Reactants $\rightleftharpoons$ Products

To what extent a reaction will achieve completion?

- The foundation of the concept of equilibrium relies on THERMODYNAMICS.
- How fast will it achieve equilibrium? This question requires a KINETCS study.

$$2Fe + O_2 + 2H_2O \rightleftharpoons 2\,Fe(OH)_2$$

ΔH = - 272 KJ/mol

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O \qquad \Delta H = -241\ \text{KJ/mol}$$

Both spontaneous, but what about rates?

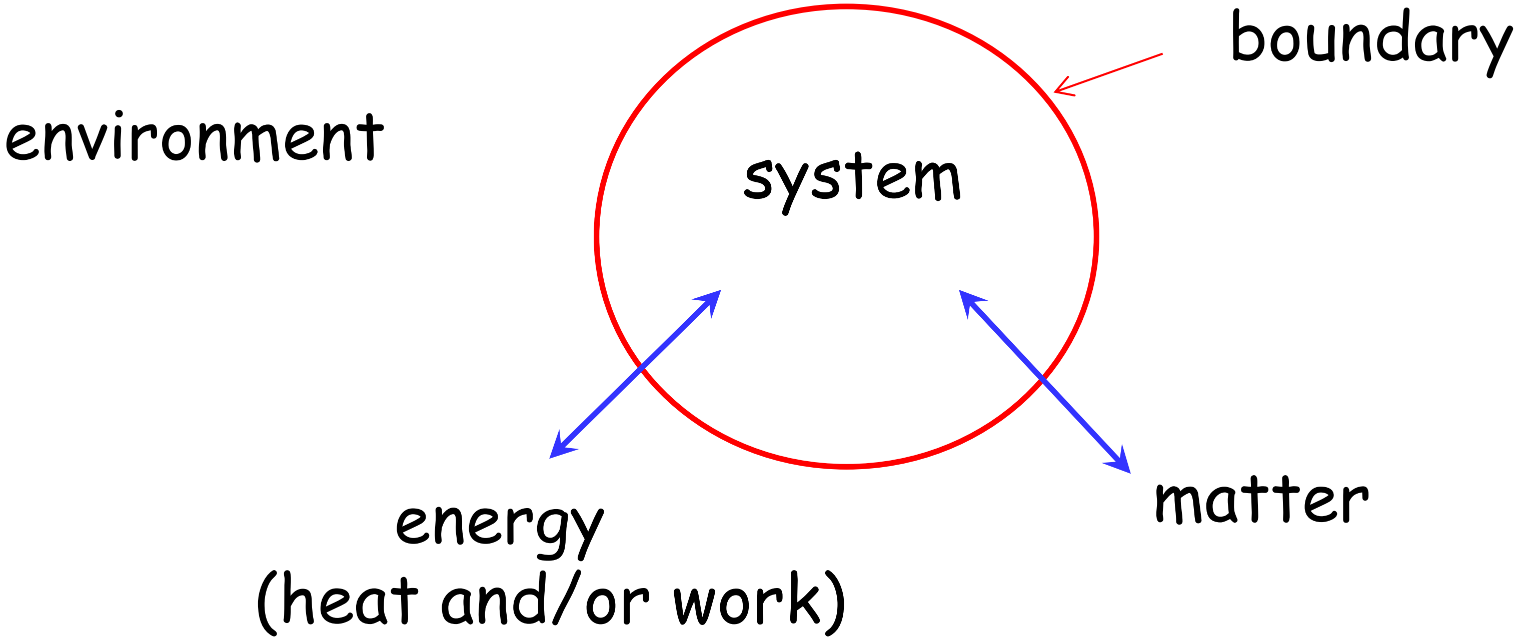
THERMODYNAMICS

Thermodynamics deals with energy transformations considering the macroscopic properties (P, V, T) of a chemico-physical system; it is therefore independent on any assumption on the nature of the particles that constitute matter.

A system represents the part of universe that we want to study (the tube in which a chemical reaction occurs, a single bacterial cell ...); therefore it has definite boundaries.

Isolated system: it does not exchange energy or matter with the environment.
Closed system: exchanges energy with the environment
Open system: exchanges energy and matter with the environment

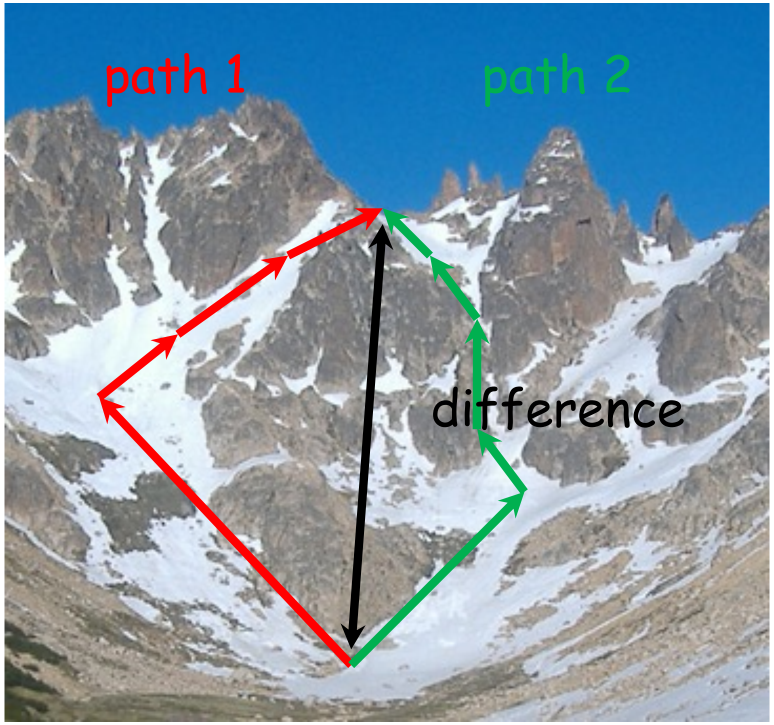
- **Isolated system:**
it does not exchange energy or matter with the environment.
- **Closed system:** exchanges energy with the environment
- **Open system:** exchanges energy and matter with the environment



The state of a system is defined by its properties

- intensive properties- **independent from the system size: P, T, d**
- extensive properties- **dependent from the system size: V, mass**

The properties of a system, both intensive and extensive, are called state functions. The state of a system is determined by their values, which are related to each other by state equations (eg, ideal gas law)



State functions depend solely on the state of the system and are independent of the "path" through which this state is reached.

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

INTERNAL ENERGY

The internal energy of a system is a state function; It includes all forms of energy (kinetic, vibrational and rotational, potential energy stored in chemical bonds, etc.) that can be exchanged through simple (non-nuclear) physical processes or chemical reactions.

Measuring the internal energy of a system in absolute terms is complex, but one can quantify the variation in internal energy (ΔE) that occurs when a system moves from one state to another:

$$\Delta E = E_f - E_i$$

E_f = *internal energy of the final state*
E_i = *internal energy of the initial state*

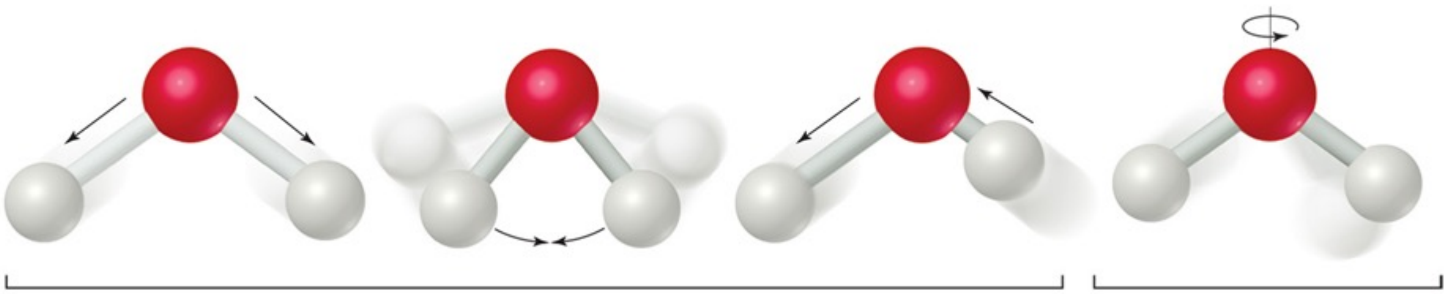
- The internal energy E of a system is the sum of the potential and kinetic energies of the atoms, molecules or ions of the system.

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

- The kinetic energy is associated with the motion of atoms, ions and molecules

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

- translation motions: displacement of the entire molecule.
- vibration motions: periodic movement of atoms within a molecule
- rotation motions: rotation of a molecule around an axis or around bonds.



Symmetric stretching

Bending

Asymmetric stretching

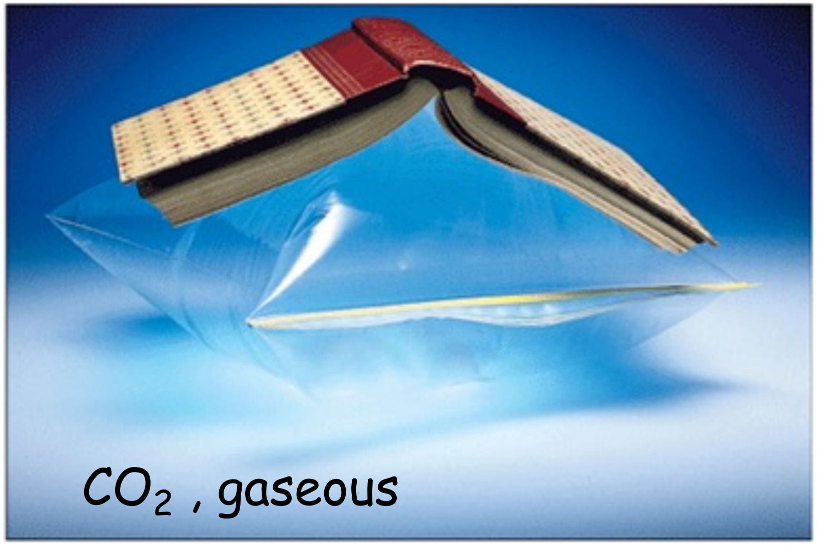
Rotation

First law of thermodynamics: conservation of energy

system = CO_2 in the zipper bag
environment = all the rest (bag, table, book, etc.)

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


CO_2 , solid


CO_2 , gaseous

CO_2 sublimation requires heat, absorbed from the environment, and at the same time the system exerts work on the environment by moving part of the atmosphere and lifting the book.

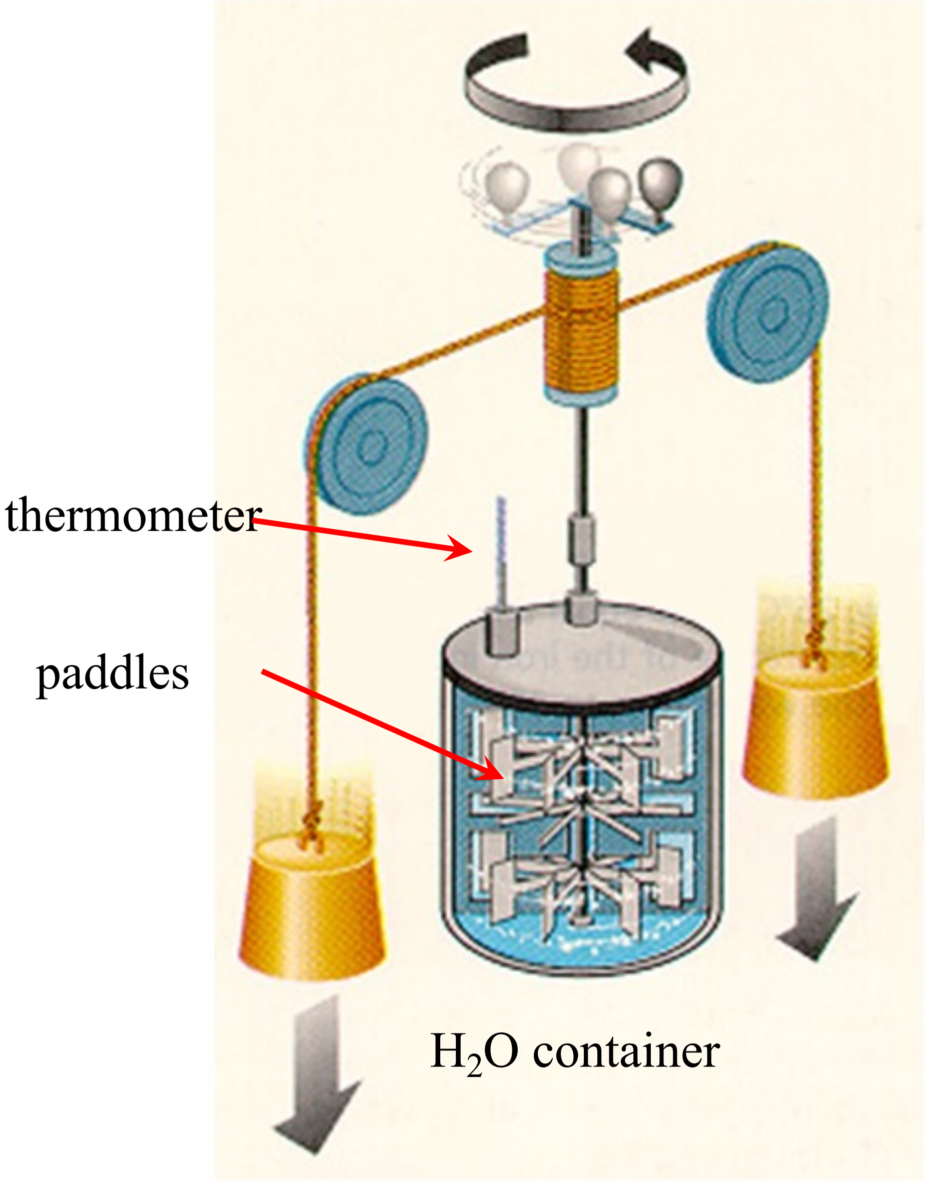
The energy variation of the system must include the heat acquired by the system and the work performed by the system.

In a closed system there are two ways to vary the internal energy: performing **work** on it (or having it perform work on the environment), or providing **heat** (or subtracting heat). Work and heat are two **forms of energy** indistinguishable by the system.

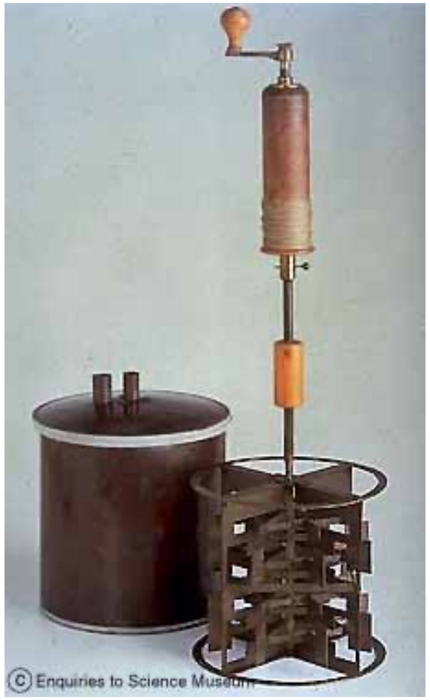
$$\boxed{\Delta E = q + w}$$

Exchange	Sign convention	Effect on E, the internal energy of the system
heat from environment to system	$q > 0$ (+)	E increases ↑
heat from system to environment	$q < 0$ (–)	E decreases ↓
work by the enviroment on the system	$w > 0$ (+)	E increases ↑
work by the system on the environment	$w < 0$ (–)	E decreases ↓

The first law of thermodynamics is based on experiments carried out by James Joule between 1843 and 1848.



The paddles are subject to a couple of forces due to the fall of two heavy weights under the effect of gravity.
As a result of this process, there is an increase in water temperature and decrease of the velocity of the drop.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When the weights have reached the ground, the temperature rise of the water contained in the calorimeter is measured, yielding in the variation of internal energy due to the mechanical action of the reel.

It is thus possible to determine the relationship between the mechanical energy input and the internal energy variation measured in calories given by the product of the water mass for the rise in temperature.

By this experiment (and others), Joule determined the mechanical equivalent of heat equivalent to 4,186 J/cal.

Work and heat allow the transfer of energy between objects.

I Principle of thermodynamics

$$\Delta E = E_f - E_i = q + w$$

The variation of the internal energy of a closed system is given by the algebraic sum of the heat exchanged between the system and the environment and the work done by the system or performed on it. This expression can be considered a mathematical formulation of the first principle.

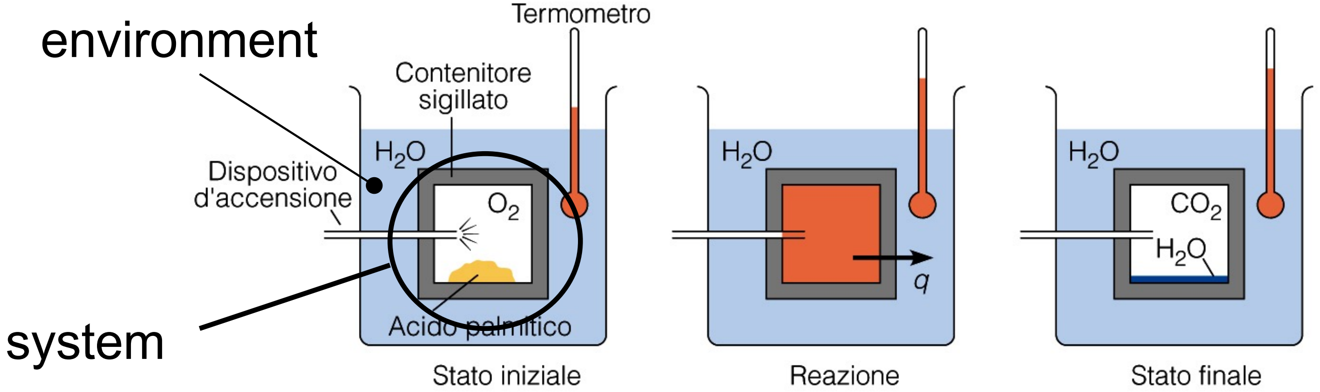
A more general statement of the First Principle is :

"In an isolated system the internal energy is constant."

I° Principle or law of energy conservation:

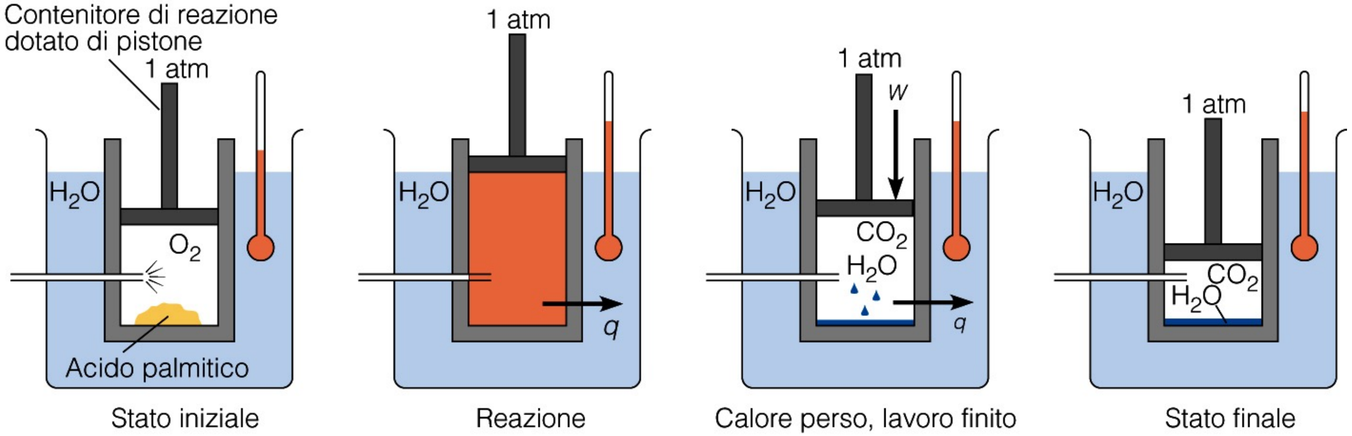
The internal energy of a closed system can change only upon exchange of heat or work with the environment $\Delta E = q + W$

$$CH_3(CH_2)_{14}COOH_{(s)} + 23O_{2\,(g)} \rightarrow 16CO_{2\,(g)} + 16H_2O_{(l)}$$



(a) Reazione a volume costante

V = cost.
$\Delta E = q$
The reaction releases E (q)



(b) Reazione a pressione costante

P = cost.
$\Delta E = q + P\Delta V$
The reaction releases heat and work

Enthalpy H

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

The thermal content of a constant pressure substance is called enthalpy H. In a chemical transformation the variation of enthalpy is:

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

In chemical and physical processes, variations of enthalpy ΔH are measured and the same sign conventions used for ΔE are applied.

- 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

Internal energy variations ΔE and enthalpy variations ΔH at constant pressure are given by :

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

The difference between ΔE and ΔH corresponds to the werk exchanged.

Work ($w = -P\Delta V$) can be neglible ($\Delta V \approx 0$) $\Delta E \approx \Delta H$ otherwise ΔE and ΔH are significatively different.

Eg.

H_2O (s) -> H_2O (l) ΔV is small w and therefore also w is small
CO_2 (s) -> CO_2 (g) ΔV is large and w is not neglible
H_2O (l) ->H_2O (g) ΔV is large and w is not neglible

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

I law of thermodynamics

-Energy can not be created or destroyed

-The total energy of the universe is constant

-Energy can be converted from one form to another or transferred from a system to the environment and vice versa.

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

-Work P-V is the work associated to a volume variation ΔV exerted against an external pressure P

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

- Sign convention for q and w

- At constant pressure the first law define ΔE, ΔH and w as:

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

When a reaction occurs with *release of heat*, it is defined as exothermic and the variation of enthalpy is negative; when a reaction occurs with *heat absorption*, it is termed endothermic and the enthalpy variation is positive.

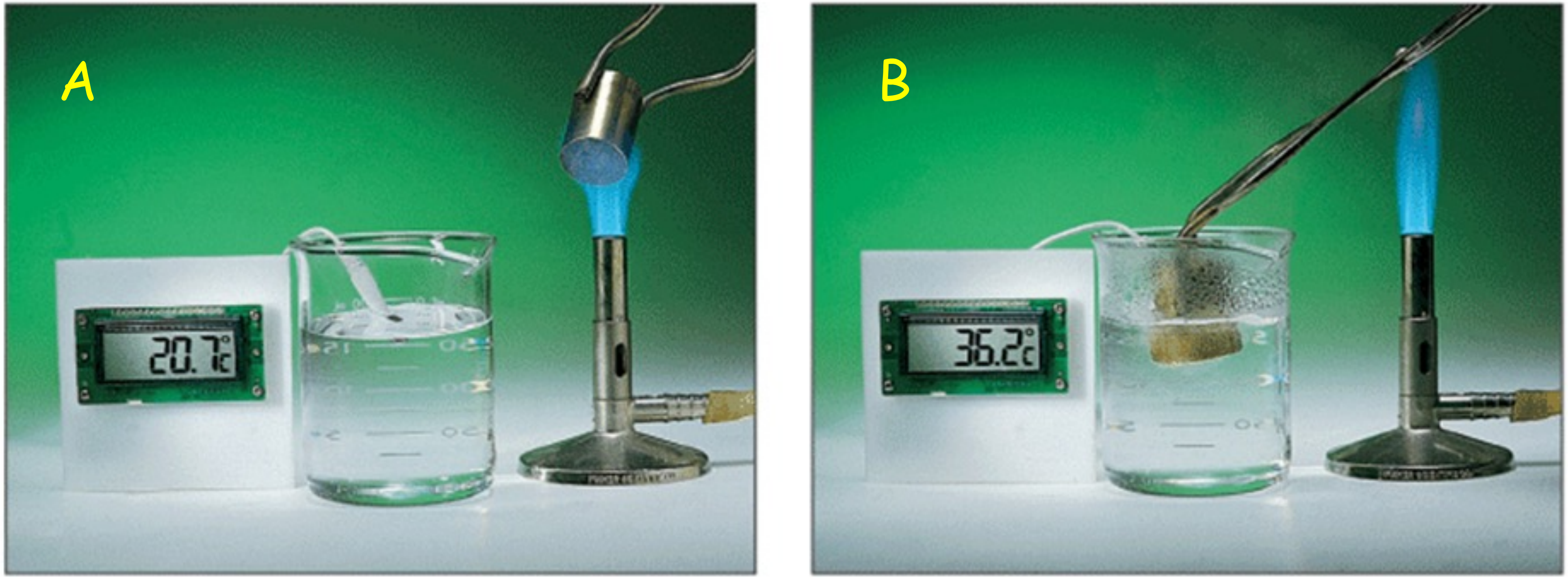
ΔH negative -> exothermic reaction-> heat released

ΔH positive -> endothermic reaction -> heat absorbed

For a chemical reaction enthalpy is defined as:

reaction (molar) enthalpy

Can we establish a criterion for spontaneity for a chemical or physical reaction?

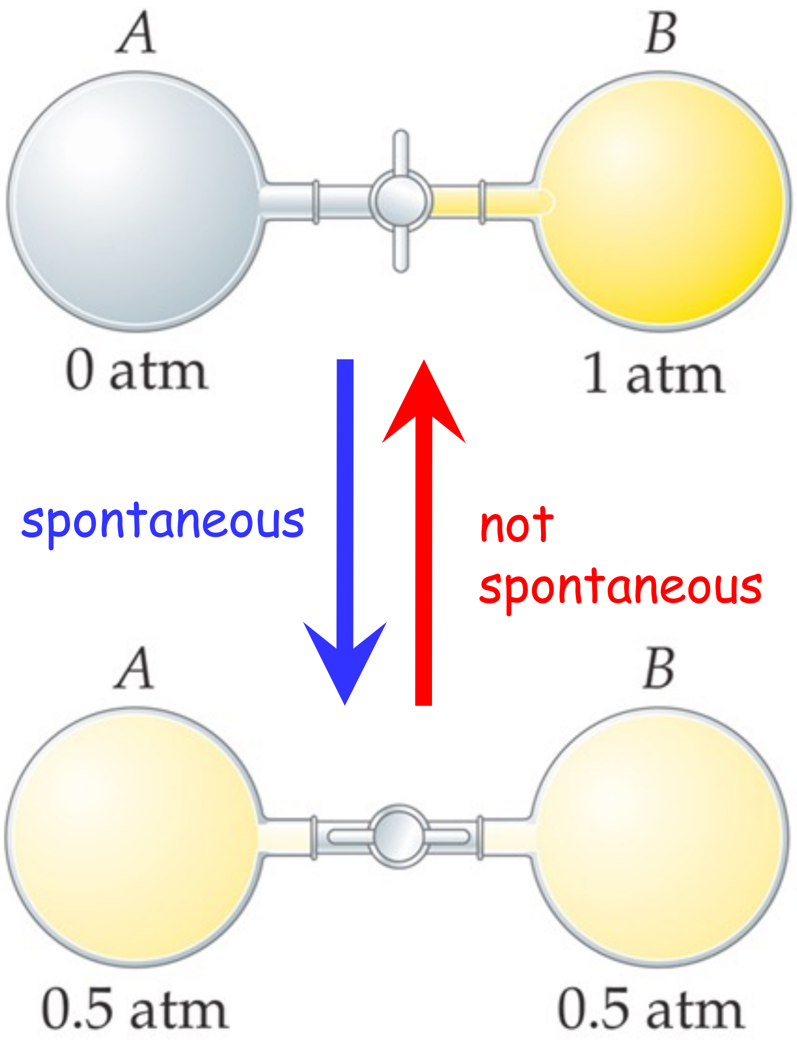


Without external intervention, it will never happen that in (B) the warm object gets warmer.

Some imeges have been taken and modified from “Chemistry” by Kotz, Treichel & Weaver, Edises 2007, III edition

Spontaneous processes

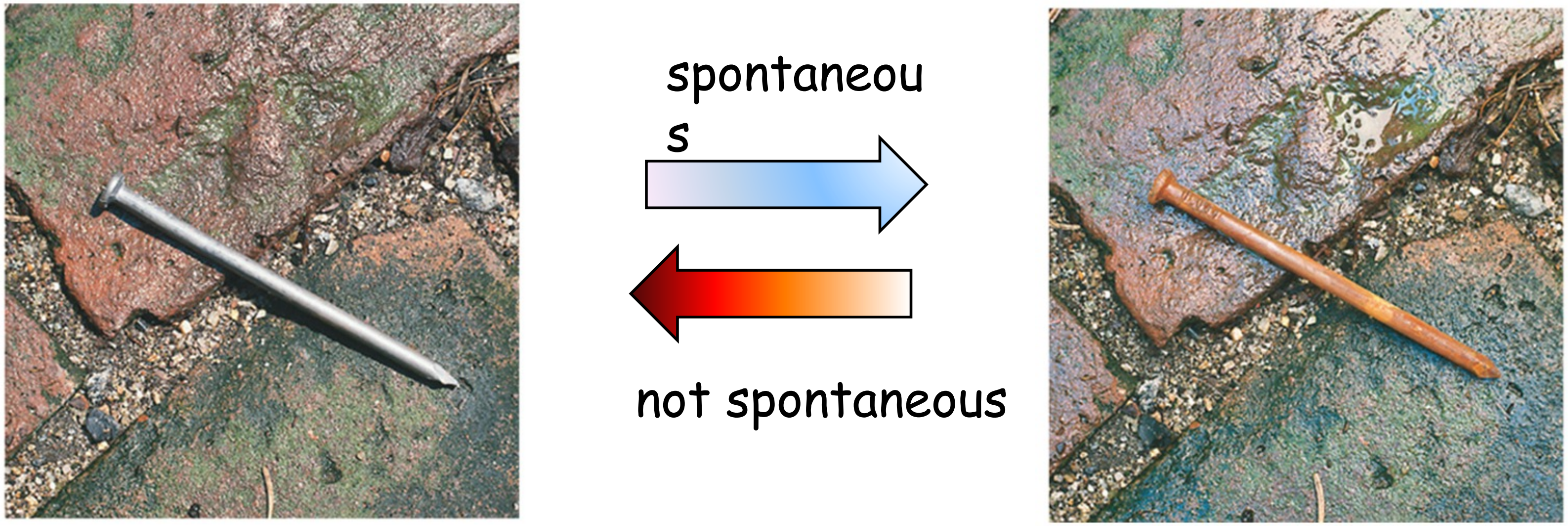
- Processes that take place without external intervention
- The gas in B will spontaneously diffuse into A



spontaneous

not spontaneous

Spontaneous processes



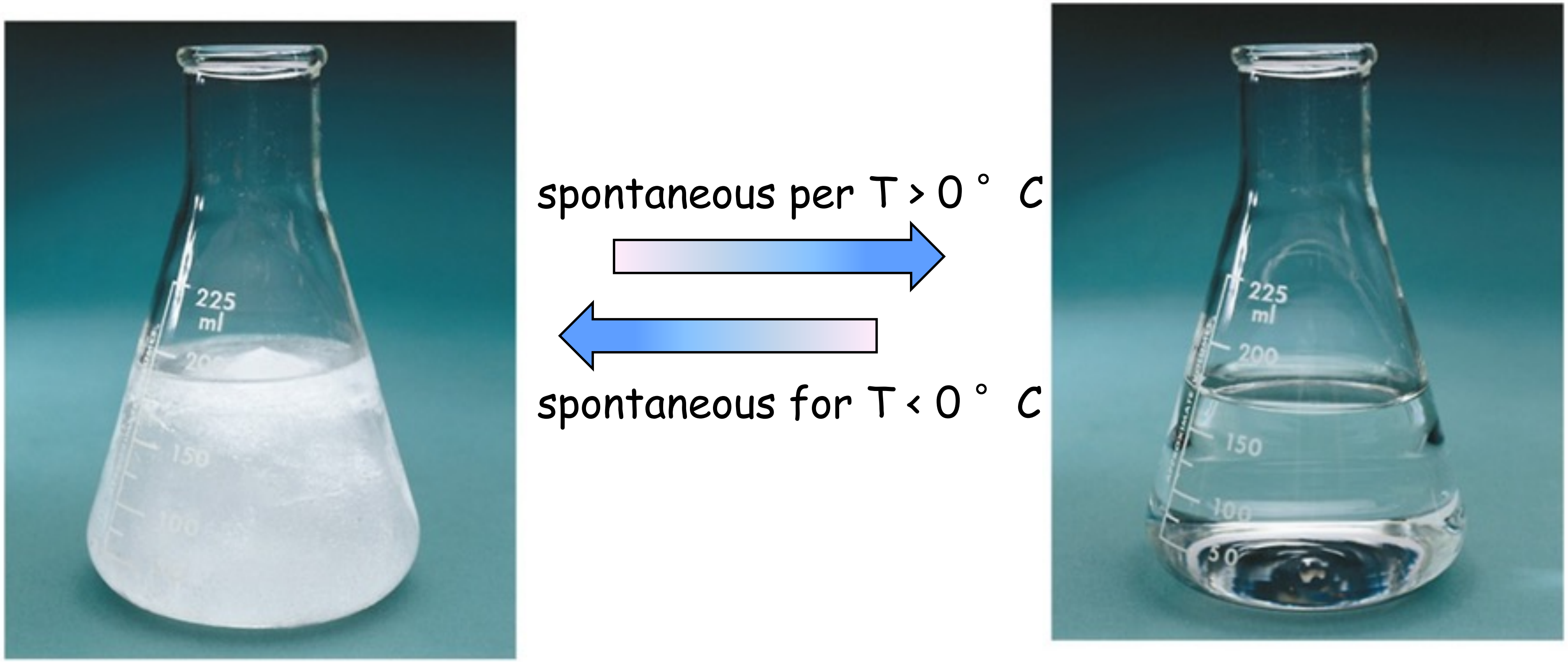
spontaneous

not spontaneous

Processes that are spontaneous in one direction are not spontaneous in the opposite one.

Spontaneous processes

- processes that are spontaneous at a temperature can be not spontaneous at another one
- above a 0°C ice melts spontaneously
- below 0°C the opposite process is spontaneous



spontaneous per $T > 0$ ° C

spontaneous for $T < 0$ ° C

Heat and spontaneity

Many chemical reactions proceed spontaneously from reagents to products and are essentially complete at equilibrium

$C_2H_5OH\ (l) + 3\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + 3\ H_2O\ (l)$ $\Delta H = -1418.0$ kJ/mol

$H^+\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (l)$ $\Delta H = -55.9$ kJ/mol

$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (l)$ $\Delta H = -438.6$ kJ/mol

These reactions, and many others are exothermic.

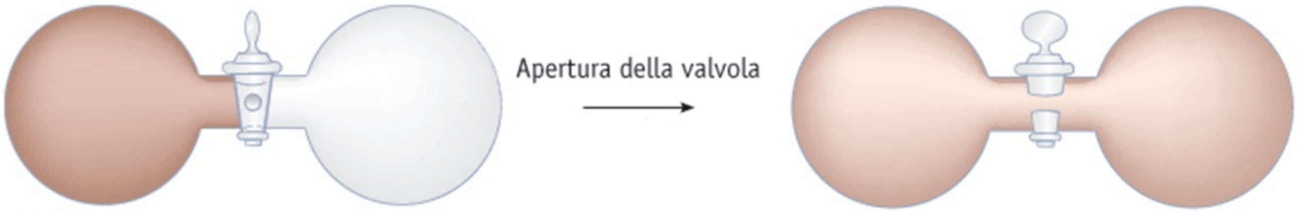
One might then surmise that heat release determines spontaneity.

However, there are many physical processes where spontaneous changes occur but are endothermic or do not involve heat transfer.

- Solubilization in water of NH_4NO_3 is spontaneous but endothermic

$NH_4NO_3\,(s) \rightarrow NH_4^+\,(aq) + NO_3^-\,(aq) \quad \Delta H = +25.7\ kJ/mol$

- Gas expansion in vacuum is isothermic



- phase transitions

$H_2O\,(s) \rightarrow H_2O\,(l) \quad \Delta H = +6.0\ kJ/mol$ a $T > 0\ °C$
$H_2O\,(s) = H_2O\,(l)$ a $T = 0\ °C$
$H_2O\,(s) \leftarrow H_2O\,(l) \quad \Delta H = -6.0\ kJ/mol$ a $T < 0\ °C$

- heat treansfer: a cold objet will absorb heat until reaching the environment temperature.

ENTROPY AND THE DIRECTION OF PROCESSES

The First Principle does not answer questions about the direction of the processes.

Not all spontaneous processes are exothermic

The sole variation of enthalpy is not enough to predict the spontaneity of a reaction.

THE SECOND PRINCIPLE OF THERMODYNAMICS

The entropy of an isolated system (Universe) tends to achieve a maximum.

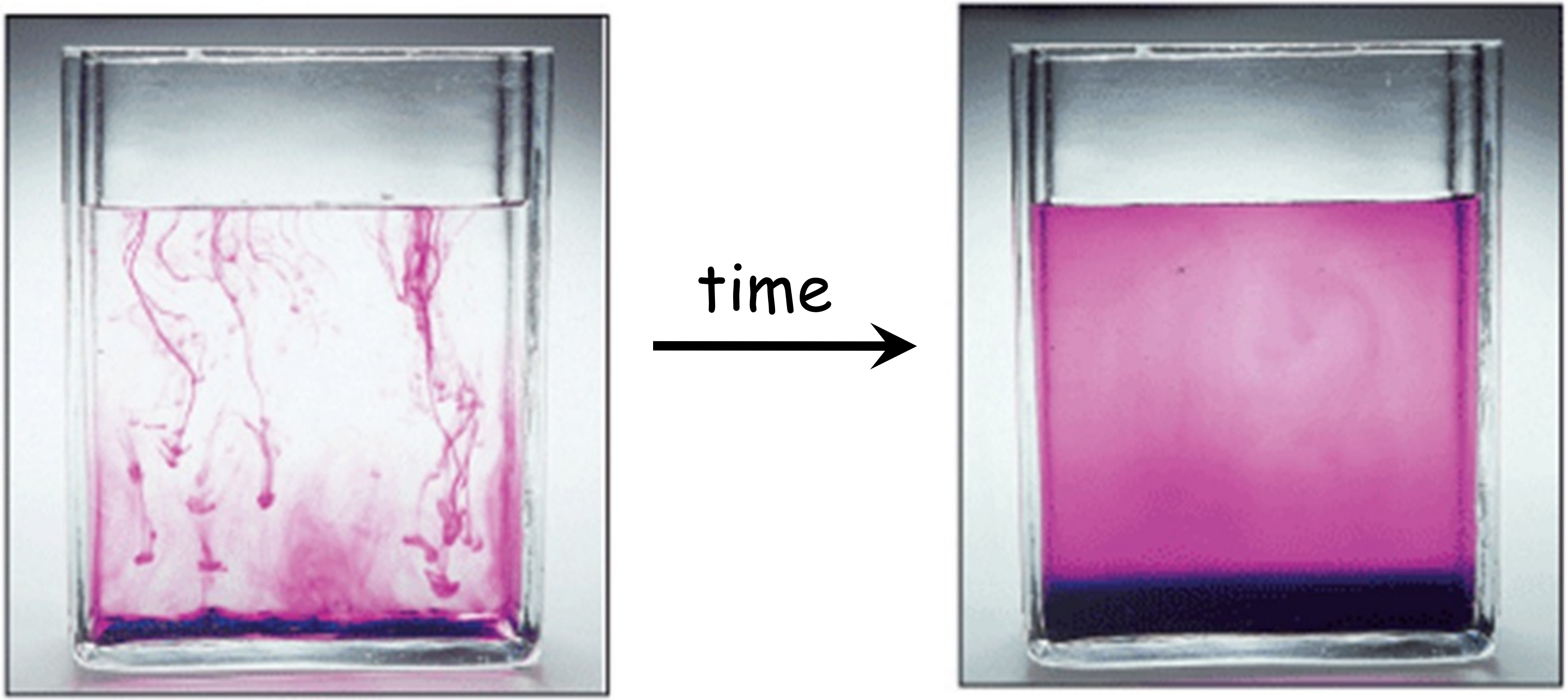
Systems spontaneously evolve toward disorder.

The degree of disorder is measured by a state function called **entropy** (**S**).

Analogy: rolling the dice

- Rolling one dice: 1/2/3/4/5/6 are equally probable
- Rolling two dice:
  - For each 1/2/3/4/5/6 are equally probable
  - The sum 7 is more probable than 6 o 8
- Why? 6 combinations (microstates) yield 7 (the macrostate): 1+6, 2+5, 3+4, 4+3, 5+2, 6+1. there are only 5 combinations that yield 6 or 8, etc.

A small amount of $KMnO_4$ is dissolved in water. The ion MnO_4^- and K^+ are dispersed homogeneously in the solution.



Entropy - S

Term introduced by R. Clausius (from Greek $\varepsilon\nu$, "inside", and $\tau\rho o\pi\eta$ "change“).

Heat irreversibility:

- heat is transfered from hot to cold, never from cold to hot.
- friction converts movement into heat, but in nature there is no process to fully transform heat into movement.

Clausius singled out two main transformations in these two classes of phenomena :

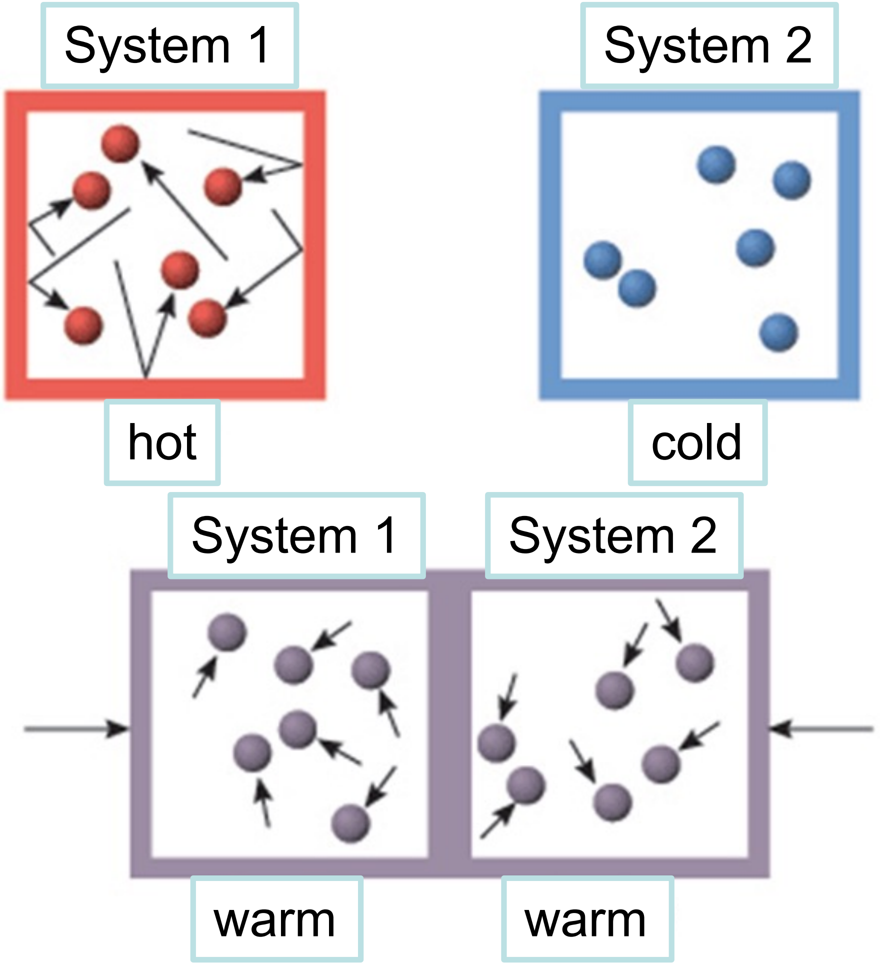
- temperature change (thermic energy moving from hot to cold)
- energy change (mechanic energy turning into thermic energy).

He hypothesized that these two types of transformations were two consequences of the same phenomenon: entropy variations.
Spontaneus transformations should then involve an increse of entropy.
The entropy variation due to a transformation is:

$$\boxed{\Delta S = \frac{Q}{T}}$$

Thermic transfer between two objects at different temperatures.

Let us consider two bodies, initially at T1 (high) and T2 (low) temperatures. Upon thermal contact the warm one transfers heat to the cold one: according to the energy conservation principle, the heat Q released by the hot object must be equal to the heat acquired by the cold object.



$$\Delta S = \Delta S_2 + \Delta S_1 = \frac{Q}{T_2} - \frac{Q}{T_1} > 0$$

This sort of onsiderations led Clausius to unify the various forms of the second principle of thermodynamics in a single statement: "the variation in entropy of the universe is always larger than zero".

Dispersion of energy and matter

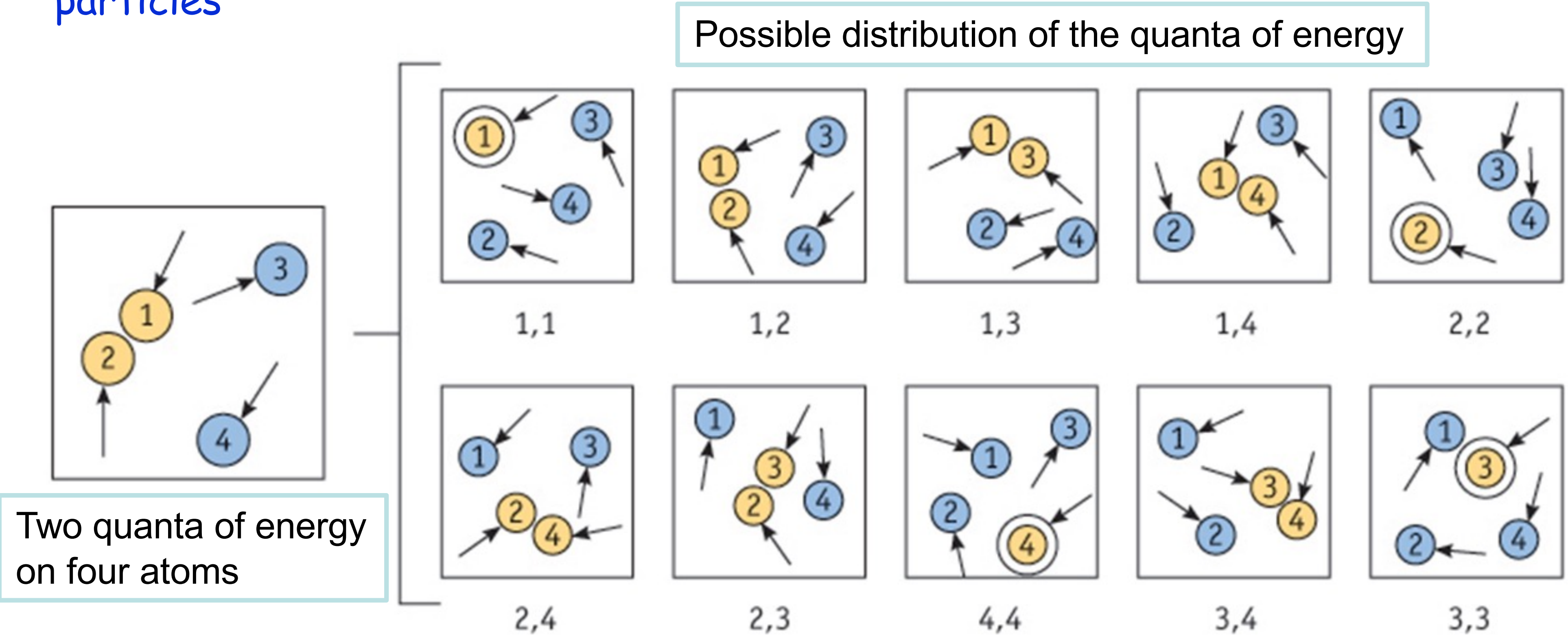
A better way of predicting whether a process is spontaneous is to consider the thermodynamic function entropy, S

The concept of entropy is born from the idea that a spontaneous transformation leads to a dispersion of energy. Often in these processes a dispersion of matter is also involved and this can contribute to the dispersal of energy in some systems.

- entropy can be seen as a function that describes the number of possible arrangements of energy and
- nature proceeds spontaneously towards the states that are most likely to exist
- these observations are the foundation of statistical thermodynamics

A statistical approach can be used to demonstrate how energy is distributed in a system. For this approach to be accurate, the system should include a large number of particles.

A simple case: the distribution of two quanta of energy on four particles



Possible distribution of the quanta of energy

Two quanta of energy on four atoms

There are 10 different ways to distribute the 2 quanta of energy on the 4 atoms. It is more likely that the energy is distributed over multiple particles, rather than being concentrated in a single position.

Boltzmann's entropy equation

Ludwig Boltzmann developed the idea of considering the energy distribution at various energy levels in order to calculate entropy

$$S = k \cdot \log w$$

Zentralfriedhof, Vienna

$k = 1.3807 \cdot 10^{-16}$ J/mol   Boltzmann constant

w = the number of different ways in which energy can be distributed in the available energy levels

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Some values of standard molar entropy at 298 K

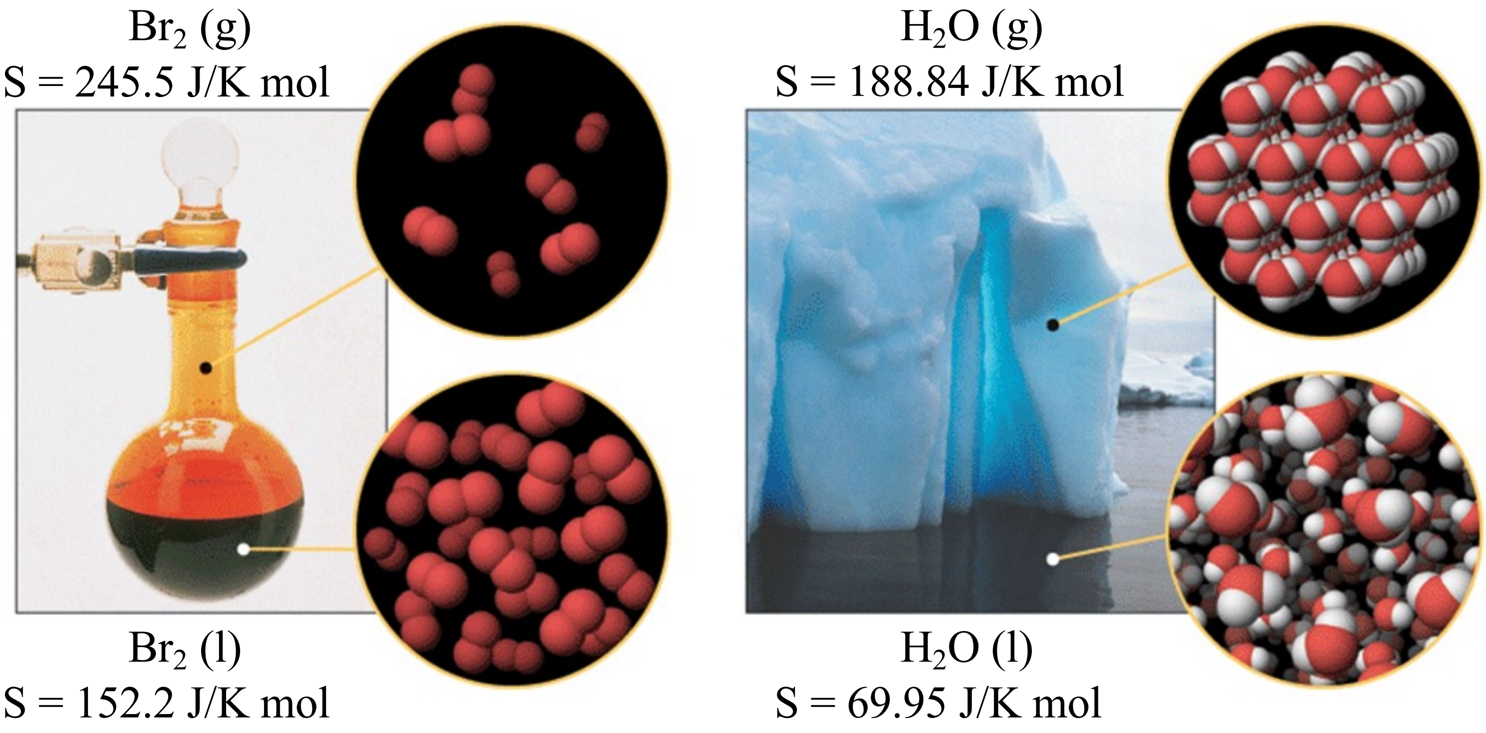
element	entropy (J/K mol)	compound	entropy (J/K mol)
C (diamond)	2.377	CH_4 (g)	186.3
C (grafite)	5.6	C_2H_6 (g)	229.2
C (vapor)	158.1	C_3H_8 (g)	270.3
Ca (s)	41.59	CH_3OH (l)	127.2
Ar (g)	154.9	CO (g)	197.7
H_2 (g)	130.7	CO_2 (g)	213.7
O_2 (g)	205.1	H_2O (g)	188.84
N_2 (g)	191.6	H_2O (l)	69.95
F_2 (g)	202.8	HCl (g)	186.2
Cl_2 (g)	223.1	NaCl (s)	72.11
Br_2 (l)	152.2	MgO (s)	26.85
I_2 (s)	116.1	$CaCO_3$ (s)	91.7

Source: NIST table (http://webbook.nist.gov)

Some useful general concepts

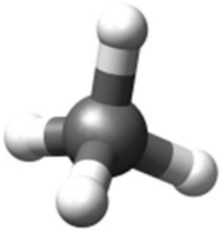
1) Comparing similar compounds: $S_{GAS} >> S_{LIQUID} >> S_{SOLID}$

In solids particles occupy almost fixed positions in a crystal lattice.
When a solid melts, its particles can adopt different positions and this increase disorder. When a liquid evaporates , the constraints due to interactions between particles become negligible and and entropy increases.
(III law of thermodynamics: at 0 K in a perfect crystal there is no disorder, i.e. S = 0).

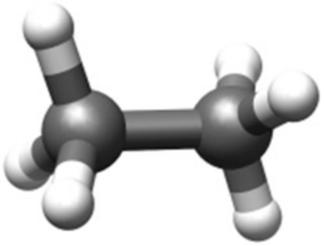


Some useful general concepts

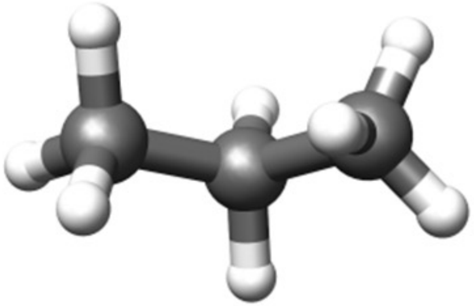
2) In general, large molecules have a larger entropy than small ones



CH_4 (g)
S = 186.3 J/K mol



C_2H_6 (g)
S = 229.3 J/K mol

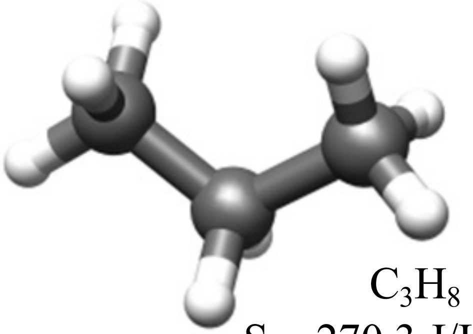


C_3H_8 (g)
S = 270.3 J/K mol

And molecules with a more complex structure have a larger entropy than simples ones.

Ar (g)
S = 154.9 J/K mol

CO_2 (g)
S = 213.7 J/K mol



C_3H_8 (g)
S = 270.3 J/K mol

More complex molecules have more chances to rotate, bend and vibrate in space. This results in a greater number of states on which energy can be distributed.

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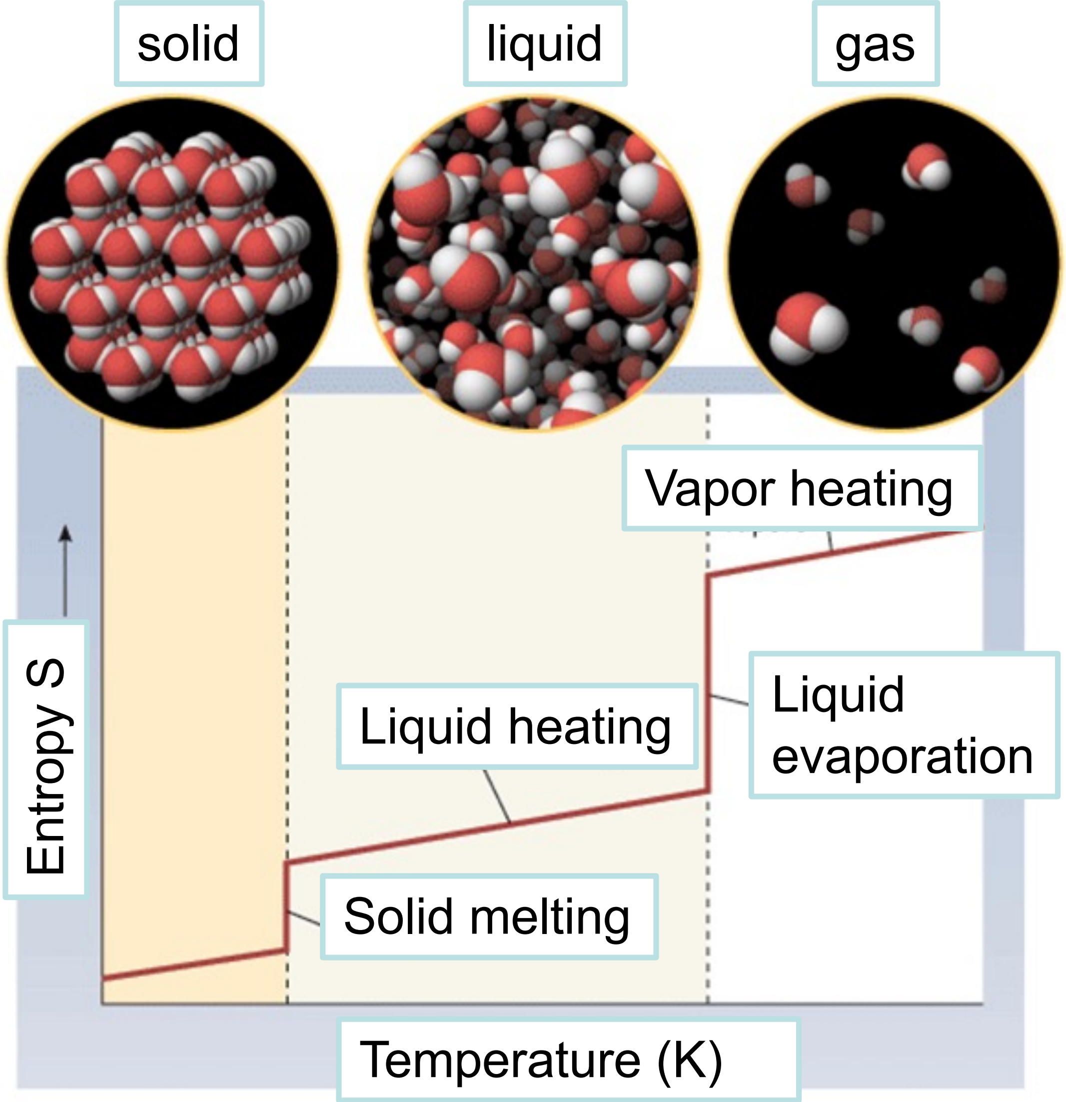
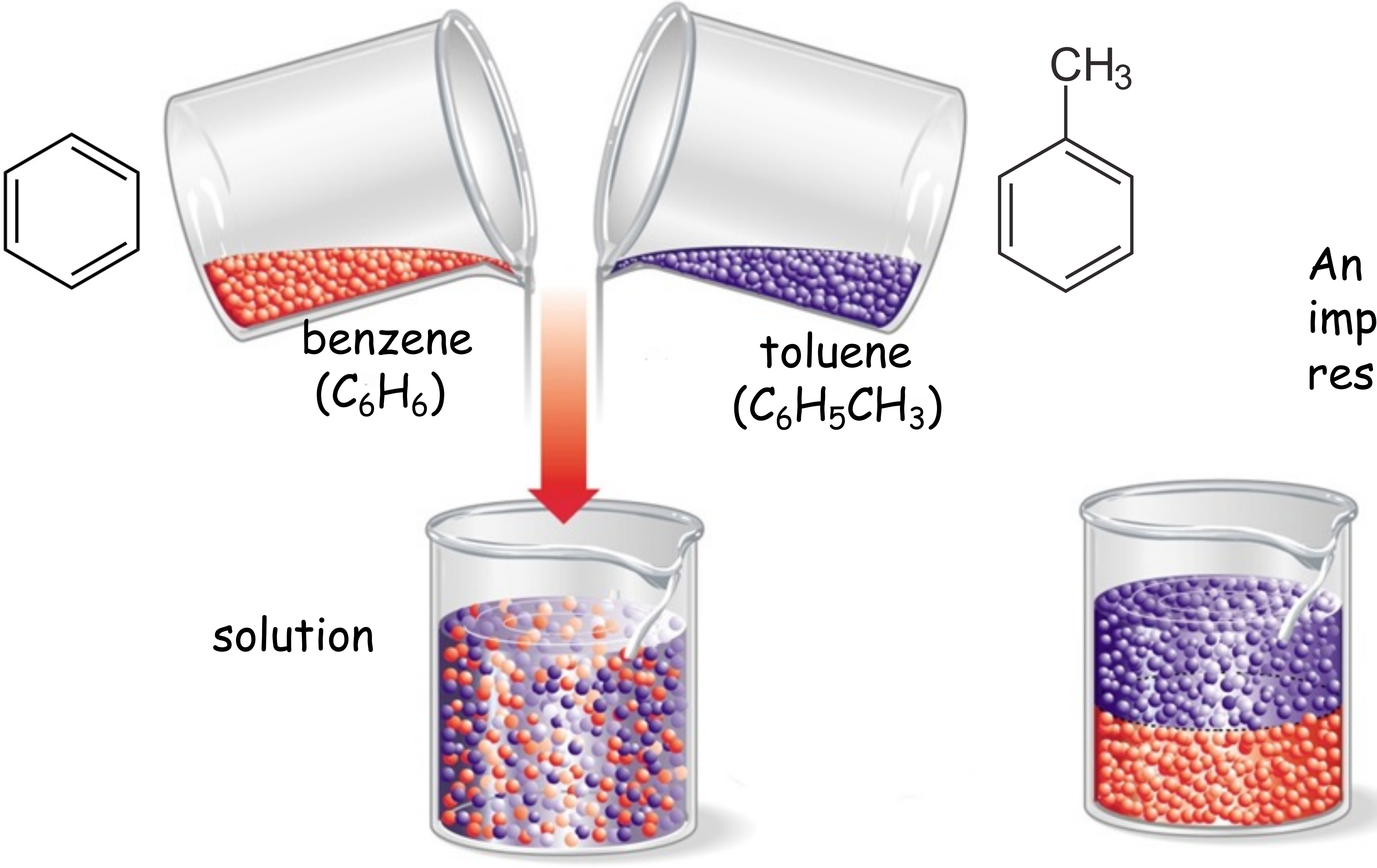
Some useful general concepts

3) For a given substance, entropy increases as temperature rises (see III law of thermodynamics).
State transitions are accompanied by large variations of entropy.



There are two natural tendencies in spontaneous processes: the tendency toward a lower energy state and the tendency towards a more disordered state



benzene
(C_6H_6)

toluene
($C_6H_5CH_3$)

An
impossible
result

solution

FREE ENERGY

Evaluating the spontaneity of a reaction by examining the variation of entropy that undergoes the system and the environment during a transformation may be unworkable. The ideal would be to focus on some property of the system, that can provide information about the direction of a spontaneous process.

This opportunity exists and it is possible to define a new state function, called Gibbs free energy (G) (since

$$G = H - TS$$

from which we obtain the fundamental relationship,
for a transformation at constant T:

$$\Delta G = \Delta H - T\Delta S$$

The spontaneity criterion for a reaction

The free energy represents the maximum energy available to perform work

$$\Delta G = \Delta H - T\Delta S$$

when $\Delta G > 0$ the process is not spontaneous
when $\Delta G = 0$ the process is at equilibrium
when $\Delta G < 0$ the process is spontaneous

Free Energy and equilibrium constant

$$\text{Reagents} \rightleftarrows \text{Products}$$

(25° C, 1 atm, 1M)
Standard conditions

$$\Delta G_0^{\text{react}} = G_0^{\text{prod}} - G_0^{\text{reag}}$$

$$\Delta G^{\text{react}} = G^{\text{prod}} - G^{\text{reag}}$$

For the generic x reagent or product:

$$G^X = G_0^X + RT \ln [X]$$

$$aA + bB \rightleftarrows cC + dD$$

$aG^X = aG_0{}^A + aRT \ln [A]$
$bG^X = bG_0{}^B + bRT \ln [B]$
$cG^X = cG_0{}^C + cRT \ln [C]$
$dG^X = dG_0{}^D + dRT \ln [D]$

$$\Delta G^{reaz} = \Delta G_0{}^{reaz} + RT \ln [C]^c [D]^d / [A]^a [B]^b$$

At equilibrium $\Delta G^{reaz} = 0$ --> $- \Delta G_0{}^{reaz} = RT \ln [C]^c [D]^d / [A]^a [B]^b$

Since at equilibrium this ratio is equal to K_{eq}

$$- \Delta G_0{}^{react} = RT \ln K_{eq} \qquad (K_{eq} = e^{- \Delta G/RT})$$

THE II PRINCIPLE AND FREE ENERGY: a thermodynamically favored process, at constant T and P, tends to proceed in the direction that minimizes free energy.

If ΔG is…	**The process is…**
Negative	Thermodynamically favoured
Zero	Reversible (equilibrium)
Positive	Thermodynamically unfavoured

Spontaneity criterion: $\Delta G < 0$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

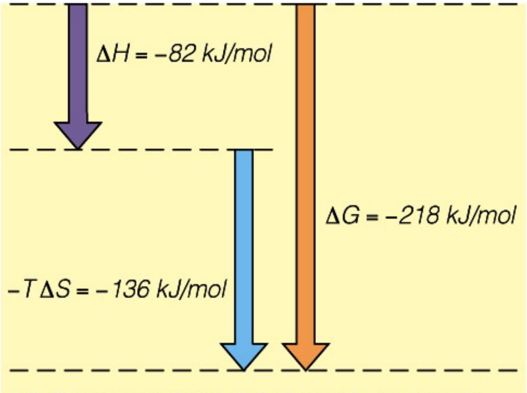
If $\Delta H<0$ and $\Delta S>0$ => ΔG is always < 0 the reaction is always spontaneous.
If $\Delta H>0$ and $\Delta S<0$ => ΔG is always > 0 the reaction is never spontaneous.

Cases where entropic and enthalpic factors give opposite contributions:

Enthalpic factor	Entropic factor	comparison	Free energy	reaction
$\Delta H > 0$	$T\Delta S > 0$	$\Delta H < T\Delta S$	$\Delta G < 0$	spontaneous
$\Delta H > 0$	$T\Delta S > 0$	$\Delta H > T\Delta S$	$\Delta G > 0$	not spontaneous
$\Delta H < 0$	$T\Delta S < 0$	$\|\Delta H\| > T\Delta S$	$\Delta G < 0$	spontaneous
$\Delta H < 0$	$T\Delta S < 0$	$\|\Delta H\| < T\Delta S$	$\Delta G > 0$	not spontaneous

For every chemical and physical transformation the competition between the enthalpy and the entropic terms determines the direction

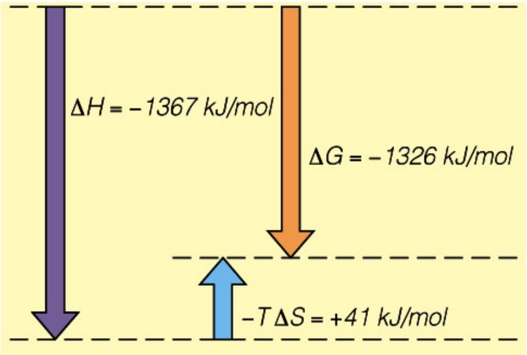
Always $\Delta G < 0$, but…



(a) Fermentazione del glucosio a etanolo

$C_6H_{12}O_6\ (s) \rightarrow 2C_2H_5OH\ (l) + 2CO_2\ (g)$

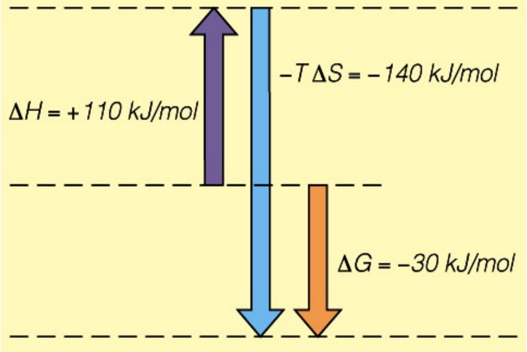
Both ΔH and ΔS favor the reaction



(b) Combustione dell'etanolo

$2C_2H_5OH\ (l) + 3O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O\ (l)$

The reaction is enthalpy driven



(c) Decomposizione del pentossido di azoto

$N_2O_5\ (s) \rightarrow 2NO_2\ (g) + 1/2O_2\ (g)$

The reaction is entropy driven

Heat is absorbed but entropy increases due to the formation of gaseous products.

… TWO IMPORTANT POINTS:

Whether a transformation is favored or not has nothing to do with its velocity. A reaction can have a $\Delta G \ll 0$ but proceed very slowly.

C (diamond) ->C (graphite) $\Delta G = - 288$ kJ/mol

The velocity of reactions is studied by kinetics.

- ✓ In an open system entropy can decrease.

(living matter)

http://biochimica.bio.uniroma1.it/didattica/bellelli.htm

Relazione fra fem e costante di equilibrio

Dalla termodinamica è possibile dimostrare che la variazione di energia libera di una reazione è uguale al lavoro utile massimo che quella reazione può produrre a T e P costanti. In una cella voltaica il lavoro è quello elettrico, e riferendosi a reagenti e prodotti in condizioni standard

$$\Delta G^{o} = -z \cdot F \cdot \Delta E^{o}$$

Data la fem standard di una cella è possibile calcolare (misurare) la costante di equilibrio della reazione di cella.

$$\Delta G^{o} = -z \cdot F \cdot \Delta E^{o} = -RT \ln K_{EQ}$$

Relationship between emf and the equilibrium constant K

Using thermodynamics it is possible to demonstrate that the free energy change of a reaction is equal to the maximum useful work that that reaction can produce to T and P constants. This corresponds the the electric work produced by a cell, and referring to reagents and products in standard conditions:

$$\Delta G^{o} = -z \cdot F \cdot \Delta E^{o}$$

If we know the standard potential we can determine the equilibrium constant of the redox reaction.

$$\Delta G^{o} = -z \cdot F \cdot \Delta E^{o} = -RT \ln K_{EQ}$$

Since

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

at constant pressure

$$\Delta S = \frac{\Delta H}{T}$$

multiplying ΔS by T, the difference between the entropic loss and ΔS is the energy available for performing work