GLOBAL IMPLICATIONS OF THE SECOND LAW OF THERMODYNAMICS

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Summary

The formulation of the second law of thermodynamics has been explained. Its significance and considerable difference of its character in comparison with other laws of physics has been stressed. Its probabilistic interpretation and the phenomenon of fluctuations has been discussed. The law of energy dissipation has been presented and the definition of exergy characterizing the quality of energy has been formulated. The causes of the formation of stable dissipative structures and the influence of solar radiation on the stable state of the terrestrial environment have been explained. The deleterious impact of the emission of waste products (and especially of CO_2) on the state of the natural environment has been presented.

The problem of the depletion of non-renewable natural resources and its evaluation by means of the ecological cost (cumulative consumption of non-renewable exergy) has been discussed. The possibilities of the conservation of the natural environment have been presented. The most important are: the reduction of exergy losses leading to an improvement of the thermodynamic imperfection of processes, the reduction of the emission of CO_2 aiming at the prevention against an increasing greenhouse effect, the

utilization of renewable energy resources ensuring the conservation of non-renewable ones and the decreased deleterious impact on the environment, the utilization of waste products ensuring a decrease of the pollution of the environment and conservation of non-renewable resources, the mitigation of the consumption of final products by means of a new tax, proportional to the ecological cost.

1. Significance of the Second Law of Thermodynamics

The second law of thermodynamics is one of the most important laws of physics. It is a sole law not symmetric in relation to time. All the real macroscopic processes are irreversible. It is impossible to restore the initial state of all the bodies taking part in the process.

For example, if a body falls from some height, its initial position can be regained but it requires to perform some work, which is connected with some consumption of fuel (if an electrical of mechanical motor is used for this purpose) or some amount of food (if a man or an animal performs the necessary work). Hence all the real processes are subject to the passage of time. Its direction cannot be changed.

The second law of thermodynamics results from observation and experiments. All the systems containing a sufficiently great amount of material particles fulfill this law. Even cosmic observations confirm this law. Only in systems containing a small amount of material particles instantaneous deviations from the second law can appear.

The mathematical formulation of the second law became possible after the introduction of the concept of entropy by Rudolf Clausius (1865). This quantity is a function of state (hence depending on the macroscopic parameters of the body) and increases when the considered body absorbs heat (delivered from external sources or formed inside the body thanks to mechanical or hydraulic friction):

$$dS = \frac{dQ + d\,Q_f}{T} \tag{1}$$

where:

$Q\,, Q_f$ = heat delivered from external sources and heat of friction,

T = absolute temperature of the body.

The mathematical formulation of the second law states that the *sum of entropy increase values of all the bodies taking part in the process* (termed also *entropy generation*) *is always positive*. For example, if a hot cup of tea cools down, its entropy decreases, but simultaneously the entropy of the environment increases and this increase is greater than the drop of entropy of the considered cup of tea.

A process occurring without any resistances (friction, temperature gradient, concentration gradient, gradient of the chemical potential) would be reversible. Such a process would run infinitely slowly and represents a border between possible and impossible processes.

According to the cited formulation every separated system tends to a state of maximum entropy. This state represents an internal equilibrium of the system. Only reversible processes are possible in the vicinity of this state. The macroscopic parameters of this state would be constant. Hence it would be a dead state. Basing upon this statement Clausius formulated the hypothesis of the thermal death of the universe. He assumed the universe to be a separated system. After a sufficiently long time all the differences of macroscopic parameters and all the processes should disappear in the universe.

We owe to Ludwig Boltzmann (1872) the molecular explanation of the second law. He stated that entropy is proportional to the logarithm of the thermodynamic probability of the macrostate of a body, where the thermodynamic probability expresses the amount of microphysical possibilities of the realization of the considered macrostate:

$$S = k \ \ln \mathrm{W} \tag{2}$$

where:

k = Boltzmann constant, $1.36\cdot 110^{-26}$ kJ/K,
W = thermodynamic probability of the considered macrostate of the body.

The macrostate is described by macroscopic parameters (temperature, pressure, volume, chemical composition). Every macrostate can be realized by means of numerous microstates. The amount of microstates representing the considered macrostate (the thermodynamic probability) is expressed by a very high number.

The concepts of the macrostate and microstate may be explained by means of the example presented in Figure 1. The closed vessel is divided into two equal parts by means of a wall with an opening. The system contains six distinguishable molecules.

Thanks to their thermal motions the distribution of the molecules between the parts of the vessel changes. Every distribution characterized by the amount of molecules contained in the left and right-hand part of the vessel represents a separate macrostate (this distribution decides, for example, about the pressure in these parts of the vessel).

Hence 7 macrostates may appear (Table 1). But thanks to the fact that the molecules are distinguishable, every macrostate can be realized by means of some microstates. For example, the macrostate characterized by 2 molecules in the left part and four in the right one can be realized by means of 15 microstates: AB, AC, AD, AE, AF, BC, BD, BE, BF, CD, CE, CF, CE, DF, EF.

The maximum amount of microstates characterizes the symmetric distribution. Hence this is the equilibrium state appearing with the greatest probability.

According to the Boltzmann's formulation the processes usually tend towards a greater probability. A more probable state represents a greater disorder (if the order is understood as, e.g., the structure of a crystal; for example, in Figure 1 the symmetric distribution denotes the greatest disorder). Hence entropy can be interpreted as a measure of the disorder.

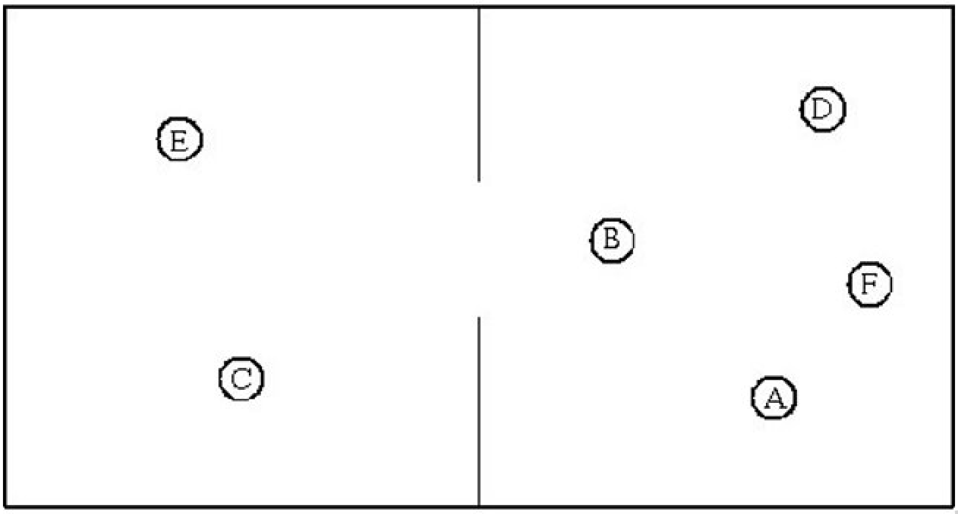

Figure 1. Distribution of molecules between two parts of the vessel.

Macrostates		Amount of microstates *W*
Amount of molecules in the part		
left	right	
6	0	1
5	1	6
4	2	15
3	3	20
2	4	15
1	5	6
0	6	1

Table 1. Macrostates and microstates in a system containing a small amount of molecules.

The theory of Boltzmann explains also, why in small systems of particles processes not obeying the second law can occur. Thanks to the chaotic thermal motions of the material particles the thermodynamic probability of the state changes and sometimes can become smaller. Such a deviation is termed *fluctuation*. The smaller the number of the considered particles, the more often fluctuations opposite to the second law can occur and the greater can be their scope. For example, in the system presented in Figure 1 the fluctuation proceeding from the symmetric distribution of the molecules to an asymmetric one has a relatively great probability.

In the Boltzmann's time many mathematicians criticized his theory. For example, Poincaré (1893) maintained that every state should appear again after a sufficiently long time, thanks to the chaotic thermal motion. Hence all the states appear repeatedly infinite times. The sharp criticism of Boltzmann's theory led him to suicide. Later his famous formula (2) has been cut into his gravestone. Even classical methods of mathematics are sufficient to overthrow the criticism of Boltzmann's theory. As proved by Smoluchowski, in macroscopic processes the observable fluctuations have a very small probability. For example, when some stone has fallen from some height, it is really not probable that the molecules of air, thanks to their thermal motion, will push it up again to its initial height. The waiting time for fluctuation leading to the initial state of the system can be much greater than the time of the existence of the universe even in small systems (e.g. in the volume of gas as great as 1 cm^3).

It should be stressed, that the microphysical reasons of irreversibility have so far not sufficiently been explained (Feynman, 2000). Almost all the subatomic phenomena are symmetric in relation to time, but according to new discoveries there exist non-symmetric (hence irreversible) phenomena. According to the actual opinion of physicists the principle of causality does not govern microphysical phenomena. Causality in the macrophysical world results only from the principle of probability characterizing the second law. Nevertheless, the theory of fluctuations helps substantially to understand the processes occurring on the Earth's surface.

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Biographical Sketch

J. Szargut was born in September 9, 1923 in Lwów. 1946–1954 assistant of the Chair of Thermal Machines of the Technical University of Silesia, 1955 PhD-degree in the Technical University of Silesia. 1957–1969 head of the Chair of Thermal Energetics of the Technical University of Silesia. 1971–1993 Director of the Institute of Thermal Technology of the Technical University of Silesia. Since 1976 member of the Polish Academy of Sciences. Since 1993 retired professor and professor for scientific research in the Institute of Thermal Technology of the Technical University of Silesia. Author or co-author of 260 scientific papers and 20 scientific and technical books.