# Heat, enthalpy and entropy

Energy considerations play a central role in virtually all processes in science and technology: Does one need to add energy to a chemical reaction so that it takes place, or does it run spontaneously and with the release of energy? How much energy is released in an organic cell as a product of metabolism? How does an engine need to be designed so that the energy of the fuel is converted into mechanical energy with optimum effect?

Different terms are used for "energy" depending on the special field. In chemistry, for example, one speaks of the "enthalpy" or the "free enthalpy" of a chemical reaction, while in thermodynamics "internal energy" and "heat" are the key parameters. How are all these terms related and what do they state?

## Heat and enthalpy are energy quantities

### Heat

**Heat (Q)** is an amount of energy. It is equivalent to the energy that is needed to raise a system from a lower temperature to a higher temperature. The greater the temperature difference ($\Delta T$) is to be, the more heat has to be input – the two quantities are directly proportional to one another. Exactly how much energy needs to be expended depends on the material. This material property is called "heat capacity" C. Referred to the mass (m) of the material, one speaks of the "specific heat capacity" (also shortened to "specific heat" which can be misunderstood): $c = C/m$.

The heat energy to be expended ("heat" for short) can thus be calculated via the formula:

$$Q = C \cdot \Delta T = c \cdot m \cdot \Delta T$$

Water, for example, has a specific heat capacity $c_{H2O} = 4.183$ kJ/ (kg K) (= 1 kcal/ (kg K) ), i.e. the amount of energy (heat) required to heat 1 kg water by 1 K is 4.183 kJ.

Note: The specific heat capacity itself is temperature-dependent. A distinction must also be made according to the type of process: If the volume remains constant, one speaks of "isochoric processes". In this case, the specific heat capacity c is characterized by an index "V" (for constant volume), abbreviated to: $c_V$. If, on the other hand, the pressure remains constant, one speaks of "isobaric processes". In this case the specific heat capacity c is characterized by an index "p" (for constant pressure), abbreviated to: $c_p$. (Pressure, volume and temperature can, of course, also change simultaneously in nature but in that case the calculations quickly become complicated so that one is generally limited to a few special cases, like those mentioned above.)

Conversely, heat can naturally also be released. For this purpose a system must go from a higher to a lower temperature, in other words cool down. Whether heat is transferred to the system or released from it is expressed by the corresponding sign:

| | |
|---|---|
| Input heat | positive sign |
| Output heat | negative sign |

## Internal energy

In thermodynamics, the term **internal energy (U)** is generally used if the entire energy of a closed system is meant.

With a single-atom, ideal gas this depends, for example, only on the temperature (T) of the gas:

$$U = \frac{3}{2} N \cdot k \cdot T$$

k: Boltzmann constant = $1.38 \cdot 10^{-23}$ J/K, N: number of particles.

The internal energy of a closed system is constant. Heat energy (Q) and work (W) can only be reciprocally converted. This 1st law of thermodynamics is expressed as a formula thus:

$$\Delta U = 0 = \Delta Q + \Delta W$$

In the case of a not closed system the convention applied is that work or thermal energy absorbed by the system is given a positive sign while heat or thermal energy given off by the system is given a negative sign. This produces the following equations for a

- Heat engine (for example, a gas or steam turbine):     $\Delta U = \Delta Q - \Delta W$
- Inverse heat engine (for example, a heat pump):     $\Delta U = \Delta W - \Delta Q$

## Enthalpy

**Enthalpy (H)** is equivalent to the "heat content" of a system:

$$H = U + p \cdot V$$

A host of reactions in chemistry run with the absorption of heat or release heat (so-called thermo-chemical reactions). The starting materials of a chemical reaction are called "educts" and the end products are termed "products". The heat that needs to be transferred in a reaction (under constant pressure) or is released is equivalent to the difference between the heat contents of the educts and the products, in other words the difference between their particular enthalpy:
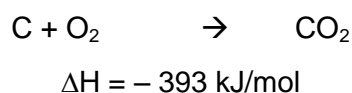
$$\Delta H = H(\text{products}) - H(\text{educts})$$

This difference is known as the **reaction enthalpy** and this can be determined experimentally.

Reactions in which heat is released ($\Delta H < 0$) are known as exothermic.

Reactions that "use up" heat ($\Delta H > 0$) are known as endothermic.

An example of an exothermic reaction is the combustion of carbon:

$$C + O_2 \quad \rightarrow \quad CO_2$$
$$\Delta H = -393 \text{ kJ/mol}$$

## Without entropy it is impossible to predict whether a process will run

The reaction enthalpy only provides information about whether heat is released or absorbed in a reaction. Although it is known that exothermic reactions run spontaneously, it cannot be deduced from this whether a reaction in which heat must be transferred (endothermic) might not also run spontaneously. In this case therefore it is not sufficient to only look at the reaction heat. Thermodynamics also needs an additional factor in order to explain why heat cannot go from a lower to a higher temperature level spontaneously (2nd law of thermodynamics).

In nature there are a very large number of processes which although they can run spontaneously can only run in one direction. These kinds of processes are called "irreversible", i.e. "not easily reversible". If, for instance, you open a gas cylinder in a room under normal atmospheric pressure, gas spontaneously flows out of the cylinder but it will certainly not flow back in spontaneously. (It can, however, be put it back into the cylinder "artificially" with great effort.) Generally speaking, every spontaneous process in nature endeavors to cause a state of maximum disorder in the affected system. The measure of this disorder is known as **entropy (S).**

In the case of processes running in a closed system, entropy never decreases when viewed from the long-term perspective. (Small statistical variations are possible in the short term.)

This can be expressed as the formula:

$$\Delta S \geq 0$$

This represents a particularly simple formulation of the 2nd law of thermodynamics.

Changes in the state of order of a system can also be caused specifically. That is what occurs, for example, during the smelting process through the application of heat. In the solid phase the body has a higher level of order (lower entropy) than in the liquid phase. During phase transition, in other words during smelting, transfer of heat does not result in an increase in the temperature, but in an increase in entropy; this is proportional to the amount of heat transferred. The increase in entropy therefore also leads to the fact that the body does not heat up as long as it is not completely molten.

### Information for specialists

- Systems can be readily returned to a state of order "artificially", i.e. their entropy can be reduced. For example, heat can be extracted from a system so that it solidifies. That means, though, that the environment of the liquid has absorbed this heat and has thus changed to a state of higher disorder. The entropy of the system as a whole (in this example: the former liquid and its environment) has therefore not been reduced.
- In statistical physics entropy is defined by the probability with which a system assumes a particular state:

$$S = k \cdot \ln(W)$$

k: Boltzmann constant, W: thermodynamic probability.

## Free enthalpy connects energy and entropy

In order to be able to tell whether a process will run "spontaneously" it is also necessary to analyze the entropy of the system in addition to the energy. For this purpose the concept of **free enthalpy**

**(G)** has been introduced. That concept establishes this connection and is a measure of the spontaneous change of a system:

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

In every spontaneous process, the free enthalpy of a system decreases. A process of this type is known as "exergonic", $\Delta G < 0$. When $\Delta G = 0$ the process stops. On the other hand, processes in which the free enthalpy increases, i.e. $\Delta G > 0$, are termed "endergonic".

Free enthalpy provides an explanation for the fact that endothermic reactions can run spontaneously if only the entropy gain in the reaction is suitably high.

An example of an exergonic, endothermic process:

$$NH_4NO_3 + H_2O \rightarrow NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H = +29 \text{ kJ/mol}$$
$$\Delta G = -4 \text{ kJ/mol}$$
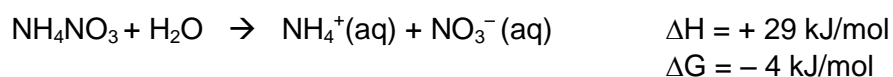
Entropy (disorder) therefore increases strongly when ammonium nitrate is dissolved in water.

## Summary

The following table provides an overview of all terms and their formulae:

| Quantity | Formula symbol | Formula |
|---|---|---|
| Energy | E | Depending on the form of energy, e.g.<br>Potential energy $\quad E_{pot} = m \cdot g \cdot h$<br>Radiation energy $\quad E_{radiation} = h \cdot \nu$ |
| Internal energy | U | $U = \dfrac{3}{2} N \cdot k \cdot T$ (single-atom ideal gas)<br>Change: $\quad \Delta U = Q + W$ |
| Heat | Q | $Q = C \cdot \Delta T = c \cdot m \cdot \Delta T$ |
| Enthalpy | H | $H = U + p \cdot V$<br>exothermic $\quad \Delta H < 0$<br>endothermic $\quad \Delta H > 0$ |
| Free enthalpy | G | $G = H - T \cdot S$<br>$\Delta G = \Delta H - T\Delta S$<br>exergonic $\qquad \Delta G < 0$<br>endergonic $\qquad \Delta G > 0$ |
| Entropy | S | $S = k \cdot \ln(W)$, where: $\Delta S \geq 0$ (this always applies) |