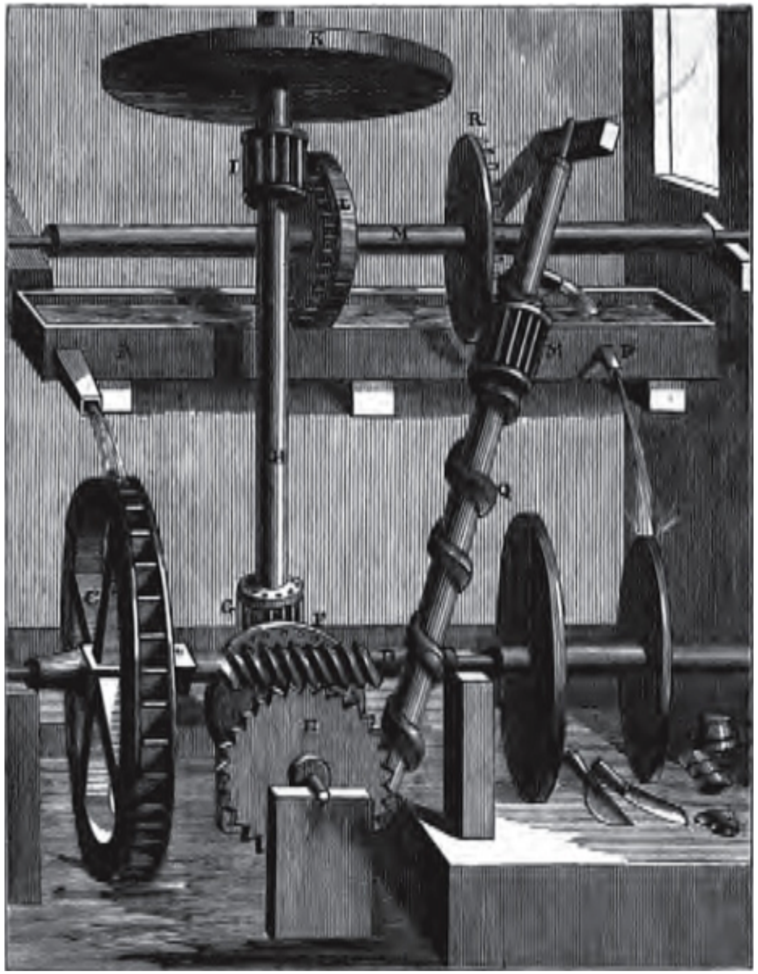
Chemistry and Introduction to Biochemistry

Thermodynamics 1



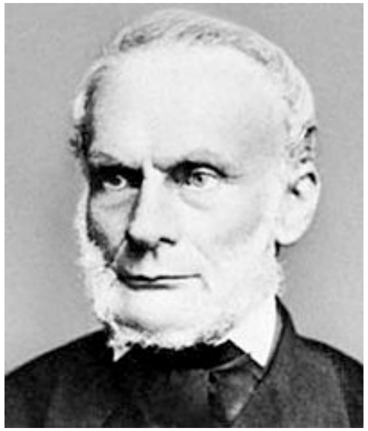
Perpetual motion machine
by R. Fludd, 1618

Fall by M.C. Escher, 1961

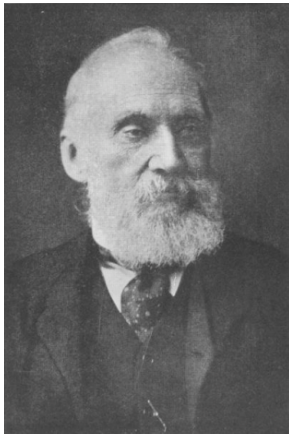
Alcune immagini sono state prese e modificate da “Chimica” di Kotz, Treichel & Weaver, Edises 2007, III edizione

Some of the most importan scientists involved in thermodynamics

James Joule
(1818 – 1889)

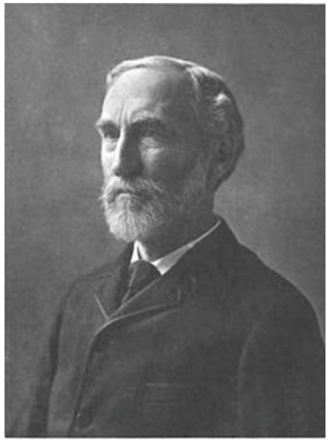


Rudolf Clausius
(1822 – 1888)



Lord Kelvin
William Thomson
(1824 –1907)

Ludwig Boltzmann
(1844 –1906)



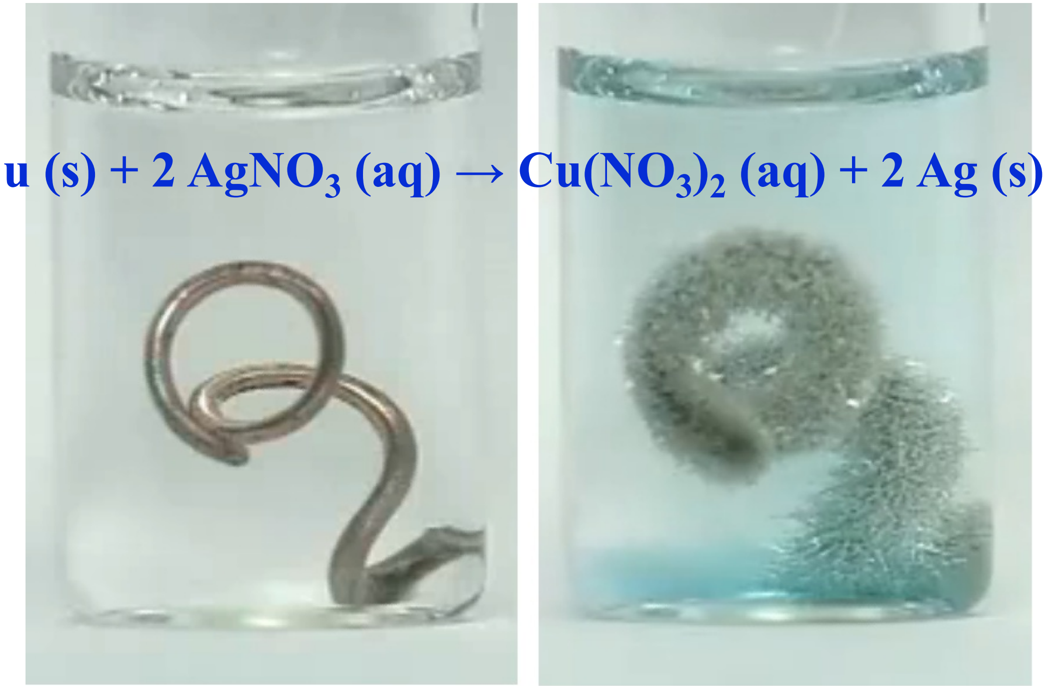
Josiah Gibbs
(1839 –1903)

Thermodynamics

- deals with energy transformations starting from macroscopic properties (P, V, T) of a system
- it is independent of any hypothesis about the nature of the particles that make up matter
- is unable to predict the temporal evolution of a transformation

Chemical thermodynamics: being able to predict whether or not a reaction will occur under certain conditions.

- in a waterfall, the water falls downwards
- a sugar cube dissolves in a cup of coffee
- at 1 atm, water freezes below 0 °C and ice melts above 0 °C
- heat flows from warmer objects to colder ones
- gas expands into an empty balloon
- iron exposed to water and air rusts

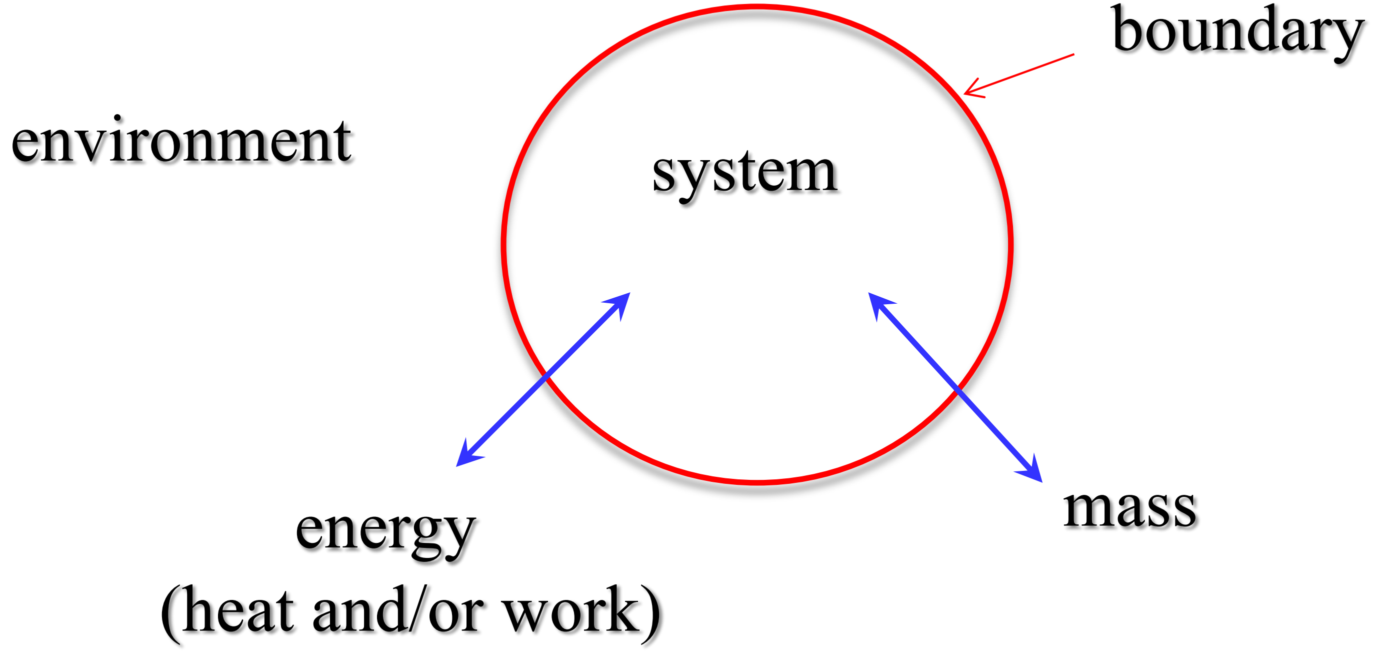


$\mathbf{Cu\ (s) + 2\ AgNO_3\ (aq) \rightarrow Cu(NO_3)_2\ (aq) + 2\ Ag\ (s)}$

Thermodynamic systems

A thermodynamic system represents that part of the universe that we want to study (the test tube in which a chemical reaction takes place, a single bacterial cell ...) and therefore has defined boundaries that separate it from the surrounding environment:

- isolated system: it does not exchange energy or matter with the environment
- closed system: energy exchanges with the environment take place
- open system: exchanges of energy and matter with the environment (living organisms) take place

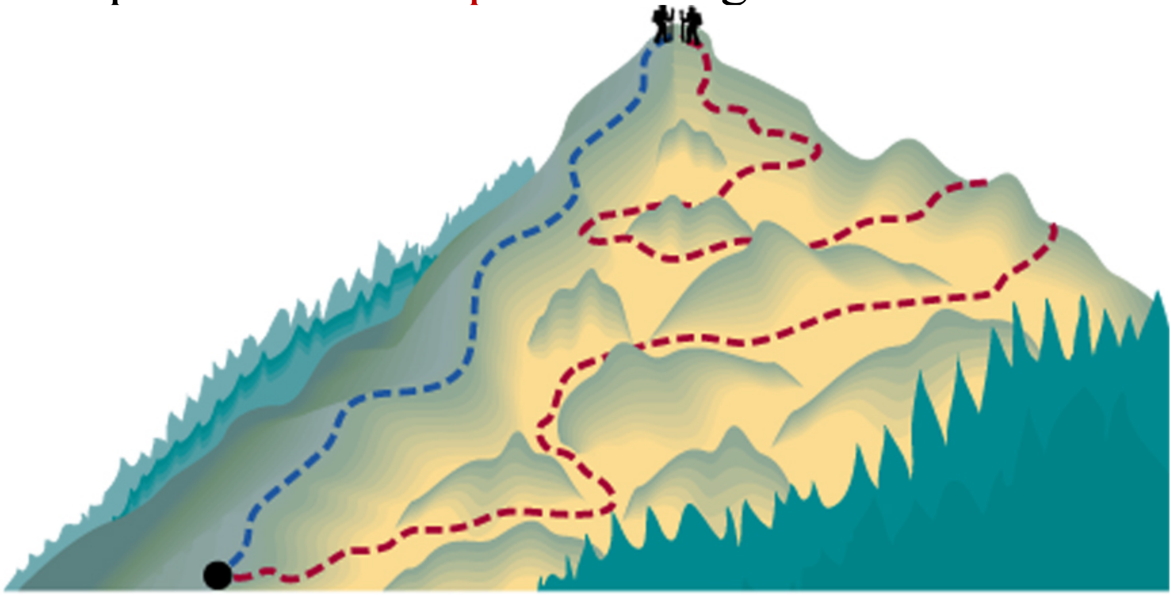


The state of a system is defined by its properties

- intensive properties - independent of system size: example, P, T, δ
- extensive properties - dependent on the size of the system: example, V, mass

The properties of a system, both intensive and extensive, are called state functions. The state of a system is determined by the values of the state functions, which are correlated with each other by equations of state (e.g. general equation of state for ideal gases)

The state functions depend exclusively on the state of the system and are independent of the "path" through which that state was reached.

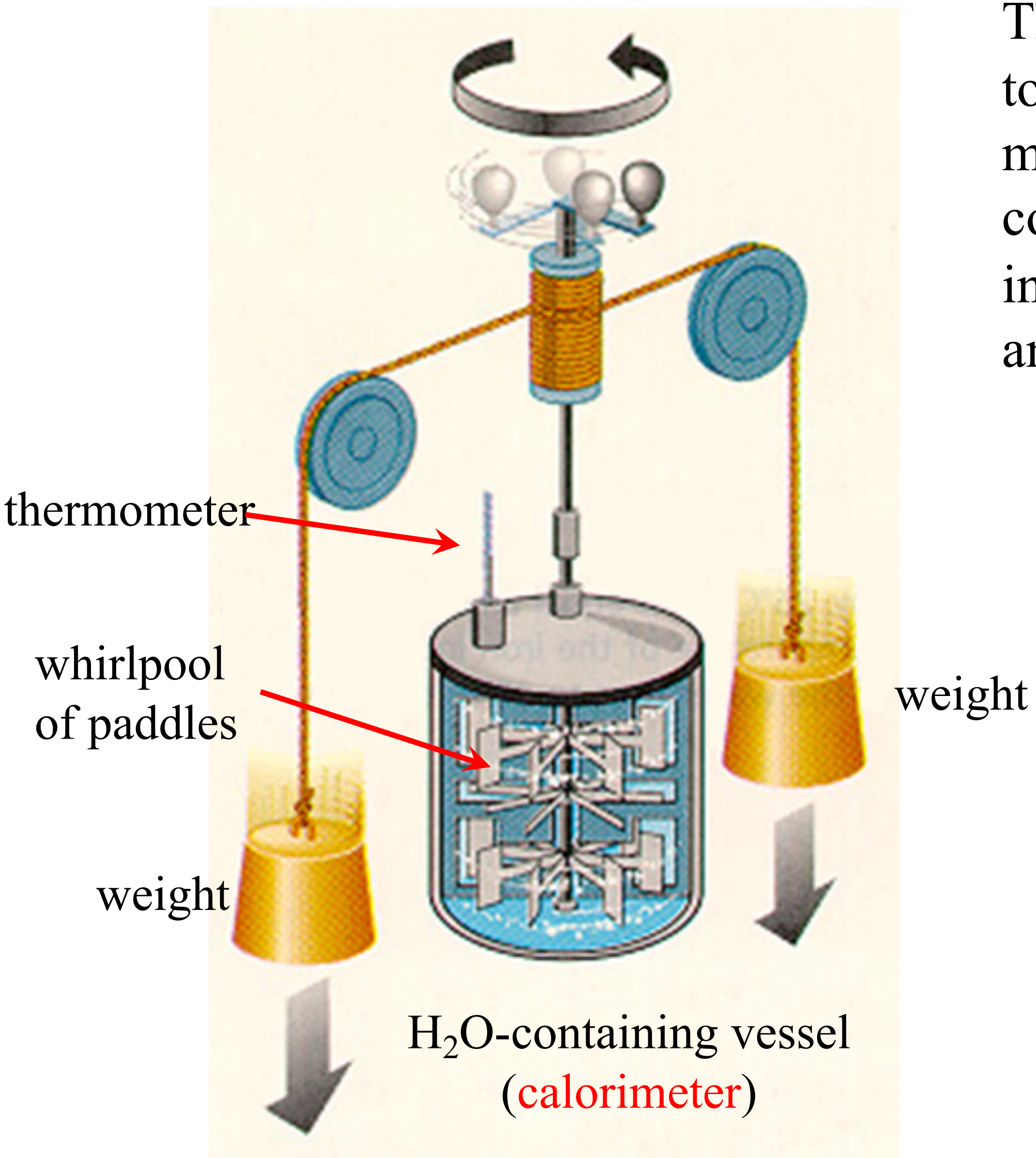


The potential energy of climber 1 and climber 2 is the same even if they have followed two different paths.

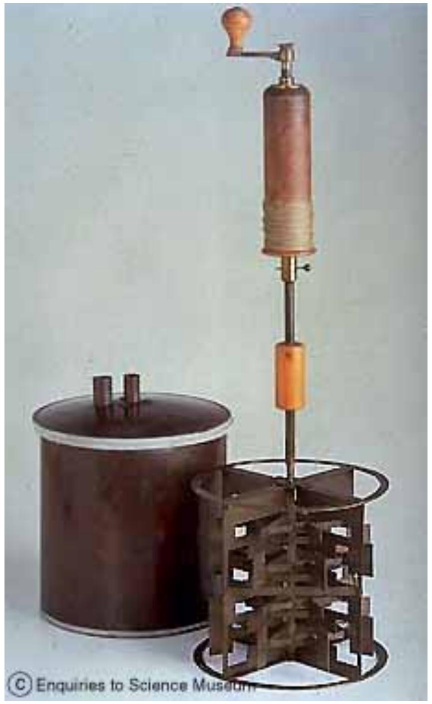
The thermodynamic state of a system is defined by establishing the quantities of all the substances present and assigning a value to any two of the three variables P, V, T.

The first law of thermodynamics

The first law of thermodynamics is essentially based on a series of experiments conducted by Joule between 1843 and 1848.



The paddles are subjected to a torque due to the fall of two large weights, free to move under the effect of gravity. As a consequence of this process, there is an increase in the temperature of the water and the slowed fall of the weights.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When the weights have reached the ground, the temperature rise of the water contained in the calorimeter is measured, obtaining the variation in internal energy deriving from the mechanical action of the whirlpool. It is therefore possible to determine the ratio between the mechanical energy introduced and the internal energy variation measured in calories given by the product of the mass of water for the temperature rise.

By means of this experiment (and others), Joule determined a value of the **mechanical equivalent of heat equal** to 4.186 J / cal.

mechanical work →

• turbulent motion of water	$\Delta T = +4.16$ °C
• electrical current	$\Delta T = +4.51$ °C
• compression of a gas	$\Delta T = +4.28$ °C
• friction between two iron blocks	$\Delta T = +4.16$ °C

Work and heat are mechanisms of **energy transfer** from one body to another

Internal energy E

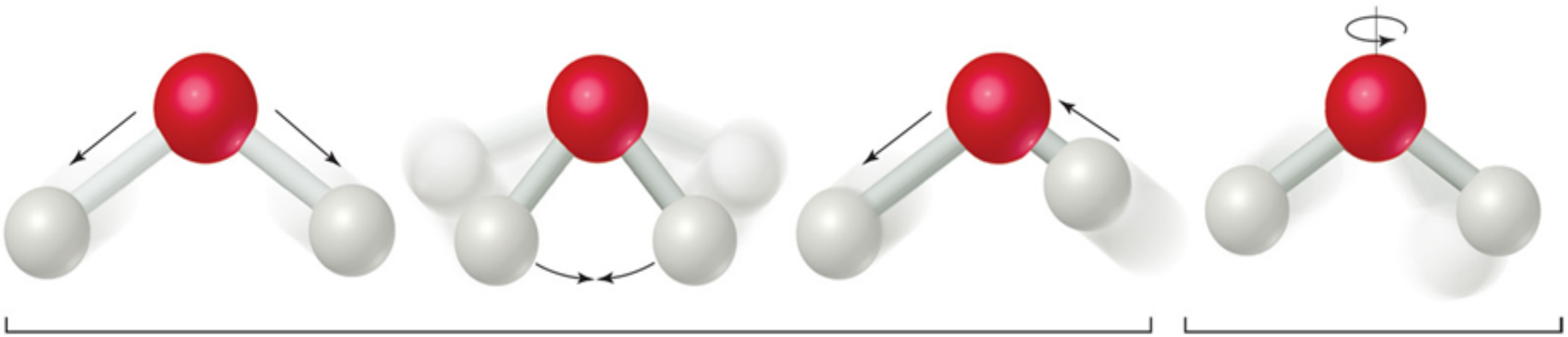
The internal energy E of a system is the sum of the potential and kinetic energies of the atoms, molecules or ions of the system.

Potential energy is the energy associated with the attractive and repulsive forces between all nuclei and electrons in the system and includes the energy associated with the bonds in molecules, the forces between ions and the forces between molecules in the liquid and solid state.

Does a glass of water have energy?

Kinetic energy is the energy associated with the motion of atoms, ions and molecules

- **translational motions**: the movement of an entire molecule from one place to another
- **vibrational motions**: the periodic movement of atoms within a molecule
- **rotational motions**: rotation of a molecule around an axis or around s-bonds



vibrational

rotational

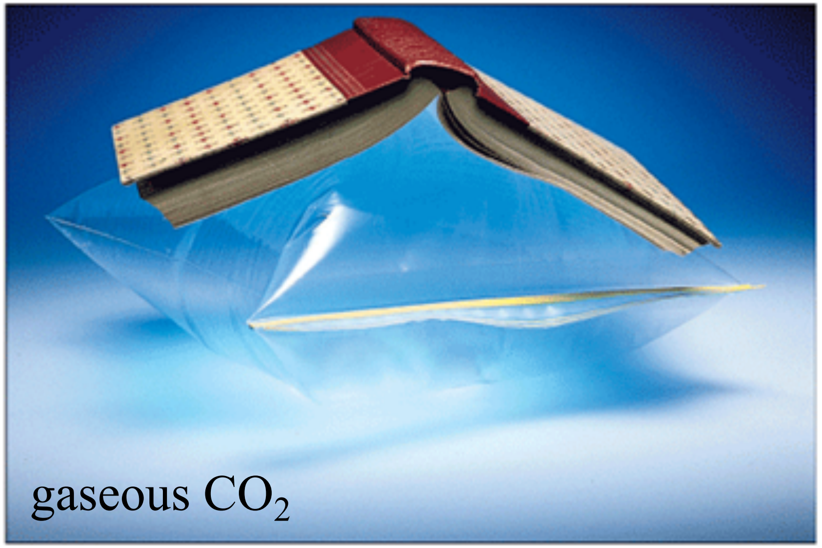
http://www2.ess.ucla.edu/~schauble/molecular_vibrations.htm

The first law of thermodynamics

system = CO_2 (s) inside the airtight bag
environment = everything else (airtight bag, table, book, etc.)

$$CO_2\ (s) + \text{heat} \rightarrow CO_2\ (g)$$

→

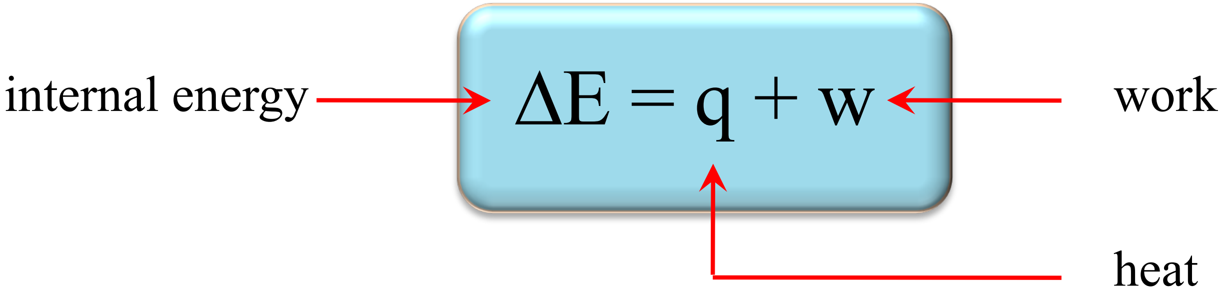


The sublimation of CO_2 requires heat, which is transferred from the environment, and at the same time the system does work on the environment by moving a part of the atmosphere and lifting a book.

A system energy balance must include the heat acquired by the system and the work expended by the system.

The first law of thermodynamics

The **change in the energy content** of a system (ΔE) will be equal to the sum of the heat transferred (q) to or from the system and the work done by or on the system (w).



internal energy

$$\Delta E = q + w$$

work

heat

This equation is the mathematical expression of the first law of thermodynamics: "*the change in energy of a system is the sum of the heat exchanged between the system and the environment and the work done by the environment on the system or by the system on the environment*" .

The quantity E in the equation has a very precise meaning in thermodynamics and and is called internal energy. The **absolute internal energy** E of a system is difficult to determine, but its variation ΔE is measurable

$$\boxed{\Delta E = E_{FINAL} - E_{INITIAL}}$$

P-V work

In CO_2 sublimation, the work performed is of a specific type, and is called P-V (pressure-volume) work.

$$CO_2\ (s) + \text{heat} \rightarrow CO_2\ (g)$$

It is the work associated with a change in volume ΔV that takes place against an external pressure P. For a system in which the external pressure is constant, it can be calculated:

work
(at constant pressure)

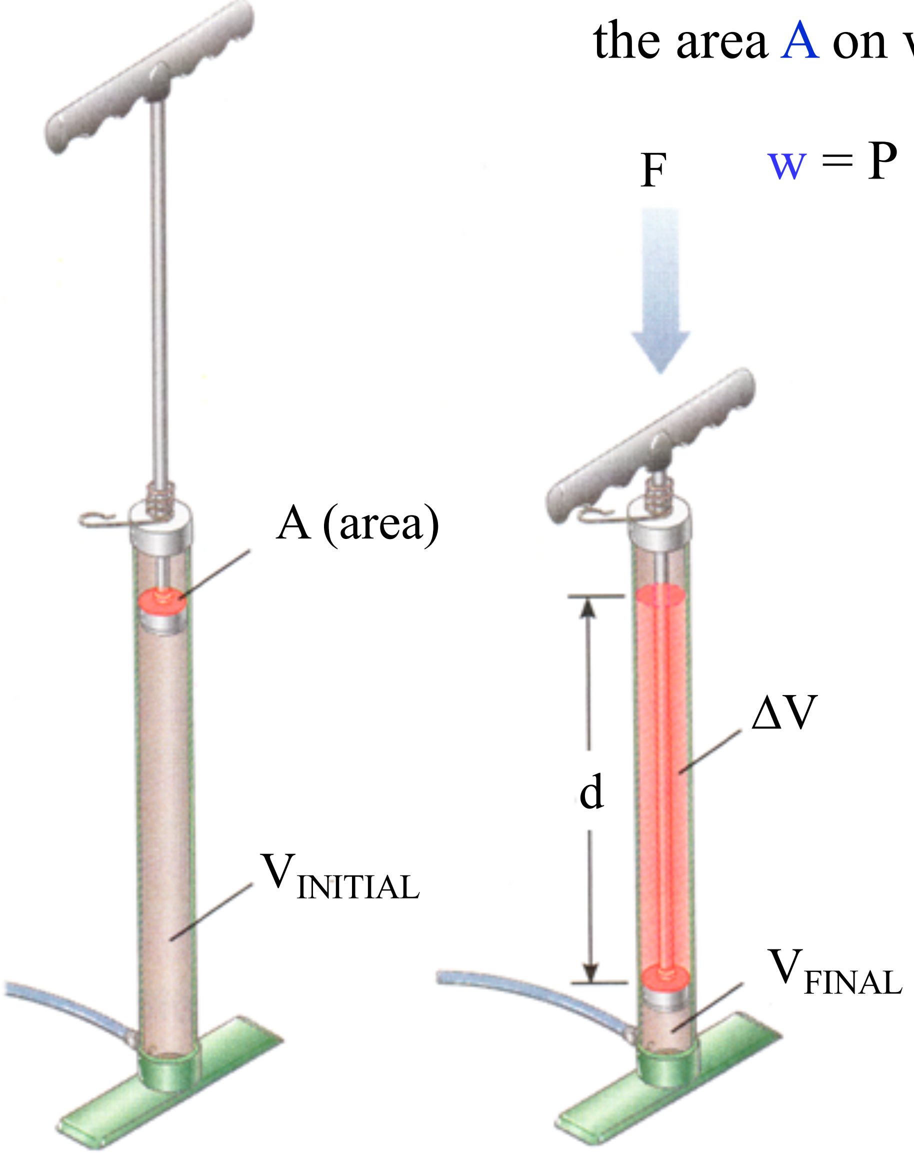
$$w = -P \cdot \Delta V$$

volume change

pressure

P-V work

The work required to lower the piston is given by: $w = F \cdot d$



The pressure P is defined as the ratio between a force F and the area A on which it is applied $P = F / A$

$$w = P \cdot A \cdot d = P \cdot (V_{FINAL} - V_{INITIAL}) = -P \cdot \Delta V$$

$$\boxed{w = -P \cdot \Delta V}$$

Lowering the piston therefore means doing work on the system, the gas contained in the cylinder. The gas is compressed to a smaller volume and consequently has a higher energy.

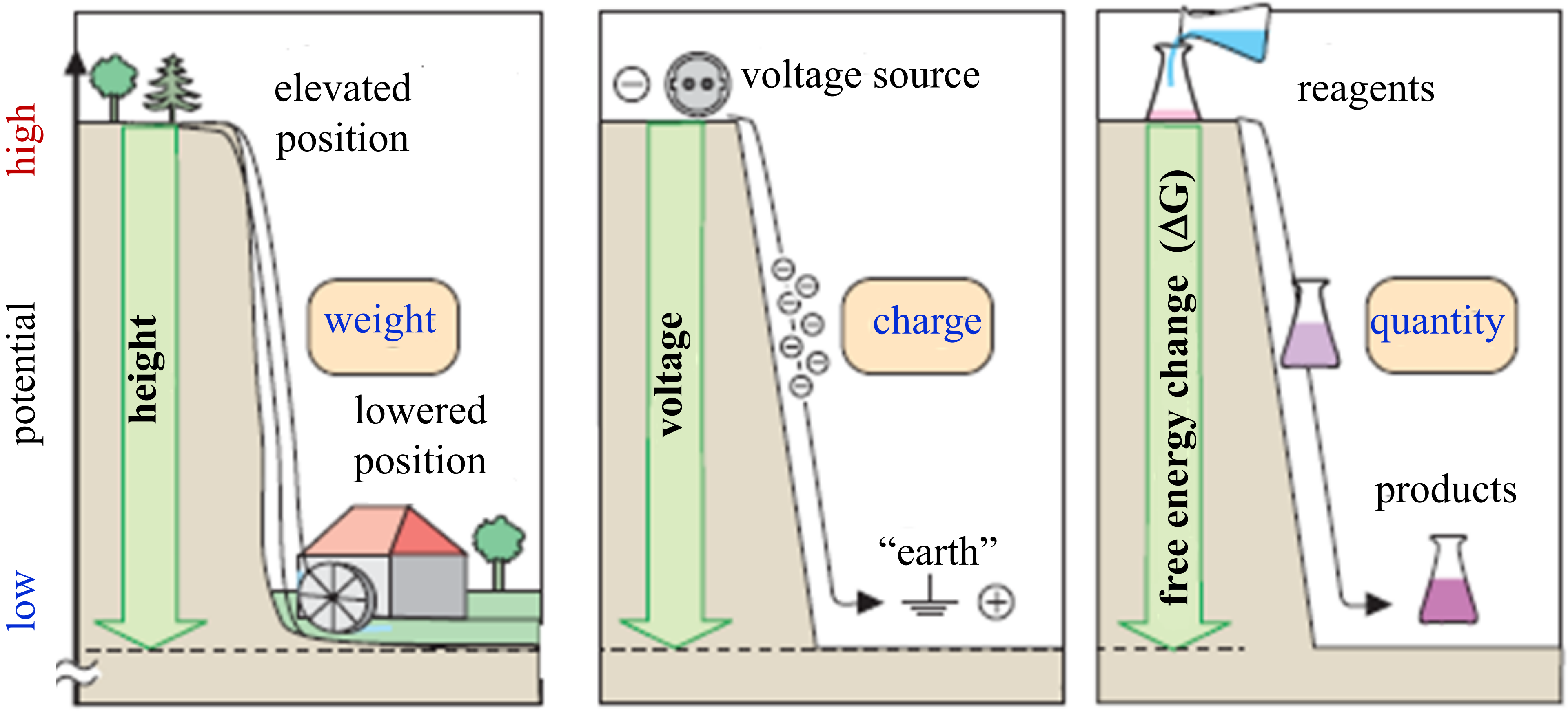
The energy has transformed from one form to another: from muscle energy used to lower the piston, to potential energy stored in the gas at higher pressure.

Convention on the signs of q and w of the system

$$\Delta E = q + w$$

change	**convention on the sign**	**effect on the internal energy E of the system**
heat transferred from the environment to the system	$q > 0$ (+)	E increases ↑
heat transferred from the system to the environment	$q < 0$ (–)	E decreases ↓
work carried out by the environment on the system	$w > 0$ (+)	E increases ↑
work carried out by the system on the environment	$w < 0$ (–)	E decreases ↓

Types of work



Mechanical work

Electrical work

Chemical work

Enthalpy H

Most of the chemical processes in living organisms take place under constant pressure. It is therefore convenient to have a specific definition of heat transfer under these conditions.

The thermal content of a substance at constant pressure is called **enthalpy** H. During a chemical transformation the change in enthalpy:

$$\Delta H = H_{FINAL} - H_{INITIAL}$$

In chemical and physical processes, a change in ΔH enthalpy is measured and the same sign conventions are applied to it as for ΔE.

- negative values of ΔH and ΔE indicate an energy transfer from the system to the environment
- positive values of ΔH and ΔE indicate an energy transfer from the environment to the system

The variations of internal energy ΔE and enthalpy ΔH are mathematically related by the general relation (at constant pressure):

$$\boxed{\Delta E = \Delta H + w}$$

That is, the difference between ΔE and ΔH is equal to the amount of energy transferred as work by or on the system.

The work term ($w = -P \cdot \Delta V$) can be small ($\Delta V \approx 0$) → $\Delta E \approx \Delta H$ or large and ΔE and ΔH differ significantly.

Example

$H_2O\ (s) \rightarrow H_2O\ (l)$ ΔV is small and therefore w is small

$CO_2\ (s) \rightarrow CO_2\ (g)$

$H_2O\ (l) \rightarrow H_2O\ (g)$ ΔV is large and therefore w is not negligible

Summing up

The internal energy E of a system includes all forms of energy (kinetic, translational, vibrational and rotational of the constituent particles, potential energy stored in chemical bonds ...) that can be exchanged through simple physical processes (non-nuclear) or chemical reactions

First law of thermodynamics

- Energy cannot be created or destroyed
- the total energy of the universe is constant
- energy can, however, be converted from one form to another or transferred from a system to the environment and vice versa.

$$\Delta E = q + w$$

The P-V work is the work associated with a change in volume ΔV that is performed against an external pressure P

$$w = -P \cdot \Delta V$$

Convention of the signs of q and w

At constant pressure, the first law of thermodynamics correlates the ΔE, ΔH and w

$$\Delta E = \Delta H + w$$

State functions

It is significant that neither heat nor work are, taken individually, state functions of the system, while their algebraic sum, that is the variation of internal energy ΔE, is.

$$\Delta E = E_{FINAL} - E_{INITIAL} = q + w$$

The value of ΔE depends on $E_{INITIAL}$ and E_{FINAL}, but a transition from the initial and final states can be performed through different paths that have different values of q and w.

Enthalpy is also a state function; e.g. the ΔH when 1 g of H_2O is heated from 20 to 50 ° C is independent of the way in which the process is conducted. Other state functions are entropy S and free energy G

Enthalpy changes in chemical reactions

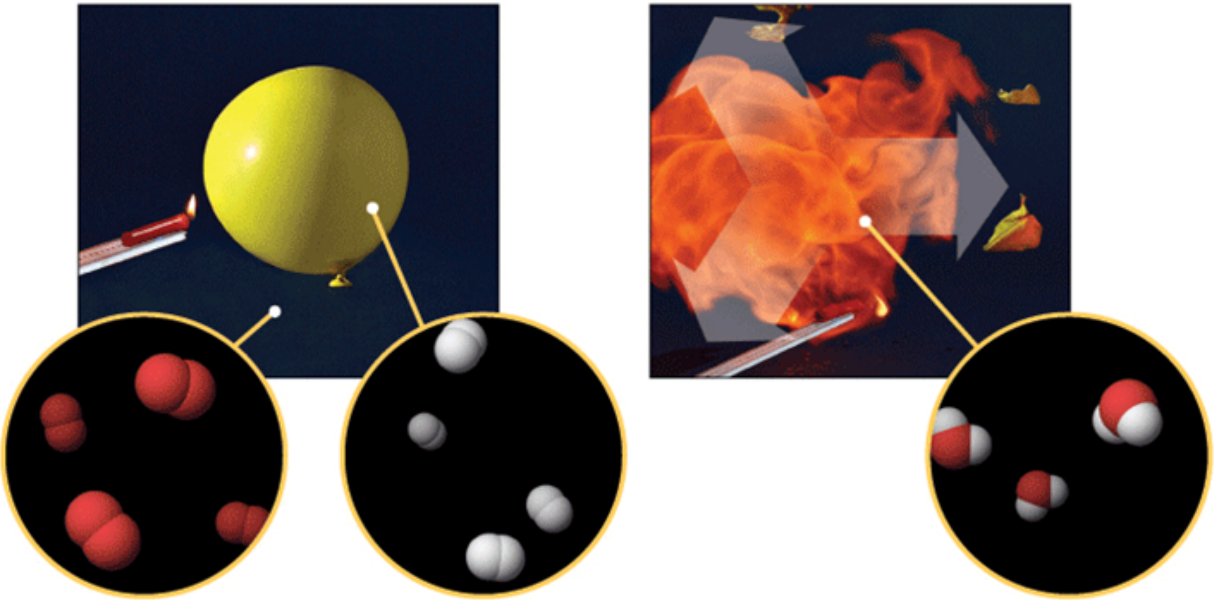
Chemical reactions are accompanied by changes in enthalpy

$$H_2O\ (g) \rightarrow H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \qquad \Delta H = +241.8\ \text{kJ a } 25\ °C$$

The water decomposition reaction is an endothermic process, that is, the reaction requires 241.8 kJ to be transferred from the environment to the system, gaseous H_2O. In the reverse reaction, the exothermic formation of H_2O, the system transfers 241.8 kJ to the environment

.

$$H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \rightarrow H_2O\ (g) \qquad \Delta H = -241.8\ \text{kJ a } 25\ °C$$



The amount of heat transferred during a chemical reaction depends on the moles of reagents used or the products formed

$$H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \rightarrow H_2O\ (g) \quad \Delta H = -241.8\ \text{kJ a } 25\ °C$$

$$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (g) \quad \Delta H = -438.6\ \text{kJ} = -241.8 \cdot 2\ \text{kJ}$$

It is also important to identify the physical state of the reactants and products in a reaction since the ΔH value also depends on whether they are solid, liquid or gaseous.

$$H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \rightarrow H_2O\ (l) \quad \Delta H = -285.8\ \text{kJ a } 25\ °C$$

The additional energy developed with respect to the gas phase reaction derives from the energy released when a mole of water vapor condenses to a mole of liquid water.

Summing up

- enthalpy changes ΔH are specific to the type of reactants and products and their physical states (solid, liquid, gas)
- ΔH has a negative value if **heat is developed** (*exothermic reaction*) and a positive value if **heat is absorbed** (*endothermic reaction*)

$$\Delta H_{\text{exothermic}} = H_{\text{FINAL}} - H_{\text{INITIAL}} < 0 \quad \rightarrow H_{\text{FINAL}} < H_{\text{INITIAL}}$$
$$\Delta H_{\text{endothermic}} = H_{\text{FINAL}} - H_{\text{INITIAL}} > 0 \quad \rightarrow H_{\text{FINAL}} > H_{\text{INITIAL}}$$

- for chemical reactions inverse of each other, the DH values are numerically identical but of **opposite sign**
- the enthalpy changes ΔH depend on the molar quantities of the reactants and products