

# 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** ( $E_{\text{internal}}$ )

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

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

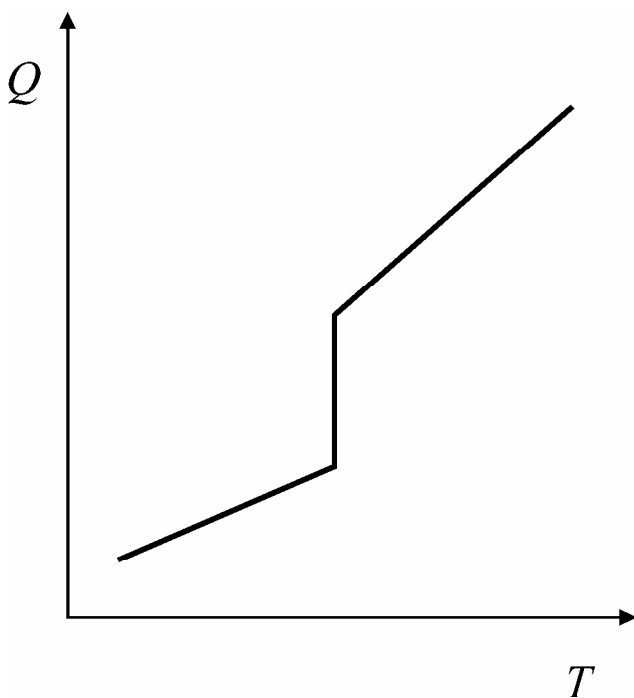
Two new quantities: **heat** ( $Q$ ) and **temperature** ( $T$ )

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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**

$$Q = L m$$

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**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 ( $\kappa \approx 10^4 \text{ GPa}^{-1}$ )

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

$$kN_A = R$$

$$N/N_A = \nu$$

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**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 ( $\Delta t$ ) 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.

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

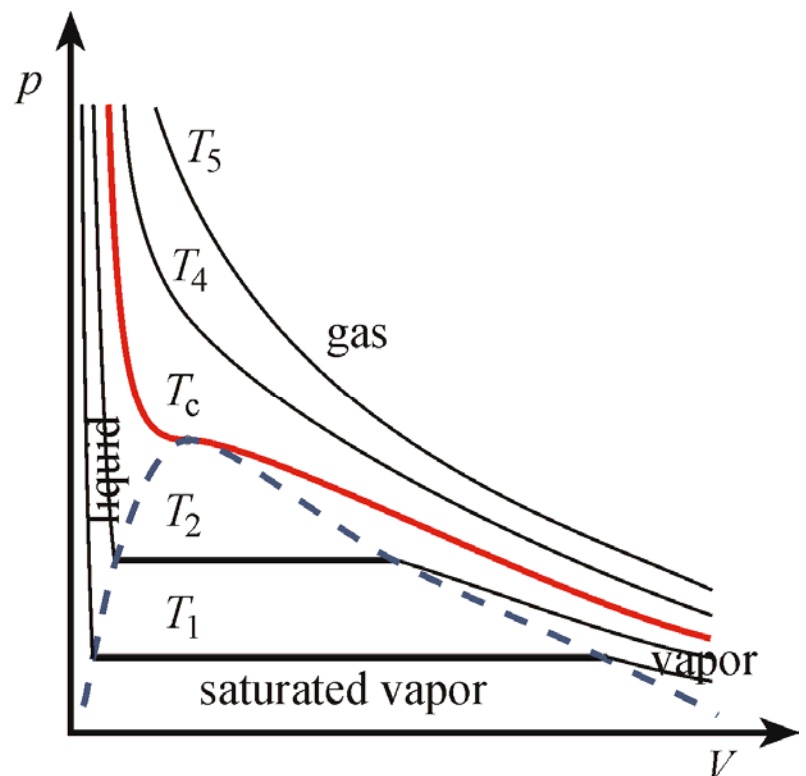
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## Real gas

vapor, saturated vapor,  
**saturated vapor pressure**

In the new model we have to take into consideration

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



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## 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.  $p$ ,  $\varphi$ ,  $\mu$ ,  $T$ )

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

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## 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  $\mu$ , **chemical potential** (change of energy):

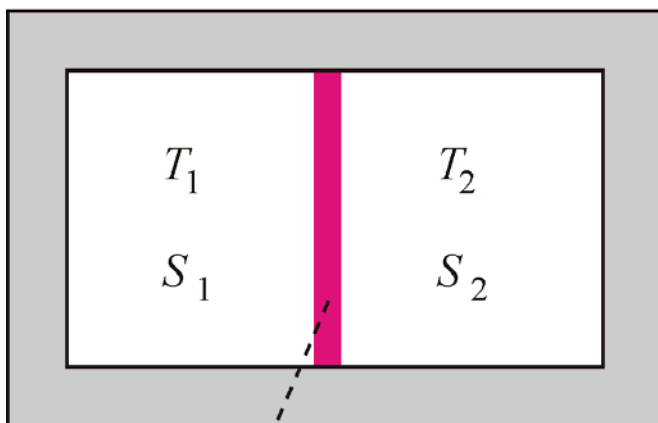
Appearance of any new particles increases the kinetic energy of the system, furthermore because of its interaction with the other particles the potential energy also changes.

**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,  $\Delta E = 0$



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

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

$S$  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**:  $\Omega$

An example:

The thermodynamic system is the air in the lecture hall

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

$\Omega$  increases during the equalization process, but it isn't additive

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

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

**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

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## 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 ( $\Delta p = 0$ )

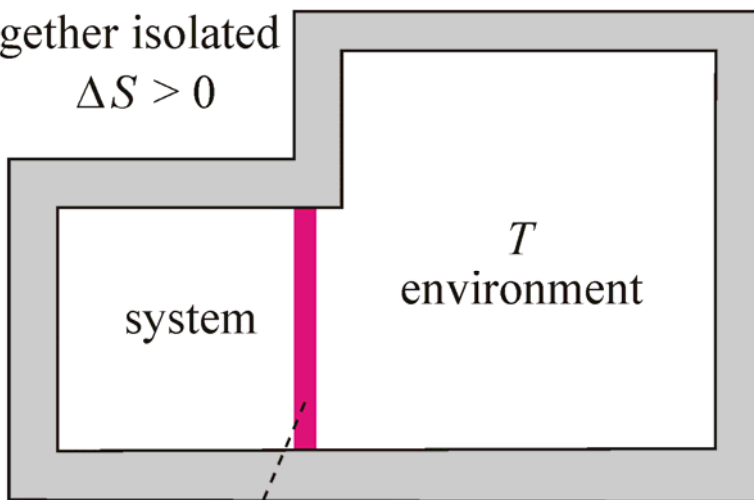
$$\Delta E = Q + W \quad \rightarrow \quad \Delta E = Q - p\Delta V, \quad \text{but } p\Delta V = \Delta p V$$

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

### Direction of processes in non-isolated systems

system and environment  
together isolated

$$\Delta S > 0$$



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

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## Boltzmann-distribution

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

Two important parameters:

$\varepsilon_i$  the possible energy of particles,  $n_i$  occupation number

Further conditions:

$$E = \sum_i n_i \varepsilon_i$$

$$N = \sum_i n_i$$

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):

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

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

E.g. barometric formula, rates of chemical reactions

