

Thermodynamics

Premises: conservation of mechanical energy (work-energy theorem)

$$mgh = \frac{1}{2}mv^2$$

$$W = \frac{1}{2}mv_2^2 - \frac{1}{2}mv_1^2 = \Delta E_{\text{kin.}}$$

Where does the energy disappear in the case of inelastic collision (or acting friction force)?

„Warms up the body” (increases the temperature)

„Becomes heat”

$$W = \Delta E_{\text{internal}}$$

One of the fundamental physical quantities is the **internal energy** (E_{internal})

Its origin: **thermal motion** of atomic **particles**, and the **interactions** among them.

Thermal interaction

New macroscopic interaction (besides the mechanical one), **heat is added** to the body

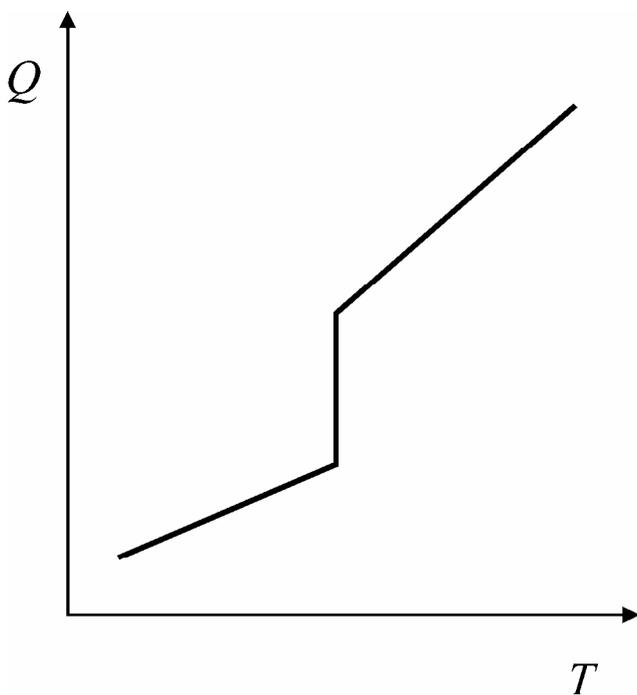
$$Q = \Delta E_{\text{internal}}$$

Two new quantities: **heat** (Q) and **temperature** (T)

What could happen because of the added heat?

The body **heats up**, means increases its temperature,
dilates, means increases its volume (see exceptions)

How can we characterize these processes?



Heat capacity (of a body):

$$C = \frac{\Delta Q}{\Delta T}$$

Specific heat capacity
(of a medium):

$$c = \frac{\Delta Q}{m\Delta T}$$

Molar heat capacity
(of a medium):

$$C_v = \frac{\Delta Q}{\nu\Delta T}$$

Latent heat of fusion or vaporization

$$Q = L m$$

Thermal expansion (free), small changes
expansion coefficients

Solids (linear):
$$\alpha = \frac{\Delta l}{l\Delta T}$$

Liquids (volumetric):
$$\beta = \frac{\Delta V}{V\Delta T}$$

Gases: they are compressible ($\kappa \approx 10^4 \text{ GPa}^{-1}$)

$$pV = NkT, \quad \text{or} \quad pV = \nu RT$$

$$kN_A = R$$

$$N/N_A = \nu$$

Ideal gas (model)

- **large number** ($N \approx N_A$, Avogadro number $\sim 10^{23}$) of **spherical** particles with **identical mass** moving randomly,
- may **collide elastically** with each other and the walls of the container,
- all other **interactions** (e.g. attraction, repulsion) and
- the **total volume of particles** are negligible

Gas mixtures

partial pressure

Interpretation of **temperature** and **pressure** (based on the model)

$$\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} kT$$

equipartition of energy

At each collision with the wall of the container the **change of momentum** is $\Delta m v = 2m v_x$,

these changes (according to the Newton's II. law) result short (Δt) impulses:

$$\Delta m v = F \Delta t$$

Taking into consideration the huge number of collisions (N is close to N_A), an **average force** will act to the wall. The quotient of this force and the area of the wall, gives the pressure.

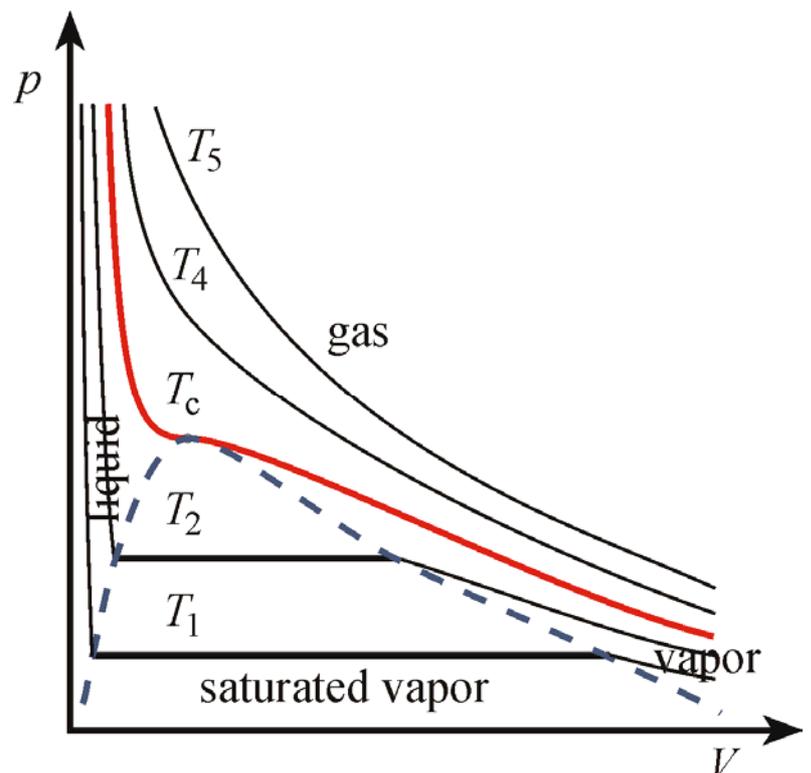
$$p = \frac{F}{A}$$

Real gas

vapor, saturated vapor,
saturated vapor pressure

In the new model we have to take into consideration

- the **interactions**, and
- the **volume of particles**



Thermodynamic system (and environment):

„many” ($\sim 10^{23}$) particles interacted with each other (macroscopic)

Major types:

Type	Matter-	Energy-
	exchange	
Isolated	—	—
Closed	—	+
Open	+	+

Characteristic quantities:

extensive: (e.g. V, q, N, E)

- proportional to the system size
- additivity: e.g. $V_1 + V_2 = V_{\text{total}}$
- (can flow)

intensive: (e.g. p, φ, μ, T)

- independent of the size of the system
- equalize
- (drive the flow)

Laws of thermodynamics

0. If the spatial distribution of intensive quantities is homogeneous, than the system is in **equilibrium**.

I. $\Delta E = Q + W$ thermal and mechanical interactions

$$W = -p\Delta V \quad (\text{see exceptions})$$

Further possible interaction

$$W_N = \mu_N \Delta N \quad \text{or} \quad W_v = \mu_v \Delta v$$

Physical meaning of μ , **chemical potential** (change of energy):

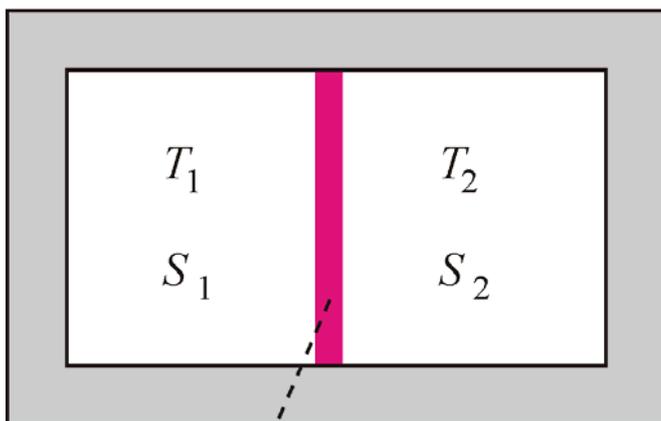
Appearance of any new particles increases the kinetic energy of the system, furthermore because of its interaction with the other particles the potential energy also changes.

II. A qualitative statement for the **direction of spontaneous processes**; in thermal interactions T equalizes, these processes are **irreversible**.

For quantitative phrasing we need to introduce the **entropy** (S); formally, if $\Delta E = Q$ than $Q = T\Delta S$

How does the entropy (S) change during thermalization?

isolated system, $\Delta E = 0$



heat-conducting wall

$$\Delta E_1 = -\Delta E_2$$

$$\begin{aligned} \Delta S &= \frac{\Delta E_1}{T_1} + \frac{\Delta E_2}{T_2} = \\ &= \Delta E_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \rightarrow \Delta S \geq 0 \end{aligned}$$

S non-conserved quantity!

Statistical interpretation of entropy

We could see that the above introduced entropy **increases**.

Is there any **other quantity** having the same feature?

Microstate: microscopic parameters of all the particles of the system (e.g. position, velocity) are known.

(all the microstates are equally probable)

Macrostate: distribution of macroscopic parameters (e.g. temperature, pressure, density, **energy**) is known.

The number of microstates that belong to the same macrostate is called **thermodynamic probability**: Ω

An example:

The thermodynamic system is the air in the lecture hall

$$\Omega_{AB} = \Omega_A \Omega_B$$

Ω increases during the equalization process, but it isn't additive

$$\ln \Omega_{AB} = \ln \Omega_A + \ln \Omega_B$$

$$S = k \ln \Omega \quad \left(\Omega = e^{\frac{S}{k}} \right)$$

III. The entropy of a singlecomponent, crystallizing material is 0 at 0 K temperature.

$$S = k \ln \Omega = k \ln 1 = 0$$

An important example: free expansion of a gas
no work, no heat, but the entropy increases

Thermodynamic potential functions

Hess's theorem:

transition heat of an overall reaction only depends on the initial and the final states.

Lemma: small change of a product (e.g. xy)

$$\Delta xy \approx x\Delta y + y\Delta x$$

Most chemical reactions pass off at constant pressure ($\Delta p = 0$)

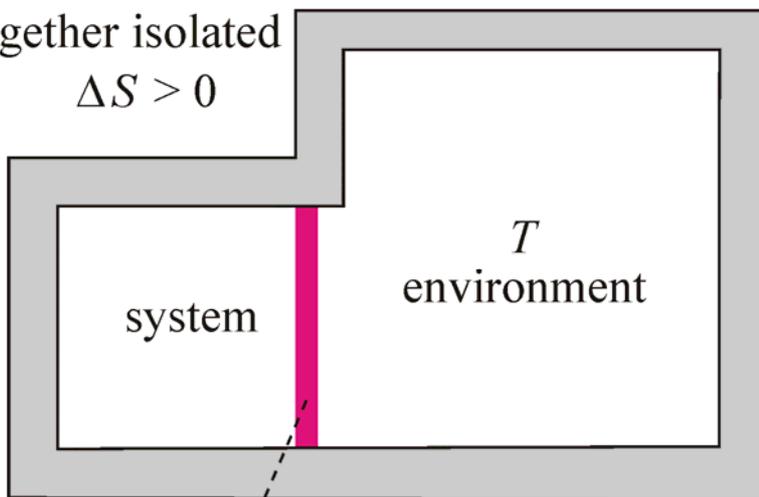
$$\Delta E = Q + W \quad \rightarrow \quad \Delta E = Q - p\Delta V, \quad \text{but } p\Delta V = \Delta pV$$

thus $\Delta(E + pV) \equiv \Delta H = Q$ **enthalpy change**

Direction of processes in non-isolated systems

system and environment
together isolated

$$\Delta S > 0$$



system

T
environment

heat-conducting wall

$$\Delta S = \Delta S_r + \Delta S_k > 0$$

$$\Delta S_k = \frac{-Q}{T}$$

$$\Delta S_r - \frac{Q}{T} > 0$$

$$*T\Delta S_r > Q = \Delta E_r$$

$$0 > \Delta E - T\Delta S, \text{ but } \Delta T = 0$$

$$\Delta(E - TS) \equiv \Delta F < 0$$

Helmholtz free energy change

If p is also constant (moving wall), than $*T\Delta S_r > Q = \Delta E_r + p\Delta V$

$$0 > \Delta E - T\Delta S + p\Delta V, \quad \text{but } \Delta T = 0 \text{ and } \Delta p = 0$$

$$\Delta(E - TS + pV) = \Delta(H - TS) \equiv \Delta G < 0$$

Gibbs free energy change

Boltzmann-distribution

Premises: equipartition **in thermal equilibrium** ($T = \text{constant}$)

Two important parameters:

ε_i the possible energy of particles, n_i occupation number

Further conditions:

$$E = \sum_i n_i \varepsilon_i \qquad N = \sum_i n_i$$

The ratio of thermodynamic **probabilities** ($\Omega_2 < \Omega_1$) of two macrostates ($\varepsilon_2 > \varepsilon_1$, $\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$):

$$\frac{p_2}{p_1} = \frac{\Omega_2}{\Omega_1} = \frac{e^{\frac{S_2}{k}}}{e^{\frac{S_1}{k}}} = e^{\frac{S_2 - S_1}{k}}$$

Decrease of entropy (the higher the energy of a state, the less probable its occupation is):

$$\Delta S = -\frac{\Delta\varepsilon}{T}$$

$$\frac{n_2}{n_1} = e^{-\frac{\Delta\varepsilon}{kT}} = e^{-\frac{\Delta E}{RT}} \qquad (kN_A = R)$$

E.g. barometric formula, rates of chemical reactions

$$T_1 < T_2 < T_3$$

