evropský
sociální
fond v ČR

EVROPSKÁ UNIE

MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY

OP Vzdělávání
pro konkurenceschopnost

INVESTICE
DO ROZVOJE
VZDĚLÁVÁNÍ

Inovace bakalářského studijního oboru Aplikovaná chemie

Reg. č.: CZ.1.07/2.2.00/15.0247

evropský sociální fond v ČR
EVROPSKÁ UNIE
MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY
OP Vzdělávání pro konkurenceschopnost
INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

Introduction to Physical Chemistry

Lecture 6

- Thermodynamic laws
  – zeroth
  – first
  – second

Lecture vocabulary:

summarize	shrnovat		
prove	dokázat		
experience	zkušenost		
contravene	odporovat		
concept	koncept, koncepce, představa		
propagation of sound	šíření zvuku		
transmission of shock waves	šíření rázových vln		
can be treated as…	může být považován za…		
heat transfer	přenos tepla		
indefinitely small change	nekonečně malá změna		
exact	přesný		
partial	částečný		
energy conservation law	zákon o zachování energie		
proof	důkaz		
consider	uvažovat		
keep in mind	mít na mysli		
assumed	považován		
independent	nezávislý		
expression	výraz, vyjádření		
tendency	tendence		
abundant internal energy	přebytečná vnitřní energie		
hypothetical	hypotetický		
violate	porušovat		
side effect	průvodní jev		
sole	výhradný		
driving force	hybná síla		
magnitude	velikost		
efficiency	účinnost		

evropský
sociální
fond v ČR
EVROPSKÁ UNIE
MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY
OP Vzdělávání
pro konkurenceschopnost
INVESTICE
DO ROZVOJE
VZDĚLÁVÁNÍ

Four laws of thermodynamics

4 laws of thermodynamics summarize the most important facts of thermodynamics.

They:

- **define fundamental physical quantities, such as temperature, energy, and entropy**
- **describe thermodynamic systems by virtue of these quantities**
- **describe the transfer of energy as heat and work in thermodynamic processes**

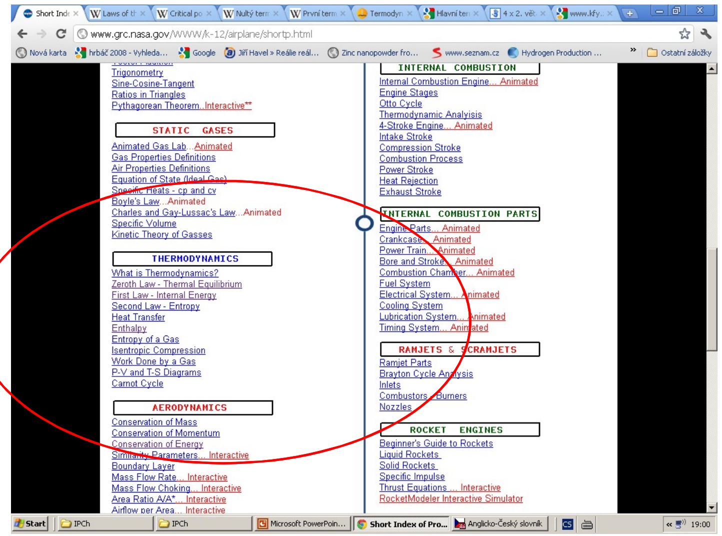
Thermodynamic laws have the character of axioms
(i.e. they cannot be proved, but we have no experience which contravenes them

Recommended reading

http://www.grc.nasa.gov/WWW/k-12/airplane/shortp.html

Hrbac recommends the web page as well

Why do I recommend this web page?
The termodynamic concepts are explained not only on basic problems, but are extended also to real-life phenomena and devices – i.e. you can learn e.g. that propagation of sound through atmosphere is an isoentropic process or that transmission of shock waves in rocket motor can be treated as an isoenthalpic process



evropský sociální fond v ČR

EVROPSKÁ UNIE

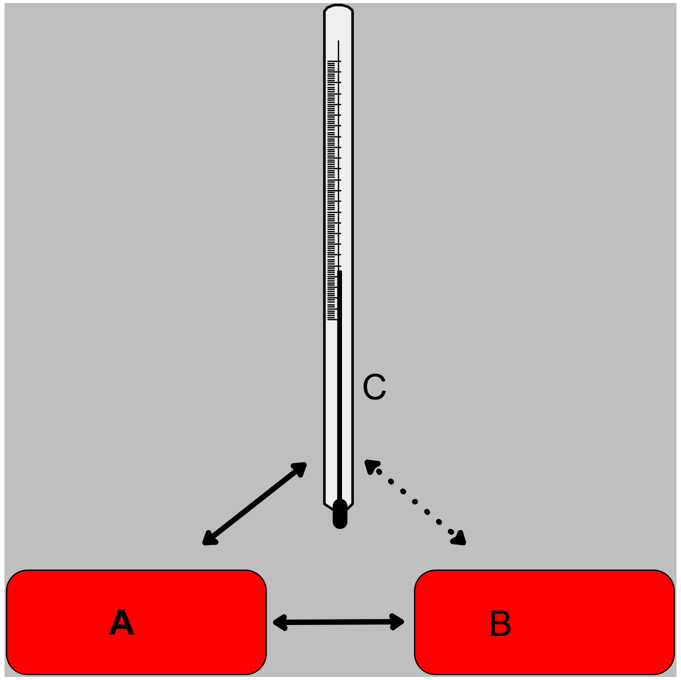
MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

OP Vzdělávání pro konkurenceschopnost

INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

Zeroth thermodynamic law

If the two thermodynamic objects are in equillibrium and stay in it after heat transfer is enabled, they have the same temperature



Objects in thermodynamic equilibrium have the same temperature.

If two or more objects are in thermodynamic equilibrium with other object, all these objects are in equilibrium

First thermodynamic law

The first law of thermodynamics defines the internal energy (U) as equal to the difference of the heat transfer (Q) into a system and the work (W) done by the system.

$$U_2 - U_1 = Q + (-W)$$

Infinitezimal (indefinitely small change in internal energy)

$$dU = \delta Q + (-\delta W)$$

Differential of quantites which are not state quantities

Exact (total) differential

Partial (non-exact) differential

First thermodynamic law is in fact the energy conservation law for the case when energy can be exchanged only in the form of heat or pressure-volume work

Internal energy of an ideal gas

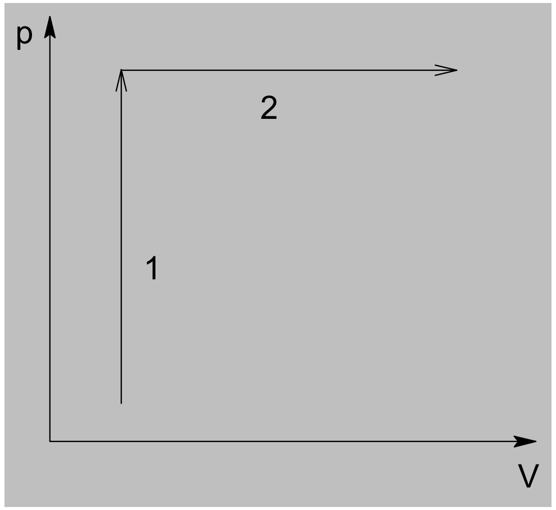
Alois Alzheimer (1864 - 1915)

For those who can't remember that the internal energy of an ideal gas is dependent *only on temperature, but not on the volume* of the gas:

Consult

The proof is on the next slide:

Internal energy of an ideal gas



Consider two processes (and keep in mind that every process can be approximated by series of such processes)

For process 1: $$dU_1 = C_V dT_{(1)}$$

This can be integrated because T is the only thing that is changing on the righthandside (C_V is assumed to be independent of T and V).

For process 2:

$$dU_2 = CpdT_{(2)} - pdV$$

C_p is constant (i.e. not a function of T or V) so it can be integrated directly. Using the ideal gas law: pV = nRT we easily see that pdV+Vdp=nRdT. For constant pressure Vdp is zero and therefore pdV=nRdT. Therefore:

$$dU_2 = CpdT_{(2)} - nRdT_{(2)}$$

As we know Mayer's eq. (C_p=C_V+R) we see that dU_2=CvdT_2. Thus

$$dU_{1+2} = C_V dT_{(1)} + C_V dT_{(2)} = C_V dT_{1+2}$$

Second thermodynamic law

The second law of thermodynamics is an expression of the tendency that over time, differences in temperature, pressure, and chemical potential equilibrate in an isolated physical system.

The law deduces:

- **the principle of the increase of entropy**
- **explains the phenomenon of irreversibility in nature**
- **declares the impossibility of machines that generate usable energy from the abundant internal energy of nature by the processes called perpetual motion of the second kind**

evropský
sociální
fond v ČR

EVROPSKÁ UNIE

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

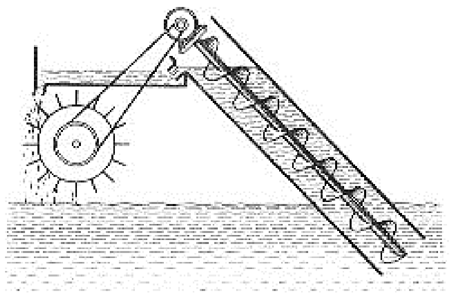
OP Vzdělávání
pro konkurenceschopnost

INVESTICE
DO ROZVOJE
VZDĚLÁVÁNÍ

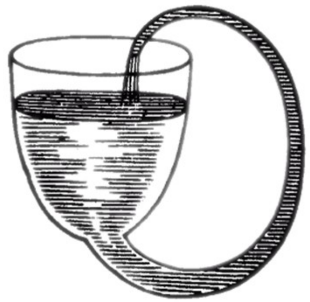
Perpetuum mobile

Perpetual motion describes hypothetical machines that operate or produce useful work indefinitely and, more generally, hypothetical machines that produce more work or energy than they consume, whether they might operate indefinitely or not.

The "Overbalanced Wheel" 1200's



"water screw" perpetual motion machine



Boyle's self flowing flask

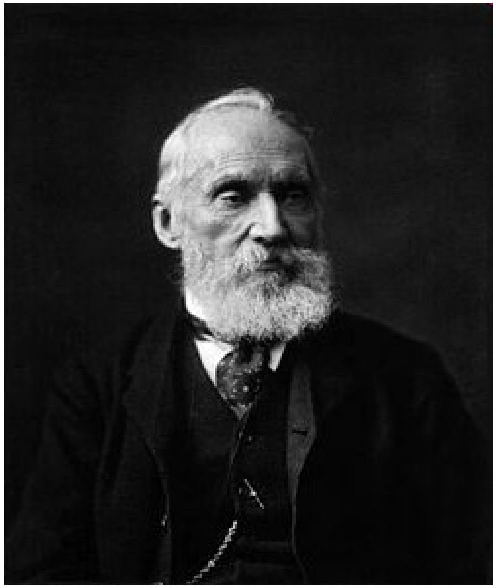
•A perpetual motion machine of the first kind produces work without the input of energy. It thus violates the first law of thermodynamics: the law of conservation of energy.

•A perpetual motion machine of the second kind is a machine which spontaneously converts thermal energy into mechanical work. When the thermal energy is equivalent to the work done, this does not violate the law of conservation of energy. However it does violate the more subtle second law of thermodynamics (see also entropy). The signature of a perpetual motion machine of the second kind is that there is only one heat reservoir involved, which is being spontaneously cooled without involving a transfer of heat to a cooler reservoir. This conversion of heat into useful work, without any side effect, is impossible, according to the second law of thermodynamics.

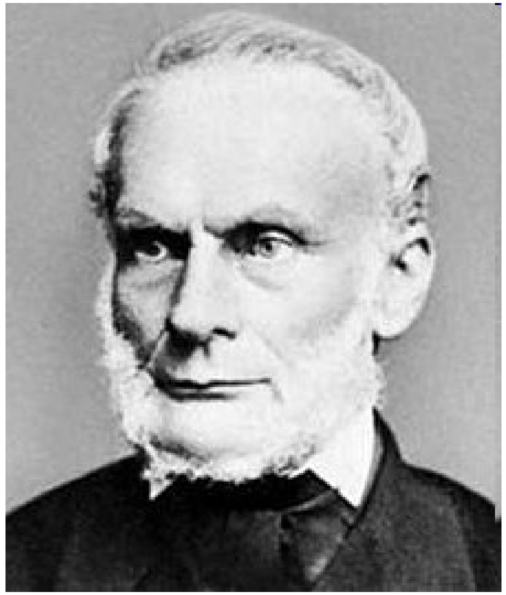
Second thermodynamic law

Clausius statement

No process is possible whose sole result is the transfer of heat from a body of lower temperature to a body of higher temperature



William Thomson, 1st Baron Kelvin OM, GCVO, PC, PRS, PRSE, (1824 –1907)

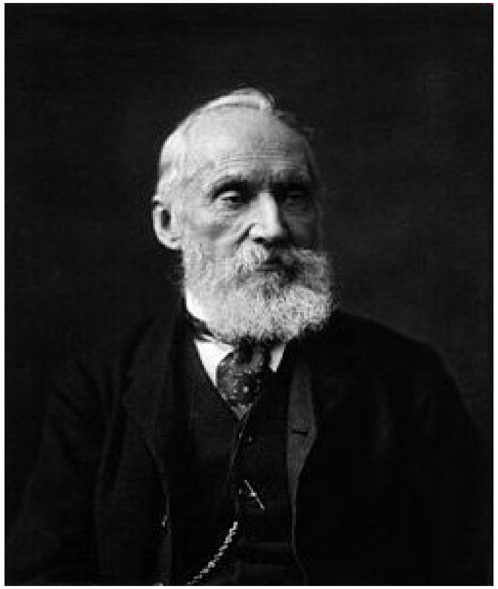


Rudolf Clausius (1822-1888)

Kelvin statement

No cyclic process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work

Lord Kelvin



**OM,
GCVO,
PC,
PRS,
PRSE**

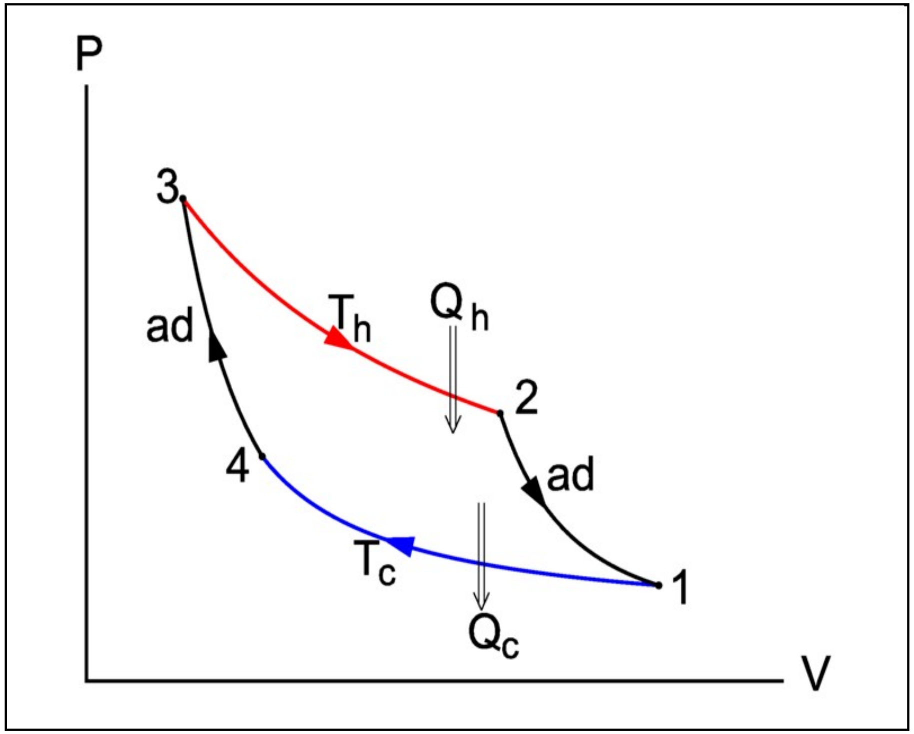
**Privy Council of the United Kingdom
President of the Royal Society (PRS)
President of the Royal Society of Edinburgh**

Order of Merit

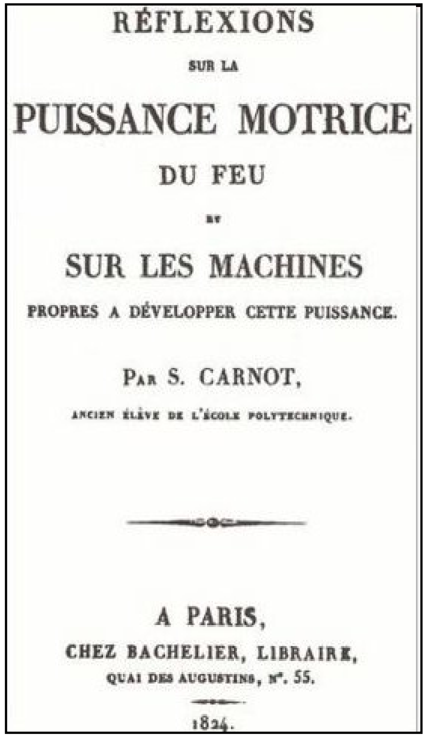
Grades of the Royal Victorian Order:

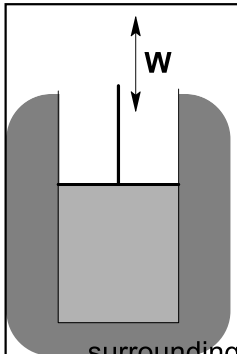
Grade (English)	Knight/Dame Grand Cross	Knight/Dame Commander	Commander	Lieutenant	Member	Medal
Grade (French)[n 1]			*Commandeur*	*Lieutenant*	*Membre*	*Medaille*
Prefix	Sir/Dame	Sir/Dame				
Post-nominal letters	GCVO	KCVO/DCVO	CVO	LVO	MVO	RVM
Insignia						

Carnot cycle



Essay about the driving force of fire


RÉFLEXIONS
SUR LA
PUISSANCE MOTRICE
DU FEU
ET
SUR LES MACHINES
PROPRES A DÉVELOPPER CETTE PUISSANCE.
PAR S. CARNOT,
ANCIEN ÉLÈVE DE L'ÉCOLE POLYTECHNIQUE.
A PARIS,
CHEZ BACHELIER, LIBRAIRE,
QUAI DES AUGUSTINS, N°. 55.
1824.



surroundings: (thermostatting bath or thermal insulation, depending on the phase of the cycle)

1. Isothermal. rev. expansion ... in bath T_h accepts Q_2 releases $-W_1$

$$-W_1 = RT_h \ln(V_2/V_1) = Q_2 \quad \text{(for 1 mole of ideal gas)}$$

2. Adiabatic rev expansion ... Q = const , releases $-W_2$

$$-W_2 = -C_v\,(T_h - T_c) = \Delta U$$

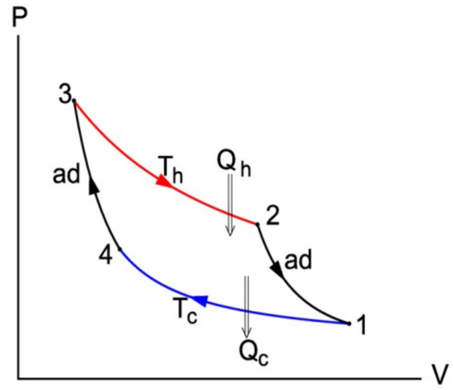
3. Isothermal. rev. compression ...in bath Tc releases Q_1 , accepts W_3

$$W_3 = -RT_c \ln(V_4/V_3) = -Q_1$$

4. Adiabat. Rev. compression ... Q = const, accepts W_4

$$W_4 = C_v(T_c - T_h) = -C_v(T_c - T_h) - W_4 = -C_v(T_c - T_h) = \Delta U$$

Carnot cycle



1. Izoth. rev. expansion … in bath T_h accepts Q_2 releases $-W_1$

   $- W_1 = RT_h \ln(V_2/V_1) = Q_2$

2. Adiabatic rev. expansion … Q = const , releases $-W_2$

   $- W_2 = - C_v (T_h – T_c)$

3. Izoth. rev. compression …in bath Tc releases Q_1 , accepts W_3

   $W_3 = - RT_c \ln(V_4/V_3) = - Q_1$

4. Adiabat. rev. compression … Q = const, accepts W_4

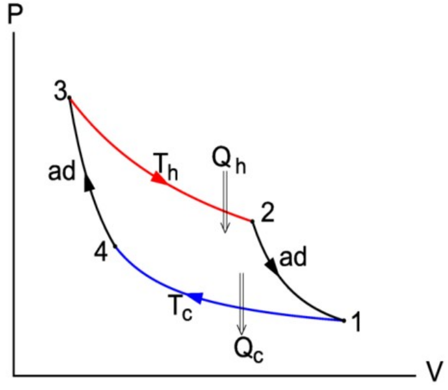
   $W_4 = C_v(T_c – T_h) = - C_v(T_c – T_h)$ $- W_4 = - C_v(T_c – T_h)$

Because during isothermal process the internal energy is not changed and the gas returns to its original state (i.e. to the state with original internal energy), the works $-W_2$ and W_4 are equal (u can see directly from the expressions that these works have the same magnitude).

Therefore, the work made by the Carnot engine depends only on the difference between $-W_1$ and W_3. That is:

$$-W = - W_1 - W_3 = RT_h \ln(V_2/V_1) + RT_c \ln(V_4/V_3).$$

Carnot cycle – efficiency and entropy



From the description of adiabatic phases

$T_c V_2^{\kappa-1} = T_h V_3^{\kappa-1}$; $T_h V_4^{\kappa-1} = T_c V_1^{\kappa-1}$

follows: that $V_2/V_1 = V_3/V_4 = -(V_4/V_3)$

Therefore $W = -W_1 - W_3 = R(T_h - T_c)\ln(V_2/V_1)$

The engine efficiency η **:**

$$\eta = -W/Q_h$$

$$\eta = (Q_h + Q_c)/Q_h = (T_h - T_c)/T_h$$

$$1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H} \quad \Rightarrow \quad \frac{Q_H}{T_H} = \frac{Q_C}{T_C} \quad or \quad \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0$$

This can be generalized as an integral around a reversible cycle:

$$\oint \frac{dQ}{T} = 0$$ **(Clausius theorem)** $$\frac{dQ}{T} = dS$$

A new thermodynamic state quantity called Entropy is introduced this way

esf evropský sociální fond v ČR

EVROPSKÁ UNIE

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

OP Vzdělávání pro konkurenceschopnost

INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ