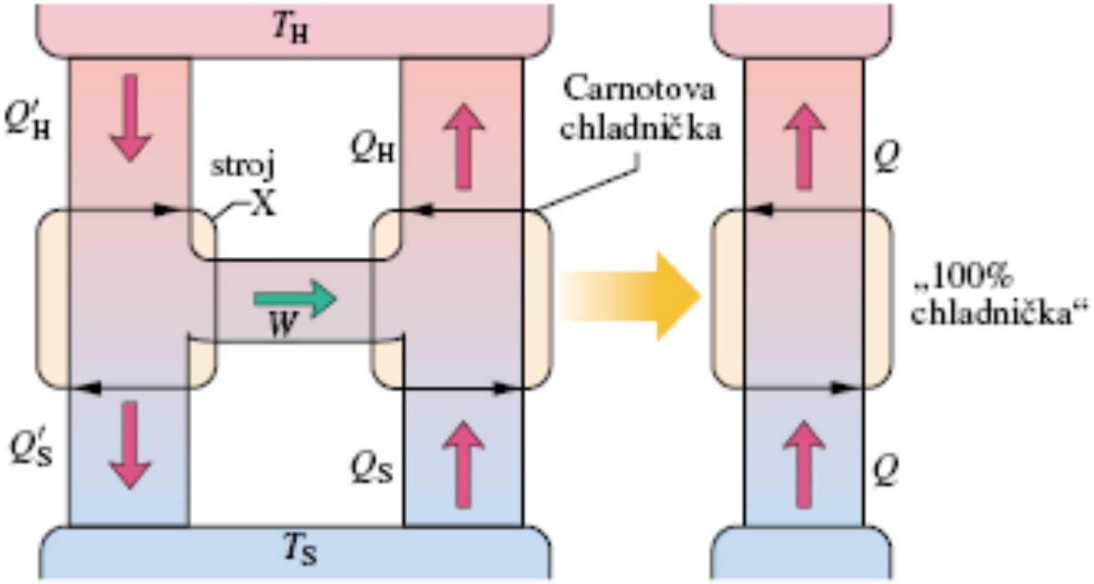
Other formulations of second law of thermodynamics

No device is possible whose sole effect is to transfer heat from one system at a temperature T_L into a second system at a higher temperature T_H

Heat cannot flow spontaneously from cold to hot system.

Efficiency of real engines

Could exist any real heat engine with higher efficiency as Carnot engine?



Let

$$\eta_X = \frac{|W|}{|Q_H'|} > \frac{|W|}{|Q_H|} = \eta_C$$

It holds $|Q_H| > |Q_H'|$

$$W = |Q_H| - |Q_S| = |Q_H'| - |Q_S'|$$

$$Q = |Q_H| - |Q_H'| = |Q_S| - |Q_S'| > 0$$

controversy!

Thermodynamic temperature

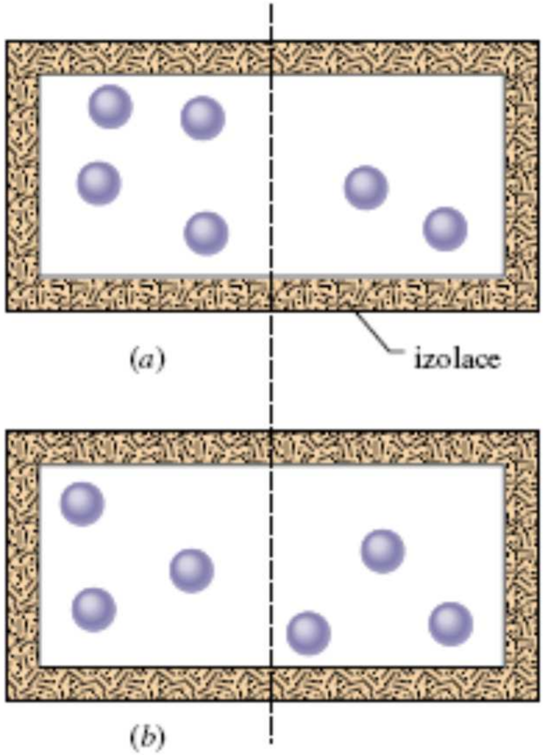
Carnot cycle is also the possibility for the definition of thermodynamic temperature independently from any thermally dependent effect or medium

$$\eta_C = 1 - \frac{T_S}{T_H}$$

All reversible and periodic heat engines working between the same temperatures have the same efficiency

Statistical physics

Entropy definition based on the microscopic arrangement of molecules

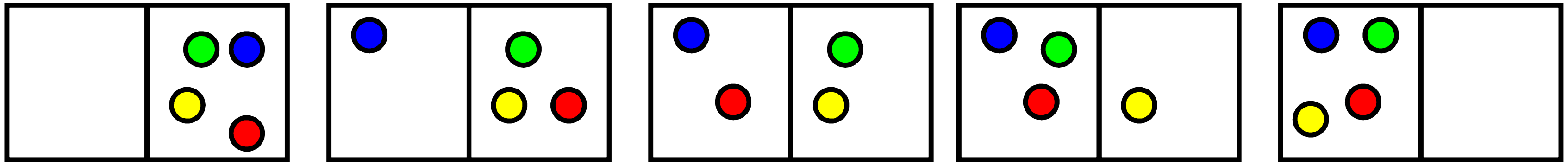


- microstate
- macrostate (configuration)

Every microstate has the same probability.

Entropy
and configuration probability

Multiplicity of microstate



1 possibility	**4 possibilities**	**6 possibilities**	**4 possibilities**	**1 possibility**
-abcd	a-bcd	ab-cd	abc-d	abcd-
	b-acd	ac-bd	abd-c	
	c-abd	ad-bc	acd-b	
	d-abc	bc-ad	bcd-a	
		bd-ac		
		cd-ab		

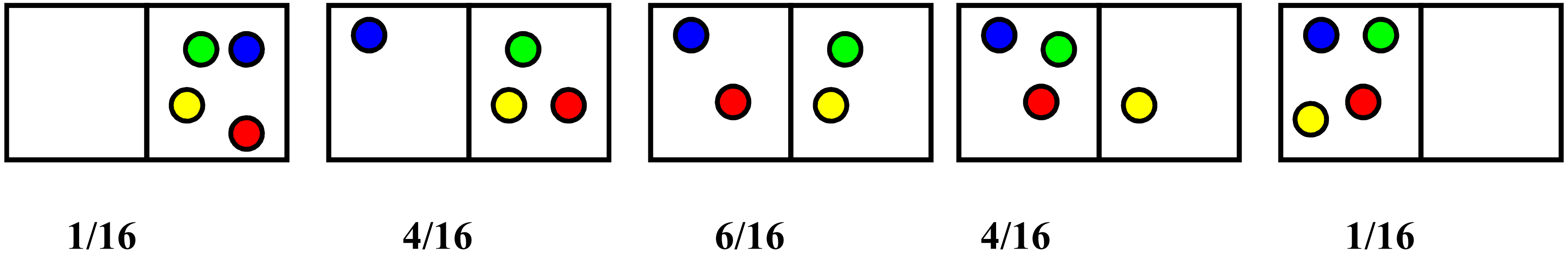
Multiplicity of microstate

Configuration multiplicity

$$W = \frac{N!}{n!(N-n)!} = \binom{N}{n}$$

Total number of configurations 2^N

Probability of configuration



State of system

Macrostate with the highest probability.

None possibility to decide what microstate defines such macrostate.

Conclusions are valid for the high particle number (see 10^{23} molecules in 1 mole)!

Probability and entropy

Entropy is an additive quantity – entropies of two subsystems sum together, probabilities multiply (independent phenomena)

$$S(W) = S(W_1) + S(W_2)$$
$$W = W_1 W_2$$

Stirling's formula $\ln N! \approx N \ln N - N$

Ludwig Boltzmann, 1877

$$S = k_B \ln W$$

Third law of thermodynamics

Thermodynamic temperature scale is linear, but indefinite for its zero point. One mark (1K) is defined to correspond to 1^{o}C.

Molecules exhibit fundamental energy state with zero kinetic and potential energy, it corresponds to $T = 0$K temperature.

Entropy of this fundamental state is S=0.

Third law of thermodynamics

Entropy of the system at absolute zero temperature is also zero, i.e. if T=0, it is also S=0.

Absolute zero temperature is not attainable by finite number of steps.

W.Nernst, 1906 – Adiabatic process approaches isothermal process in the vicinity of absolute zero temperature.

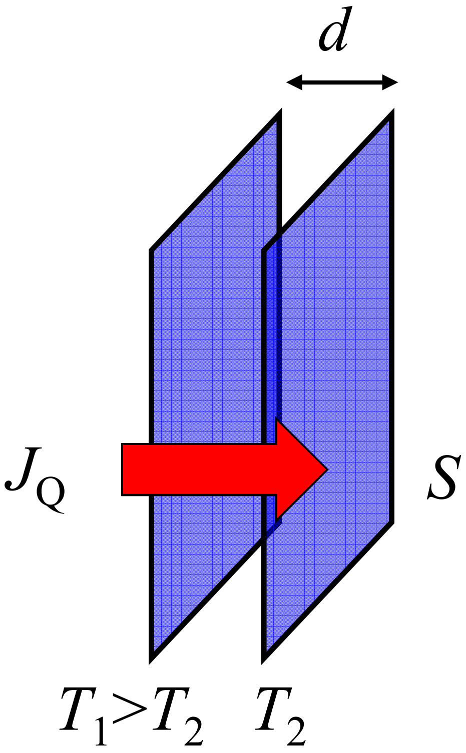
Heat transfer

- Conduction – heat exchange by contact
- Covection – heat transfer together with mass transfer – liquids and gasses
- Radiation – heat transfer by elmg. (mainly infrared) radiation

Heat conduction

Heat flux

$$J_Q = \frac{\Delta Q}{S\Delta\tau} \quad [Wm^{-2}]$$



Thermal conductivity

$\lambda[\mathrm{Wm^{-1}K^{-1}}]$

$$J_Q = \lambda\frac{T_1 - T_2}{d}$$

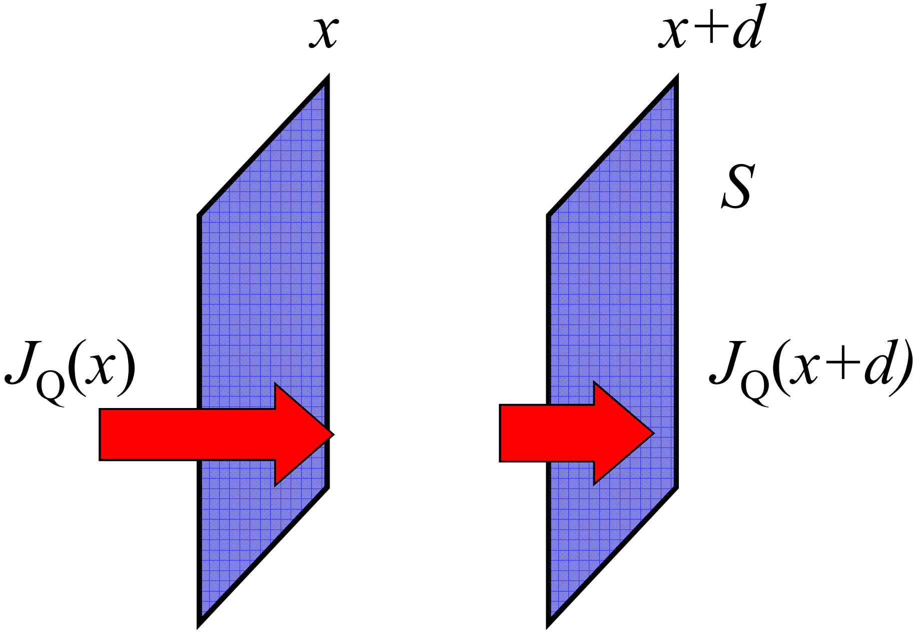
Thermal conductivity

Heat conductivity property, thermal isolators have small thermal conductivity

	$\lambda[Wm^{-1}K^{-1}]$		$\lambda[Wm^{-1}K^{-1}]$
Fe	80	Water	0.598
Al	240	Castor oil	0.181
Cu	400	Air 20°C	0.025

Heat conduction equation

Heat dissipated in the volume is given by the difference of flux



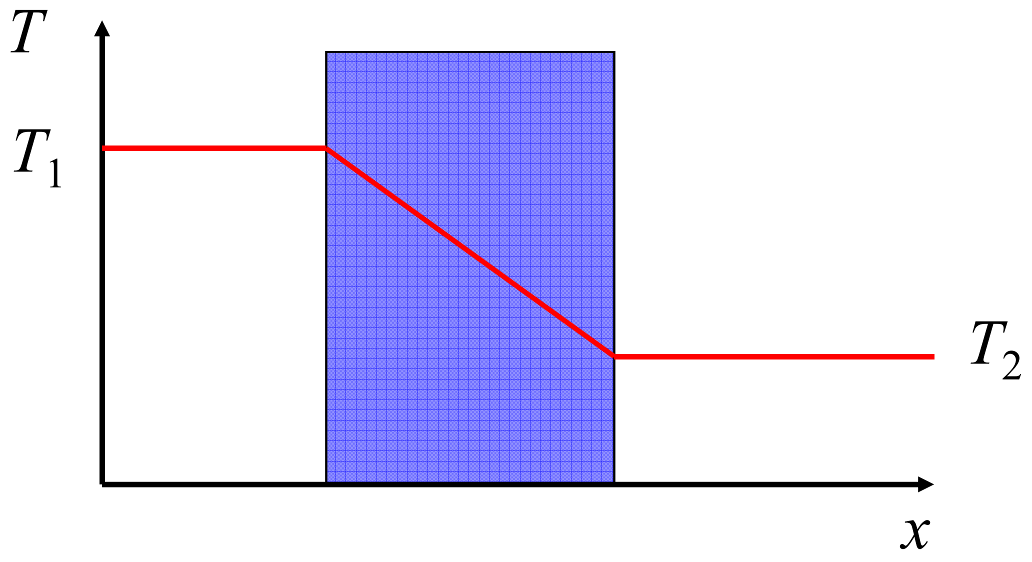
$$mc\frac{\Delta T}{\Delta \tau} = S[J_Q(x+d) - J_Q(x)]$$

$$\frac{\partial T}{\partial \tau} = \frac{\lambda}{c\rho}\frac{\partial^2 T}{\partial x^2}$$

temperature conductivity
$\chi=\lambda/c\rho[\mathrm{m^2 s^{-1}}]$

Stationary solution of heat conduction equation

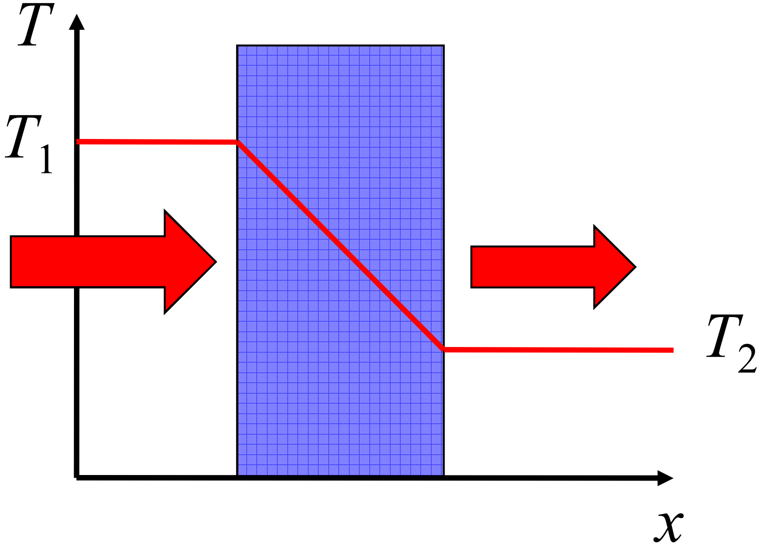
Stationary state $$\frac{\Delta T}{\Delta \tau} = 0$$



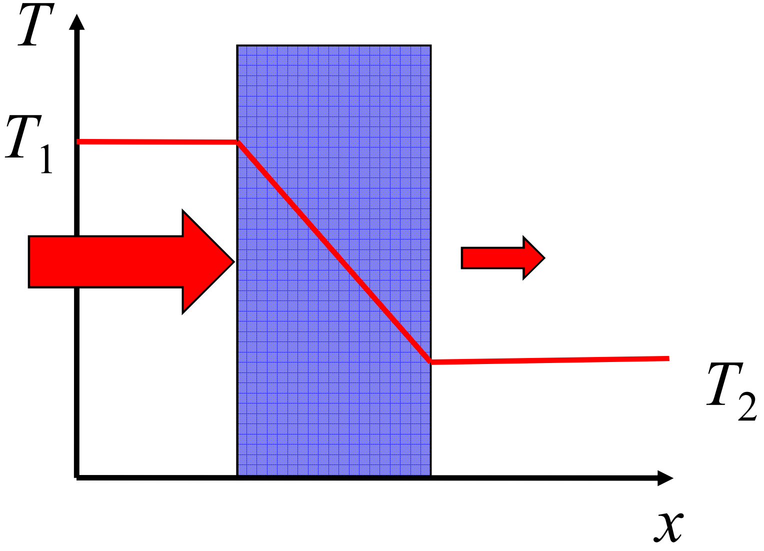
Linear profile of temperature

Thermal conductors, isolators

Conductor



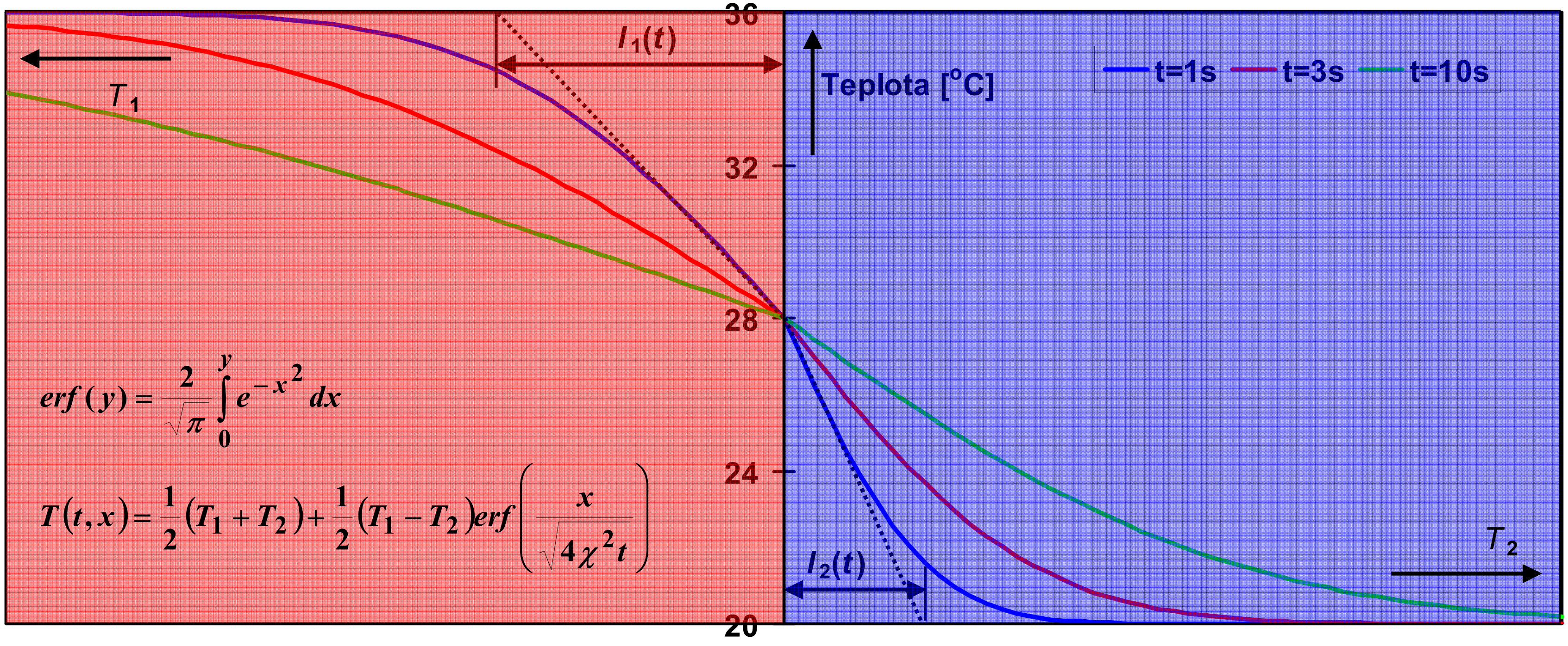
Isolator



Isolators transfer less heat at the same thickness and temperature difference, less heat losses

Nonstationary solution of heat conduction equation

Temperature profile at the interface



$$erf(y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-x^2} dx$$

$$T(t,x) = \frac{1}{2}(T_1 + T_2) + \frac{1}{2}(T_1 - T_2) erf\left(\frac{x}{\sqrt{4\chi^2 t}}\right)$$

Temperature penetration depth

Heat transfer during time τ by the difference ΔT penetrates layer of the width $l(\tau)$

$$\lambda S \tau \frac{\Delta T}{l} = l S \rho c \Delta T$$

"parabolic" law of temperature change penetration

$$\boxed{l(\tau) = \sqrt{\frac{\lambda}{\rho c}\tau}}$$

Contact temperature

Contact by the bare hand:

- Thermal insulators are „warm“
- Thermal conductors are „cold“

at the same temperature of environment below hands temperature

(and opposite above hands temperature)

Literature

Pictures used from the book:

HALLIDAY, D., RESNICK, R., WALKER, J.: Fyzika (část 2 - Termodynamika), Vutium, Brno 2000

and material data from tables:

BROŽ, J., ROSKOVEC, V., VALOUCH, M.: Fyzikální a matematické tabulky, SNTL Praha 1980