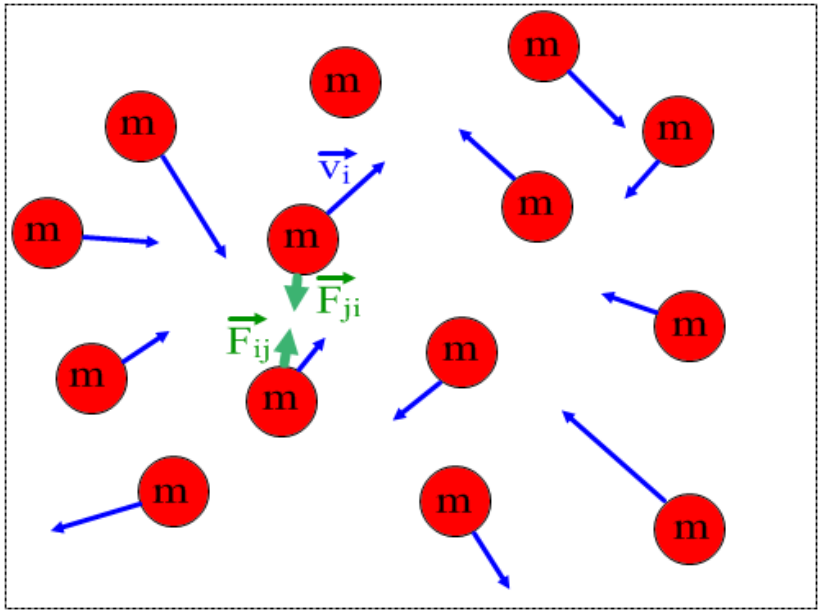
Thermodynamics

Internal energy

The **internal energy** of the system is the **kinetic energy** resulting from the disordered motion of the particles relative to each other (the center of mass of the system) and the **potential energy** associated with the Van der Waals interaction between the particles.

For N particles: $E_{int} = \sum_{i=1}^{N} E_{ki} + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} E_{Pij}$



Brownian motion: The dissolution of potassium permanganate ($KMnO_4$) in water shows that water particles collide with paint blobs at high speed. Particles therefore have velocity and thus kinetic energy. Since their number is very large, this energy is significant.

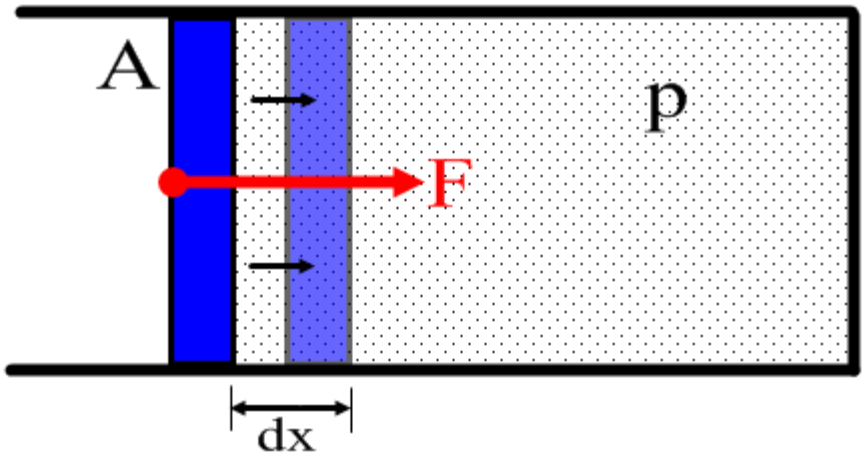
In some cases, the interactions between particles (except for elastic collisions) are negligible (ideal gases), in which case the second term is zero.

At higher temperatures, the movement is more intense, so the internal energy is greater.

The mechanical energy of ordered motion can be converted into internal energy (by e.g. friction, drag), increasing the temperature of the body.

Volumetric work

The **volumetric work** is the work done by the environment on the gas (system) while its volume changes.
The elementary work done on a freely moving piston by the environment while pushing it inward by a distance *dx*: δW

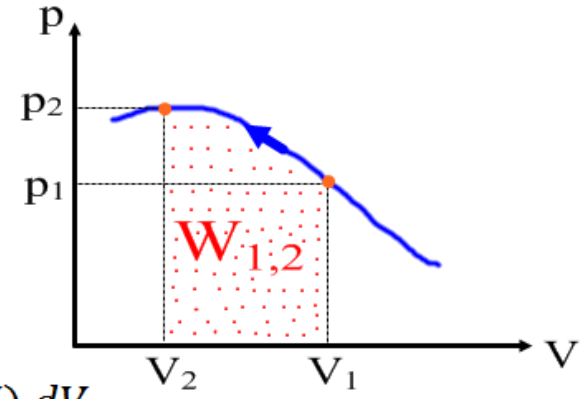


The required force for a gas with pressure *p* is: $F = pA$.

So for the elementary work: $\delta W = pAdx$
Since $Adx = -dV$

$$\delta W = -pdV$$

Meanwhile, the work done by the gas is negative because the gas pushes the piston outward (the force is opposite to the direction of displacement): $\delta W_g = -\delta W$
However, in case of expansion: $\delta W < 0$ and $\delta W_g > 0$
For a finite volume change, the pressure usually changes, so we need to integrate:
Work is represented by the area under *p*-*V* curve.



$$W_{1,2} = -\int_{V_1}^{V_2} p(V)\,dV$$

if pressure is constant:
$$W_{1,2} = -p(V_2 - V_1)$$

Heat transfer

The internal energy of a system can also increase if another system with higher temperature gives it energy. This energy transferred without macroscopic movement (work) is the **heat**.
Symbol: Q (energy the system receives from environment). Unit of measurement: J (Joule)
The energy released by the system (body, liquid, gas) to the environment is: $Q_{rel} = -Q$

Types of heat transfer:
- **heat conduction** (in the material or through contact between bodies - e.g. a hotplate)
- **convection** (the medium flows and thus carries the energy with it - e.g. central heating)
- **thermal radiation** (without any medium, in the form of electromagnetic waves – e.g. Sun)

Heat capacity: The heat required to raise the temperature of the system by 1 degree:

$$Q = C \cdot \Delta T$$ Unit of measurement: $[C]$ = J/K or J/°C

Heat capacity characterizes the system as a whole and depends on the material quality and quantity.

Specific heat: the heat capacity of a unit mass part of the system:

$C = c \cdot m$ or $Q = c \cdot m \cdot \Delta T$ Unit of measurement: $[c]$ = J/(kg·K) or J/(kg·°C)

Molar heat: the heat capacity of a one mole part of the system:

$C = c_M \cdot n$ where n is the number of moles or $Q = c_M \cdot n \cdot \Delta T$

Unit of measurement: $[c_M]$ = J/(mol·K) or J/(mol·°C)

Specific heat and molar heat are quantities that depend only on the material quality!

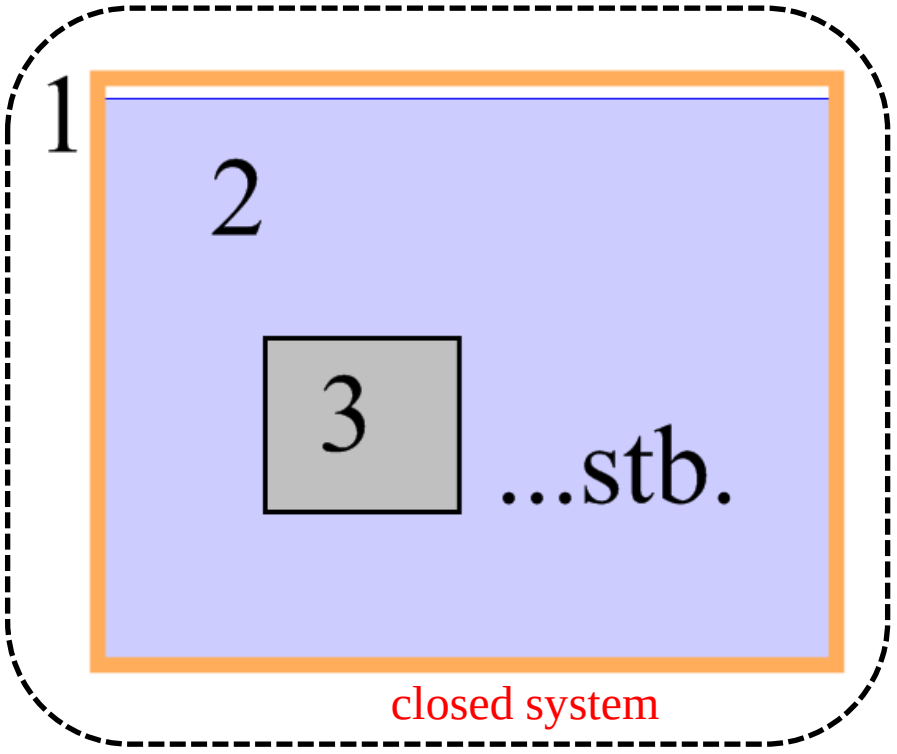
Internal energy characterizes a state of the system, while work and heat characterize a process.

Calorimetry

Calorimetry: A method for measuring the amount of heat and specific heat.
Calorimeter: An insulated container with a known heat capacity, containing a liquid with a known heat capacity.

<u>Basis of the procedure:</u> Over time, the temperature in the system equalizes, and **thermal equilibrium** is established.

The internal energy of a closed system is constant.



If Q_i is the amount of heat received by the *i*th body:

$$\sum_{i=1}^{N} Q_i = 0$$

Q can be:
$cm\Delta T$ (warming or cooling)
$-mL_c$ (heat released during combustion)
mL_f (heat absorbed during melting)
$-mL_f$ (heat released during freezing)
mL_v (heat absorbed during boiling)
$-mL_v$ (heat released during condensation)

During phase transition, the temperature doesn't change until the entire substance has changed (melting and boiling points).

<u>In the case of three bodies:</u> $Q_1 + Q_2 + Q_3 = 0$

if there is no phase transition:

$$c_1 m_1 (T_c - T_1) + c_2 m_2 (T_c - T_2) + c_3 m_3 (T_c - T_3) = 0$$

If one of the quantities (e.g. c_3) is unknown, then it can be determined from the equation.

The first law of thermodynamics

The **first law of thermodynamics** states that the change in internal energy of a system is equal to the sum of the **heat** added to the system and the **work** done on the system:

$$\Delta E_{int} = Q + W$$

Work is the volumetric work done by the environment.
Heat is the heat received from the environment (it can also be mechanical energy dissipated by friction).

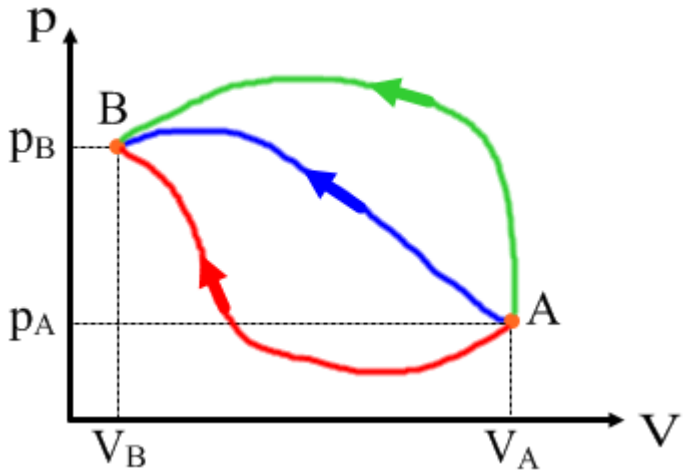
Since internal energy is a quantity characteristic of the state of the system, its change between states *A* and *B* does not depend on the process during which the change occurred:

$$\Delta E_{int} = E_{int}(B) - E_{int}(A)$$

For any cycle (starting from *A* and ending in *A*), of course:

$$\Delta E_{int} = E_{int}(A) - E_{int}(A) = 0$$

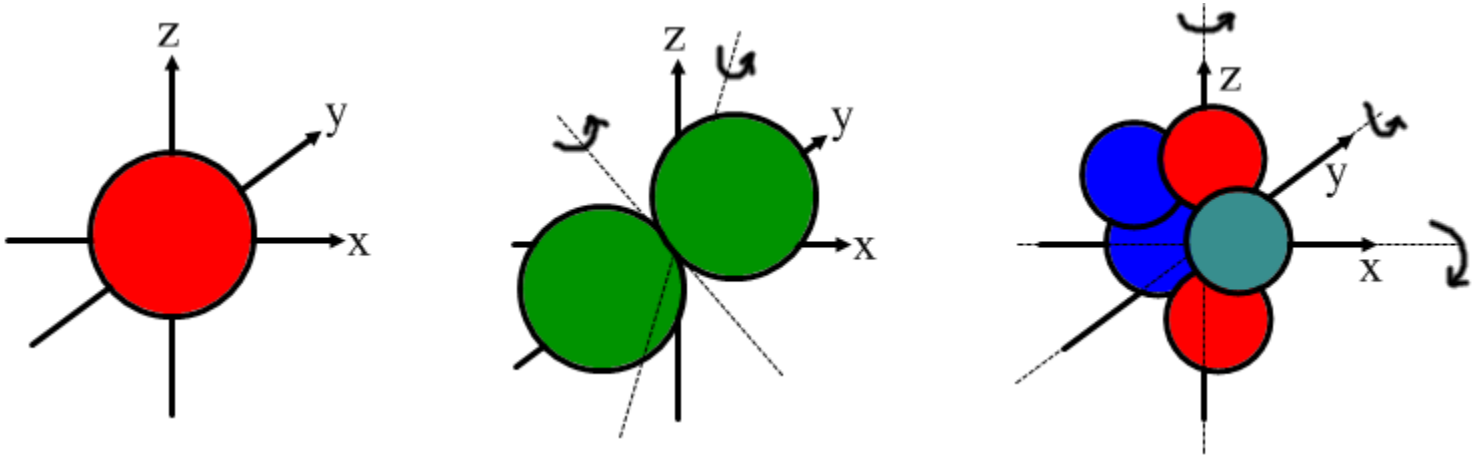
The differential form of the theorem is: $dE_{int} = \delta Q + \delta W$



Changes in the state of ideal gases

Equipartition theorem

Degrees of freedom (DoF): (f) – Number of independent ways to store energy.
e.g. moving along x, y, z directions (for a monatomic gas)
Thus: $\boldsymbol{f}$ **= 3** (for a single atom). Translational degrees of freedom (x, y, z).
Diatomic or other linear (e.g. CO_2) molecules can also rotate around two axes perpendicular to their long axes: $\boldsymbol{f}$ **= 5**. In addition to translational, they also have 2 rotational DoFs.
Polyatomic molecules can also rotate around three perpendicular axes: $\boldsymbol{f}$ **= 6**
Energy can only be stored for rotation around axes with non-negligible moment of inertia.



Equipartition theorem: For a system in equilibrium, at a certain temperature, all available degrees of freedom has the same ε_f energy if averaged over time.

For one DoF of one particle: $\varepsilon_f = \frac{1}{2}kT$

$k = 1{,}38 \cdot 10^{-23}$ J/K (Boltzmann constant)

Internal energy of an ideal gas

If for one DoF the energy on average is $\varepsilon_f = \frac{1}{2}kT$, then one particle on average has

$$\bar{\varepsilon} = f \cdot \varepsilon_f = f \cdot \frac{1}{2}kT = \frac{f}{2}kT \text{ energy.}$$

If the system consists of N particles, then the internal energy is just N times that:

$$E_{int} = \frac{f}{2}NkT = \frac{f}{2}nRT$$

where $n = N / N_A$ and $R = kN_A$

n: number of moles N_A: Avogadro number $R = 8{,}31$ J/(mol·K) is the ideal gas constant.

Thus the internal energy only depends on temperature (for given type and amount of gas).

The change in internal energy: $\Delta E_{int} = \frac{f}{2}Nk\Delta T = \frac{f}{2}nR\Delta T$

If we look at monatomic gases, then we can calculate the **root mean square velocity** of the atoms (v_{rms}):

$$E_{int} = N\bar{\varepsilon} = N\frac{3}{2}kT \quad \text{but then} \quad \bar{\varepsilon} = \frac{1}{2}m_0\overline{v^2} = \frac{3}{2}kT \rightarrow \sqrt{\overline{v^2}} = v_{rms} = \sqrt{\frac{3kT}{m_0}} = \sqrt{\frac{3RT}{M}}$$

(m_0: mass of one atom, M: molar mass)

Equation of state for ideal gases

The internal energy for monatomic ideal gases can be written in two ways:

$$E_{int} = \frac{3}{2}NkT = \frac{3}{2}nRT \qquad E_{int} = \frac{3}{2}pV \qquad \rightarrow \qquad pV = NkT = nRT$$

This is true not only for monatomic ideal gases but also for polyatomic molecules, in any state of the given ideal gas. Hence the name of the equation…

Equation of state: In all states of an ideal gas, the following relationship holds between the state variables:

$pV = NkT$ or $pV = nRT$

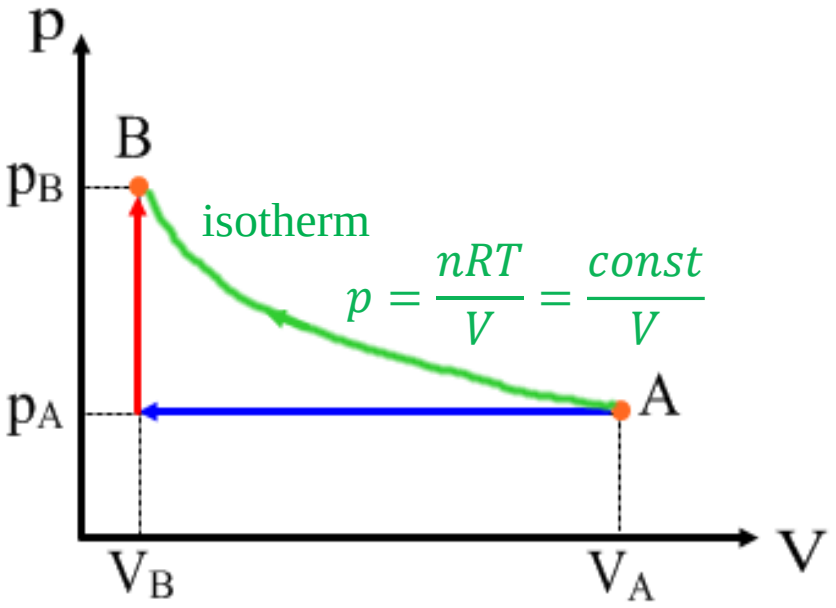
So the internal energy can be written many ways: $E_{int} = \frac{f}{2}NkT = \frac{f}{2}nRT$

In the case where the amount of gas is constant (N = constant, or n = constant), we obtain the **combined gas law** from the equation of state.

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

Special changes in the state of ideal gases

The amount of gas is always given, so n = constant!



- isobaric: the pressure is also constant ($pV = nRT$)
  (V/T = const. $W = -p\Delta V = -nR\Delta T$)

- isochoric: the volume is also constant ($pV = nRT$)
  (p/T = const. $W = 0$)

- isothermal: the temperature is also constant
  ($pV = nRT$) thus (pV = const.)

$$\delta W = -pdV$$

$$W = -\int_{V_1}^{V_2} pdV = -nRT\int_{V_1}^{V_2}\frac{dV}{V} = -nRT[\ln V]_{V_1}^{V_2} =$$

$$= -nRT\ln\left(\frac{V_2}{V_1}\right) = nRT\ln\left(\frac{V_1}{V_2}\right) = p_1V_1\ln\left(\frac{V_1}{V_2}\right)$$

- adiabatic: the heat transferred is zero $Q = 0$ (*later*…)

Isobaric and isochoric molar heat

The change in internal energy for an isochoric process (V = constant, so $W = 0$):

$$Q = c_{MV} n \Delta T \qquad \Delta E_{int} = \frac{f}{2} nR\Delta T = Q$$

isochoric molar heat: $c_{MV} = \frac{f}{2} R$

The change in internal energy during an isobaric process is:

$$\Delta E_{int} = \frac{f}{2} nR\Delta T = Q + W = Q - p\Delta V = Q - nR\Delta T$$

$$\frac{f}{2} nR\Delta T + nR\Delta T = Q$$

$$Q = c_{Mp} n \Delta T \qquad Q = \left(\frac{f}{2} + 1\right) nR\Delta T$$

isobaric molar heat: $c_{Mp} = \left(\frac{f}{2} + 1\right) R$

The ratio of the two molar heats (specific heats) is the **adiabatic exponent**:

$$\kappa = \frac{c_{Mp}}{c_{MV}} = \frac{c_p}{c_V} = \frac{\frac{f}{2} + 1}{\frac{f}{2}} = \frac{f + 2}{f} \qquad \kappa = \frac{5}{3}, \frac{7}{5}, \frac{4}{3}$$

Adiabatic change of state

During the process, heat transfer is zero: $Q = 0 \rightarrow \Delta E_{int} = W$

The change in internal energy: $dE_{int} = \delta W \rightarrow \frac{f}{2} nRdT = -pdV$

Since: $nRT = pV \rightarrow nRdT = pdV + dpV$

$$\frac{f}{2}(pdV + dpV) = -pdV$$

$$\frac{f}{2} pdV + pdV = -\frac{f}{2} Vdp$$

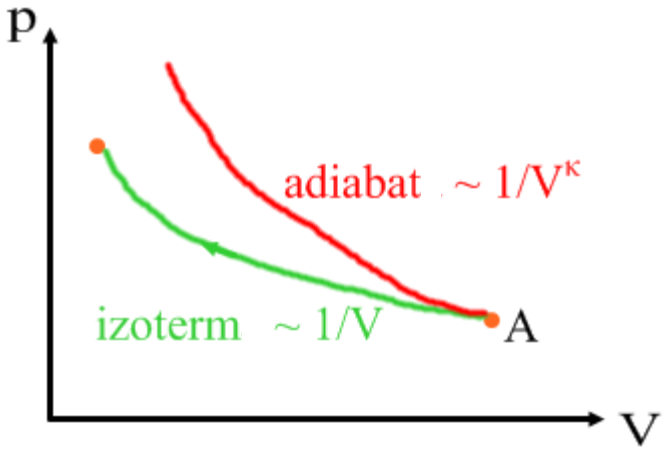
$$\left(\frac{f}{2} + 1\right)\frac{dV}{V} = -\frac{f}{2}\frac{dp}{p}$$

$$\kappa \frac{dV}{V} = -\frac{dp}{p} \rightarrow \kappa \int_{V_1}^{V_2} \frac{dV}{V} = -\int_{p_1}^{p_2} \frac{dp}{p}$$

$$\kappa \cdot [\ln V]_{V_1}^{V_2} = -[\ln p]_{p_1}^{p_2}$$

$$\kappa \cdot \ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{p_1}{p_2}\right)$$

$$\left(\frac{V_2}{V_1}\right)^{\kappa} = \frac{p_1}{p_2}$$



Poisson equation: $p_1 V_1^{\kappa} = p_2 V_2^{\kappa}$