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LECTURE No7

DISSIPATIVE FUNCTION ENTROPY AND STABILITY

Stationary state. Prigogine principle of minimum entropy production. Time hierarchy of stationary states

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Dissipative function. Entropy and Stability

The second principle of thermodynamics states that an isolated system moves spontaneously towards maximum entropy. When this state is achieved, then the system is in thermodynamic equilibrium.

The *entropy production* is always positive, but can approach zero asymptotically.

The condition $\sigma = 0$ means an idealized reversible process. Thermodynamically, a process is defined as being reversible if it can be repeated an arbitrary number of times without requiring the supply of additional energy.

In contrast to a closed system, where as a result of energy transformations only an entropy increase is possible, in an open system an entropy decrease is even possible. This can be done if substances are incorporated which have a low entropy content, in exchange for entropy-rich substances which are being extruded.

To characterize this process, an entropy flux ($\frac{dS_e}{dt}$) is formulated which penetrates the whole system, and, the total entropy balance of the system can be written.

Thermodynamically based classification of stationary states

We define a *stationary state* as a state in which the structure and parameters are time independent.

The reasons leading to this quality can be quite different. The water level of a lake can be time independent (i.e. constant), either because there is no inflow into the lake, and no outflow, or because inflow and outflow are equal to each other. These two kinds of stationary states can be distinguished by their entropy production. In the first case no energy is required to maintain this state, therefore there is no entropy production, the system is in thermodynamic equilibrium ($\sigma = 0$).

In contrast, the lake with exactly the same in- and outflow is in a *steady state*. This is a stationary state with entropy production ($\sigma > 0$). A steady state cannot be defined by its kinetic properties.

The presence, or the absence of entropy production indicates whether the given stationary state is a thermodynamic equilibrium ($\sigma = 0$), or whether it is a steady state ($\sigma > 0$). Furthermore, in the case of thermodynamic equilibrium, **global** and **local** equilibria must be distinguished.

In case of a *global equilibrium*, the function of free energy indicates only one minimum - no alteration, however strong it may be, can bring the system into another equilibrium state. E.g. equilibrium distribution of particular kinds of ions between the cell and its environment.

In the case of *local equilibrium*, the energetic function indicates two or more minima which are separated by more or less large energy barriers.

Entropy production is not only an indicator for distinguishing between the equilibrium state and steady state, but is also important for some stability considerations.

$$\sigma = \frac{dS_i}{dt} = \sum_{k=1}^{n} X_k J_k > 0$$

Prigogine was able to show that systems tend to develop towards a reduced entropy production. This is the *Prigogine principle of minimal entropy production.*

Systems which are not far from thermodynamic equilibrium, and which are kept in imbalance by continuously acting forces consequently may move towards a steady state, the stability of which is included in this criterion.

It is still controversial as to whether the Prigogine principle can be applied to large systems which include a great number of different subsystems, particularly those which are far from equilibrium.

If a system deviates from the region of linear approaches, then the Prigogine principle is no longer valid. In contrast to steady states in the scope of linear thermodynamic approaches which are always stable and do not show any kinds of metastability, systems in the region of non-linear approaches show more complicated behavior.

The living organism as a whole, when considered within a limited period of time, is in a stationary state with entropy production, i.e. in a steady state. It is made up of a great number of subsystems which are ordered in a defined time hierarchy. The steady state of the system as a whole does not imply that all of the sub-systems are also in a steady state.

A large proportion of them, particularly those with a short time constant, are in thermodynamic equilibrium. If the system as a whole changes its parameters slowly, then these sub-systems are capable of following such changes quickly, so that they almost completely adapt within their characteristic time, and thus are always in a stationary state. This is sometimes called a *quasi-stationary,* or *quasi-equilibrium* state.

The following example will illustrate this: the water content of a tissue depends on the ionic composition of its cells. Sodium and potassium ions are being actively transported against passive fluxes, giving rise to a steady state. In this way the active transport, and the corresponding passive fluxes regulate the osmotic properties of the cells. The characteristic time of the water flux is much shorter than that of the cations. As a result, the water in the interior of the cells is always in osmotic equilibrium with the surrounding medium.

Physiological steady state

The environment of living organisms is absolutely essential for them, not only as a source of free energy but also as a source of raw material. Living organisms are open systems because they exchange both energy and matter with their surroundings.

Although living organisms may appear to be in equilibrium, because they may not change visibly as we observe them over a period of time, actually they usually exist in a steady state, that condition of an open system in which the rate of transfer of matter and energy from the environment into the system is exactly balanced by the rate of transfer of matter and energy out of the system.

It is therefore part of molecular logic of the living state that the cell is a non-equilibrium system, a machine for extracting free energy from the environment, which it causes to increase in randomness.

Moreover, living cells are highly efficient in handling energy and matter. The analysis of the magnitude and the efficiency of energy exchanges in steady state or open systems is much more complex than in closed systems **(Non-equilibrium or irreversible thermodynamics).**

OPEN SYSTEMS IN A STEADY STATE:

1. An open system in a steady state is capable of doing work (systems at equilibrium can do no work).
2. Non-equilibrium processes can be regulated.
3. In non-equilibrium thermodynamics, the steady state may be considered to be an ordered state of an open system.

The state in which the rate of entropy production is minimal, the system is operating with maximum efficiency under the prevailing conditions. Life is a constant struggle against the tendency to produce entropy. The synthesis of large and information rich macromolecules, the formation of structural cells, the development of organization, all these are antientropic doom imposed on all natural phenomena. Under the 2nd law of thermodynamics, living organisms choose the least evil - they produce entropy at a minimum rate by maintaining a steady state.

Steady state:

1. Constant flow of matter and release of waste products of metabolism.

2. Constant loss of free energy, which maintains the constant concentration of substances in the system.

3. Constant values of thermodynamic parameters, including internal energy and entropy.

Thermodynamic equilibrium	Steady state
1. $S=const$, $dS=0$, $S=S_{max}$	$dS=0$, $S<S_{max}$
2. $dG=0$, $G=G_{min}$	$dG=0$, $G> G_{min}$
3. $J_i=0$ no thermodynamic flows	$J_i \neq 0$ but their sum is 0
4. $X_i=0$ no thermodynamic forces	$X_i \neq 0$