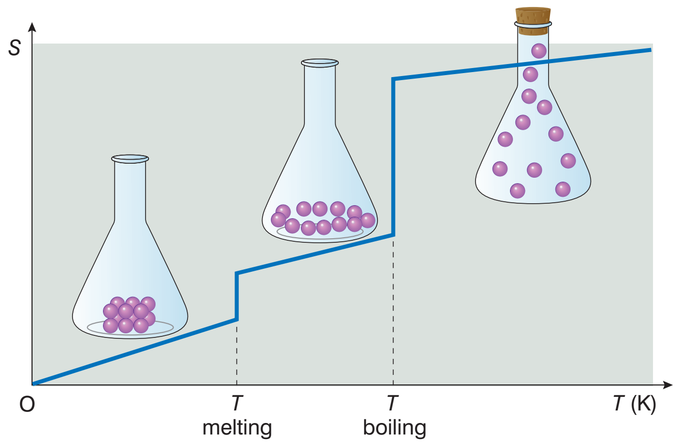
Every day we can observe around us **irreversible spontaneous phenomena**: these phenomena are characterised by the fact that they lead to a net *dispersion of energy*.

The **entropy (S)** is the magnitude that measures the degree of dispersion of the energy of a system and the symbol for its unit is J/K. For all pure and crystalline substances entropy is zero at 0 K (absolute zero) as under these conditions there is only one way to distribute the energy of the system.

With regard to entropy change with temperature for a generic substance, it can be observed that the major variations of entropy correspond to changes of state (when temperature remains constant) in which the greatest variation in the degree of freedom of the particles of the system occurs, and therefore an increase in the ways the energy of the system is dispersed.



In an isolated system, only those changes that result in an increase in energy dispersion, and therefore an increase in entropy, can occur. In other words, the entropy of the final system must be greater than the initial state:

Since $\Delta S = (S_{final} - S_{initial})$, it follows that $(S_{final} - S_{initial}) > 0$.

The fundamental principles that govern all transformations in the universe, and therefore chemical reactions, can be summarised as follows:

- the total energy of the universe is constant;
- the total entropy of the universe is increasing.

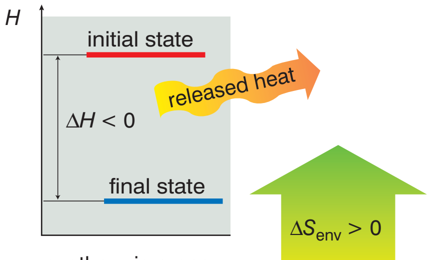
Normally, no chemical changes occur in an isolated system and for this reason to evaluate the change of entropy in the universe it is necessary to take into account both variations of entropy in the system and in the environment. The second law can therefore be written in the following form:

$$\Delta S_{univ} = (\Delta S_{sys} + \Delta S_{env}) > 0$$

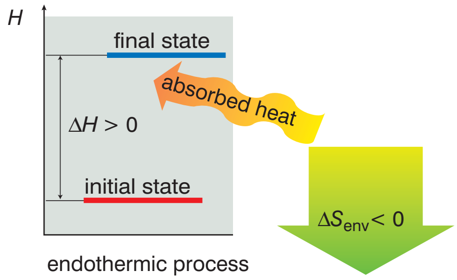
Evaluation of the *change in entropy of the environment* depends on the influence transformations have on energy, that is in the two following situations:

An *exothermic transformation* **($\Delta H < 0$)** is always accompanied by an increase in the entropy of the environment **($\Delta S_{env} > 0$)**.

An *endothermic transformation* **($\Delta H > 0$)** is always accompanied by a decrease in the entropy of the environment **($\Delta S_{env} < 0$)**.



exothermic process



endothermic process

To predict the *change in entropy of a system* as a result of a transformation it is necessary to distinguish three different situations.

- When $\boldsymbol{\Delta S_{sys} > 0}$, changes of state lead to an increased freedom of movement of the particles of the system (melting, evaporation, sublimation), and naturally entropy decreases in the reverse changes of state.
- When $\boldsymbol{\Delta S_{sys} > 0}$, in chemical reactions there is an increase in the number of species in the gaseous state. For example:

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

  Of course, the entropy decreases in reactions in which the opposite occurs.
- When $\boldsymbol{\Delta S_{sys} \sim 0}$, in chemical reactions both the reactants and the products are in the same liquid or solid state.

To predict whether a given chemical reaction can occur it is useful to remember the following criteria:

- all exothermic reactions that lead to an increase in the entropy of the system ($\Delta S_{env} > 0$ and $\Delta S_{sys} > 0$) are **possible reactions**;
- all endothermic reactions that would lead to a decrease in the entropy of the system ($\Delta S_{env} < 0$ and $\Delta S_{sys} < 0$) are **impossible reactions**;
- reactions in which ΔS_{env} and ΔS_{sys} have opposite signs are **possible reactions only under certain conditions**.

In the latter case, system temperature is crucial: an increase in temperature can make endothermic transformations possible which result in an increase in the entropy of the system; and conversely, a decrease in temperature can make exothermic transformations possible which reduce the entropy of the system.

Free energy (***G***) is a thermodynamic quantity which enables the feasibility of a transformation, that takes place at a certain temperature, to be predicted based on the values ΔH and ΔS_{sys}. The relationship between these three quantities is given by the *Gibbs equation*:

$$\boldsymbol{\Delta G = \Delta H - T \cdot \Delta S}$$

A transformation can only occur if $\boldsymbol{\Delta G < 0}$, and this certainly occurs if both the factors $\boldsymbol{\Delta H < 0}$ and $\boldsymbol{\Delta S_{sys} > 0}$ are favourable. In the event that these factors are not favourable the determining factor is the value of temperature at which the transformation takes place.