Properties of open thermodynamic systems as the consequence of their stability

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Efficiency of chemical machines-Hydrogen Fuel Cells
Energetic limitations of population growth
Dynamics of ecological system with migration
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- How is the stability of thermodynamically non-equilibrium state connected with entropy production?
- Why the non-equilibrium steady state is maintained by a negative entropy flux?
- How formulate the efficiency of thermal machines, chemical reactors and stability of biological systems?
- The applications to Hydrogen Fuel Cells, to the population growth and the stability of the ecological systems.
On fait la science avec des faits, comme on fait une maison avec des pierres: mais une accumulation de faits n’est pas plus une science qu’un tas de pierres n’est une maison.

We make science with facts, as we make a house with stones: But an accumulation of facts is no more a science than a heap of stones is a house.

Henri Poincaré

An open and growing system evolves and it is stable.
A closed system goes to equilibrium, biologically is dead.
Evolution
What is thermodynamics

- Thermodynamics results from the general outcomes of energy and matter transformation, so that it can be considered as a dialectics of matter and field.
- Thermodynamics deals with real objects, i.e. thermodynamic systems, consisted of many interacting parts, i.e. thermodynamic subsystems like atoms, molecules, and even cells, genes, living individuals, etc.
- The elementary thermodynamic subsystem used in the thermodynamics is a material point (individual), which is a part of solid bodies, fluids, biological system or its parts and/or ecological system.
- The interaction is understood as effects between bodies in the nature, such as energy transformation, momentum changes and matter exchange.
- The elementary terms used in thermodynamics are "collective" quantities temperature, energy, entropy, and work.
EXAMPLES OF OPEN SYSTEMS

Solids and fluids
Living cells - blood
Living tissue

Animals and human being

EARTH
Time evolution of relevant quantities

Global form of the balance laws is

\[ \frac{d\Phi}{dt} = \mathcal{J}(\phi) + \mathcal{P}(\phi), \quad \text{for} \quad \Phi = \int_{\mathcal{V}} \phi d\nu \]

This time change \((d/dt)\) of the quantity \(\Phi\) is caused by

\[ \mathcal{J}(\phi) = \int_{\partial\mathcal{V}} j \, da \quad \text{the flux through the boundary and} \]

\[ \mathcal{P}(\phi) = \int_{\mathcal{V}} \sigma(\phi) d\nu \quad \text{by the total production of this quantity} \ \phi \]
General form of balance laws

The change of the extensive quantity $\Phi$ in the body with volume $\mathcal{V}$ can be compensated by the flux $J(\Phi)$ thorough the surface $\partial\mathcal{V}$ and/or by the production $P(\Phi)$ in the body.
Measured extensive quantities

All important measurable extended quantities are defined by their balance laws. The convenient set of such quantities $\Phi(t)$ applied for the time evolution (physical description) of the real physical system, which occupied the volume $V$, with the boundary $\partial V$ have the following physical interpretation

$$\Phi = \begin{pmatrix}
\rho_\alpha, \rho_m, \rho_e \\
D, B \\
\rho \\
\rho_\alpha v_\alpha, \rho v \\
x \times \rho_\alpha v_\alpha, x \times \rho v \\
\frac{\rho_\alpha v_\alpha^2}{2}, \frac{\rho v^2}{2} \\
\rho_\alpha u_\alpha, \rho u \\
\rho_\alpha s_\alpha, \rho s
\end{pmatrix}$$

- chem. components, el. and mag. charges
- electric and magnetic inductions fields
- mass
- momentum
- momentum of momentum
- mechanical energy
- internal energy
- entropy
Balance of internal energy follows from the balance of total energy. I. Law of Thermodynamics

\[
\dot{U} - \dot{Q} = \int_V \left[ (t_{el} + t_{dis}) : \nabla v + j_e \mathcal{E} + \rho \mathcal{E} \left( \frac{\mathcal{P}}{\rho} \right) + \rho \mathcal{B} \left( \frac{\mathcal{M}}{\rho} \right) \right] \, d\nu + Q^{EX}
\]

\[
\rho \dot{u} = -\frac{\partial q^i}{\partial x^i} + t^{ij} \frac{\partial v_j}{\partial x^i} + j^i_e \mathcal{E}_i + \rho \mathcal{E}_i \left( \frac{\mathcal{P}_i}{\rho} \right) + \rho B_i \left( \frac{\mathcal{M}_i}{\rho} \right) + Q^{EX}
\]

\[
dU - dQ = -pdV + \sum_\alpha \mu_\alpha dN_\alpha \quad \text{classical form}
\]

\[
\dot{U} = \int_V \rho \dot{u} d\nu, \quad \dot{Q} = -\int_{\partial V} \mathbf{q} d\mathbf{a} \quad \text{added heat}
\]

The stress tensor \( t^{li} \equiv t = t_{el} + t_{dis} \) expresses the effects of the external surface forces on the boundary of the body and \( b \) are the external volume forces, e.g., gravitational and electromagnetic forces. Here \( u \) is the specific internal energy, \( \mathbf{q} \) is the heat flux vector, \( Q = Q^{EM} + Q^{EX} \) where \( Q^{EM} \) describes the electromagnetic interaction and \( Q^{EX} \) corresponds to the other form of interactions.
Entropy balance-general concept

All actual cyclical processes $\mathcal{C}$ running in the system $\mathcal{V}$ during which it is possible to measure the temperature $T$ at any moment, must to fulfil the inequality

$$\oint \frac{dQ}{T} = \int_{t_1}^{t_2} \frac{\dot{Q}}{T} dt \leq 0 \quad \text{Clausius inequality}$$

i.e., some amount of heat has to be removed from the system

Entropy is defined by the inequality

$$TdS = TdS_{ir} + TdS_{eq} \geq dQ \quad \text{for} \quad TdS_{eq} = dQ$$

$$T\dot{S} = T\dot{S}_{ir} + T\dot{S}_{eq} \geq \dot{Q} \quad \text{for} \quad T\dot{S}_{eq} = \dot{Q}$$

$$\dot{S} - J(S) = \mathcal{P}(S) \geq 0 \quad \text{II. Law of Thermodynamics}$$

for

$$S = \int_{\mathcal{V}} \rho sd\nu, \quad J(S) = \int_{\partial\mathcal{V}} -\frac{q}{T} da + \frac{\tilde{q}}{T} d\nu,$$

$$\mathcal{P}(S) = \int_{\mathcal{V}} \sigma(S)d\nu \geq 0 \quad \text{entropy production is always positive}$$
Cyclic process

I. Law of Thermodynamics - Balance of total energy

\[ W_{BE} + W_{EG} + W_{GB} + \Delta Q_B + \Delta Q_E + \Delta Q_G = \text{Total Energy is const.} \]

For \( \Delta Q_B < 0, \Delta Q_E < 0, \Delta Q_G < 0 \) ... are removed

II. Law of Thermodynamics - Process Irreversibility

\[ W_{BE} > W_{GB} \]
Reversible and irreversible processes

\[ \oint \frac{dQ}{T} = \int_1^2 \frac{dQ}{T} + \int_2^1 \frac{dQ}{T} \]

ir\(\iff\)d\(\text{Q}=0\)

eq\(\iff\)TdS\(_{\text{eq}}=dQ\)

\(\text{eq} \Rightarrow TdS_{\text{eq}} = dQ\)

All periodic processes are composed from the irreversible part "ir" and irreversible part "eq". The entropy of isolated system reach maximum.
Entropy production and damping of fluctuations

The entropy is a convex function of its parameters, which fluctuates around the stable reference state $S_0$, which can be even the non-equilibrium state. For the purely equilibrium state $S_{eq}$ the fluctuations disappear. In the reference state the entropy has local maximum, i.e., $dS|_0 = 0$.

The probability of fluctuations is $Pr \sim \exp \left[ \frac{S-S_0}{k} \right] = \exp \left[ \frac{d^2S_0}{2k} \right]$. 

\[ S - S_0 = dS_0 + \frac{1}{2} d^2S_0 \]

$P(S)$

$S_0$

$S$

fluctuations are damped

minimum of entropy production

fluctuations

REFERENCE STATE

$\frac{1}{2} d^2S_0 = \delta^2 P(S) = \sum \delta J_\alpha \delta X_\alpha > 0$

$\frac{1}{2} d^2S_0 < 0$
Entropy production for chemically reacting mixture

Typical form of transport processes $J$ and their driving forces $X$ in the thermodynamic systems (chemical devices). Corresponding entropy production is

$$\mathcal{P}(S) = \sum_{\alpha} J_{\alpha} X_{\alpha} \geq 0$$

$$= \mathcal{P}(S_0) + \delta \mathcal{P}(S_0) + \ldots \geq 0$$

$$= \sum_{\alpha} \delta J_{\alpha} \delta X_{\alpha} = \frac{1}{2} d^2 S_{eq} \geq 0$$

<table>
<thead>
<tr>
<th>Flux $J_{\alpha}$</th>
<th>Force $X_{\alpha}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>heat flux</td>
<td>$j_q$</td>
</tr>
<tr>
<td>thermodiffusion</td>
<td>$j_{D\alpha} h_{\alpha}$</td>
</tr>
<tr>
<td>concentration diffusion</td>
<td>$j_{D\alpha}$</td>
</tr>
<tr>
<td>electric current</td>
<td>$j_{e,\alpha}$</td>
</tr>
<tr>
<td>visco-plastic processes for solids</td>
<td>$t_{dis}(T, d, t_{dis})$</td>
</tr>
<tr>
<td>viscosity</td>
<td>$t_{dis} = \sum_{\alpha} \rho_{\alpha} v_{D\alpha} \otimes v_{D\alpha}$</td>
</tr>
<tr>
<td>swelling</td>
<td>$t_{dis} \alpha \cdot \nabla (\frac{1}{T})$</td>
</tr>
<tr>
<td>capillary flux</td>
<td>$j_{Dc}$</td>
</tr>
<tr>
<td>chemical reaction and phase transition</td>
<td>$\dot{\zeta}_{\rho}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Force $X_{\alpha}$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>heat release</td>
<td>$\nabla \left( \frac{1}{T} \right)$</td>
</tr>
<tr>
<td>fuel delivery</td>
<td>$\nabla \left( \frac{1}{T} \right)$</td>
</tr>
<tr>
<td>water diff. in PEM</td>
<td>$\left( \frac{\nabla \mu_{\alpha}}{T} \right)$</td>
</tr>
<tr>
<td>proton flux</td>
<td>$\dot{F}<em>{\alpha} = - \frac{z</em>{\alpha}}{M_{\alpha} T} \nabla \phi$</td>
</tr>
<tr>
<td>at CL and GDL</td>
<td>$\dot{A}<em>{\rho} = \frac{A</em>{\rho}}{T}$</td>
</tr>
</tbody>
</table>
Stability of the reference (equilibrium) state

\[ \dot{S} - \underbrace{\mathcal{J}(S)}_{\text{interaction with surroundings}} = \underbrace{\mathcal{P}(S) \geq 0}_{\text{production inside}} \]

Balance of entropy

The entropy closed the reference state is

\[ S = S_0 + \underbrace{\delta S_0}_{\text{shift of the reference state}} + \frac{1}{2} \underbrace{\delta^2 S_0}_{\text{fluctuations inside the system}} + \cdots \]

\[ \mathcal{J}(S) = \mathcal{J}(S_0) + \underbrace{\delta \mathcal{J}(S_0)}_{\text{change of external fluxes}} + \underbrace{\delta^2 \mathcal{J}(S_0)}_{\text{change of internal fluxes}} + \cdots \]

\[ \mathcal{P}(S) = \mathcal{P}(S_0) + \underbrace{\delta \mathcal{P}(S_0)}_{\text{change of production}} + \underbrace{\delta^2 \mathcal{P}(S_0)}_{\text{change of change of production}} + \cdots \]

= 0 minimum \quad \geq 0 \text{ excess of entropy}
Stability of the reference (equilibrium) state II

The time change of global entropy is

\[ \dot{S} = \dot{S}_0 + \delta \dot{S}_0 + \frac{1}{2} \delta^2 \dot{S}_0 + \cdots \]

Entropy balance (1)

\[ \dot{S} - \mathcal{J}(S) - \mathcal{P}(S) = 0 \]

has form

\[
\begin{align*}
\dot{S}_{eq} - \mathcal{J}(S_{eq}) & = 0, \mathcal{P}(S_{eq}) = 0 \\
\delta \dot{S}_0 - \delta \mathcal{J}(S_0) & = 0 \\
-\mathcal{P}(S_0) - \frac{1}{2} \delta^2 \dot{S}_0 - \delta^2 \mathcal{J}(S_0) - \delta \mathcal{P}(S_0) - \delta^2 \mathcal{P}(S_0) & = 0
\end{align*}
\]

\rightarrow 0\text{ non-equilibrium processes inside}
Thermodynamic stability condition 1

The reference (equilibrium) state is defined as

\[ \dot{S}_{eq} = J(S_{eq}), \quad \text{when} \quad P(S_{eq}) = 0 \quad \text{for equilibrium state} \ S_{eq} \]

\[ \delta S_0 = \delta J(S_0) = P(S_0) \geq 0 \quad \text{for non-equilibrium state} \ S_0 \]

The reference state \( S_0 \) is stable under the following conditions

\[ \frac{1}{2} \delta^2 S_0 = \delta^2 P(S) = \sum_{\alpha} \delta J_\alpha \delta X_\alpha \geq 0 \]

\[ \delta P(S_0) = 0 \quad \text{and} \quad \delta^2 J(S_0) = 0 \]

which are satisfied inside the system. Their meaning is

- **Minimum of entropy production**
  \[ \delta P(S_0) = 0 \]

- **Additional condition for minimum of entropy production**
  \[ \delta^2 J(S_0) = 0 \quad \text{so called endoreversible entropy flux} \]

  in the state of with minimum entropy are external entropy fluxes mutually compensated

- **Attenuation of the fluctuations**
  \[ \frac{1}{2} \delta^2 S_0 = \sum_{\alpha} \delta J_\alpha \delta X_\alpha \geq 0 \]
Thermodynamic stability II - Minimum entropy production concept

For the known magnitude of the entropy flux $\mathcal{J}(S_0)$ the entropy production can be calculated as

$$\mathcal{P}(S_0) = \frac{1}{2} d^2 S_0 \geq 0$$

$$\delta \mathcal{P}(S_0) = 0$$

$$\delta^2 \mathcal{P}(S_0) = \frac{1}{2} d^2 S_0 \geq 0$$

$$\delta \mathcal{J}(S_0) = \mathcal{J}(S_0)$$

$$\delta^2 \mathcal{J}(S_0)_{t_{in}} = 0$$

$$\dot{S}_0 = \mathcal{J}(S_0) + \mathcal{P}(S_0)$$

For the known magnitude of the entropy flux $\mathcal{J}(S_0)$ the entropy production can be calculated as

$$- \mathcal{J}(S_0) = \mathcal{P}(S_0) - \dot{S}_0$$

for steady state $= 0$

system is fed by negative entropy flux
Applications

- Entropy balance of Earth
- Efficiency of thermal machines
- Hydrogen fuel cell with polymer electrolyte membrane.
- Energetic limitations of population growth.
- Dynamics of ecological system with migration
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**ENTROPY BALANCE OF THE EARTH**

\[ J_S(\varepsilon) = 3.83 \cdot 10^{36} \text{ W} \]

\[ J(S) = -5.37 \cdot 10^{14} \text{ W K}^{-1} \]

\[ J_Z(\varepsilon) = 1.23 \cdot 10^{17} \text{ W} \]

\[ J_Z(S) = 1.23 \cdot 10^{17} \text{ W} \]

**ENTROPY FLUX OF THE EARTH**

\[ J(S) = \frac{4}{3} \left( \frac{J_Z(\varepsilon)}{T_S} - \frac{J_Z(\varepsilon)}{T_Z} \right) = -5.37 \cdot 10^{14} \text{ W K}^{-1} \]

**Photosynthesis**

\[ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{carbohydrate} \]

**Living cells**

\[ \text{carbohydrate} + \text{O}_2 \]

ELI (Extreme Light Infrastructure-Dolní Břežany)

power 10 PW = \( 10^{16} \) W, energy 2 kJ in 130 fs = \( 1.3 \cdot 10^{-13} \) s
Earth total energy income $5.46 \cdot 10^{24}$ J/year

Sun radiation 0.5 $\mu$m
Earth radiation 8 $\mu$m at 25°C
DYNAMICAL EQUILIBRIUM ASSUMPTION

\[ -J(S) = P(S) = 5.37 \cdot 10^{14} \text{[W/K]} \]

\[ P_{rad}(S) = 0.94P(S) \ldots \text{absorption and emission of energy} \]

\[ P_{transf}(S) = 0.06P(S) \ldots \text{material changes on earth surface} \]

and movement of atmosphere

Civilisation controls the power about \(10^{13} \text{ W}\)

\[ P(S) = 3 \cdot 10^{10} \text{W/K} \div 0.0008P_{transf}(S) \]
Transformation of solid body vortex to potential vortex

**Vortex tube transformation**

\[ \mathbf{v}_{\text{rot}} \rightarrow \mathbf{v}_{\text{pot}} \]

**Balanced laws**

- Mass... \( \text{div} \mathbf{v} = 0 \)
- Momentum... \( \mathbf{v} \times \text{rot} \mathbf{v} = \text{grad} h_c - T \text{grad} s \)
- Energy... \( \dot{h}_c = 0 \)
- Entropy... \( T \text{grad} s = \text{condensation heat} \)
Tropical cyclone structure

For a tropical cyclone of radius $r_o = 15$ km, the acceleration acting on the elements of air is $h_{vl} \frac{\partial c_w}{\partial r} = 4.2 \text{ m s}^{-2}$

For a tornado of radius $r_o = 50$ m, the acceleration acting on the elements of air is $h_{vl} \frac{\partial c_w}{\partial r} = 65 \text{ g} = 640 \text{ m s}^{-2}$
Conclusion following from the energy balance formulated by the total enthalpy

\[ \Delta Q = \Delta H_c - \Delta_{ir} W_{mech}, \quad \Delta, p = 0, \quad T\Delta S_{ir} = \text{viscous dissipation, phase transition heat, etc} \]

\[ \Delta_{ir} W_{mech} = T\Delta S_{ir} - \mathbf{v} \times \mathbf{rot} \mathbf{v}, \quad \Gamma = \oint_C \mathbf{v} ds = \oint_A \mathbf{rot} \mathbf{v} da - \text{circulation} \]
Energy balance of the Earth

Flux of energy $5.5 \cdot 10^{21}$ J year$^{-1}$ is used to form the new biomass and it is consumed from 99% by photosynthesis

$$n\text{CO}_2 + 2n\text{H}_2\text{O} + mh\nu \rightarrow (\text{CH}_2\text{O})n + n\text{O}_2 + n\text{H}_2\text{O}.$$ 

CO$_2$ fixation needs the Gibbs free energy $\Delta G = 450$kJ mol$^{-1}$ and 8 - 12 photons in range of wavelengths 400 - 700 nm with energy in range 300 - 170 kJ mol$^{-1}$.

- The total enthalpy needed for release of one molecule of oxygen is $\Delta H = 1360 - 8400$kJ mol$^{-1}$. In case of $n = 1$ the product of photosynthesis is CH$_2$O (formaldehyde).

- Higher carbohydrates can be produced by higher energy, e.g. for glucose C$_6$H$_{12}$O$_6$ are parameters $n = 6$ and $m = 6(8 - 12)$.

Maximal efficiency of photosynthesis is

$$\eta_{\text{photo}} = \frac{\Delta G}{\Delta H} = \frac{450}{1360} = 33\%$$
Biomass production

Assuming that 60% of energy used by photosynthesis is immediately consumed for respiration, there is only 40% of energy for forming of the new biomass (the net annual production of biosphere, NPB).

The energetic flux $J(NPB) = 2.2 \cdot 10^{21} \text{ J year}^{-1}$ is consumed to form the new biomass.

- Technical civilization generates energy of $5.7 \cdot 10^{20} \text{ J year}^{-1}$ (data for 2013), from which just 15% is generated by renewable sources and rest of energy is produced by fossil fuels.

- Human civilization is able to produce energy, which is equal to 40% of the energetic flux $J \text{ year}^{-1}$.

- One human being is part of biosphere with estimated energetic consumption of $4 \cdot 10^9 \text{ J year}^{-1}$, so that for population of six billions humans is consumption equals to $2.4 \cdot 10^{19} \text{ J year}^{-1}$.

- At present time human civilization consume approximately 1.1% of the total energetic flux needed to form biosphere.
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Global form of the energy balance for thermal machines

Energy conversion in the closed cycle at constant internal energy $U$.

$$T \Delta S = T (\Delta S_{eq} + \Delta S_{ir}) \geq \Delta Q = \Delta U + \tilde{W}_{\text{exp}},$$

where $\Delta Q = \Delta Q_{\text{in}} - \Delta Q_{\text{out}}$ is the difference of the incoming and of the outgoing heat from the system.
Efficiency of thermal machines

The temperatures $T_3, T_4$ can be eliminated using transport equations and introduced in the entropy balance

$$\frac{\mathcal{J}_{q1}}{T_1 - \frac{\mathcal{J}_{q1}}{\alpha_H}} = \frac{\mathcal{J}_{q2}}{T_2 + \frac{\mathcal{J}_{q2}}{\alpha_L}}$$

This is an additional condition for a state with minimal entropy production. Non-dimensional form of the balance of energy is

$$\dot{w}_{\text{exp, norm}} = \frac{\dot{W}_{\text{exp}}}{\dot{W}_{\text{exp, ref}}} = \frac{\eta[(1 - \frac{T_2}{T_1} - \eta)]}{(1 - \eta)}$$

for $\dot{W}_{\text{exp, ref}} = \frac{\alpha_H \alpha_L T_1}{\alpha_H + \alpha_L}$

where $\dot{W}_{\text{exp, ref}}$ is a reference mechanical power of the endoreversible thermal machine and depends on the transfer coefficients $\alpha_H, \alpha_L$ and can be determined experimentally only. At the efficiency $\eta_{th} = 1 - T_1/T_2$, which is defined by the classical Carnot formula, is the mechanical work output equal to zero.

Maximum work output is carried out for the Chambadal-Novikov-Curson-Ahlborn efficiency.

$$\frac{\partial \dot{w}_{\text{vol}}}{\partial \eta} = 0, \quad \text{for} \quad \eta_{\text{max}} = 1 - \sqrt{1 - \eta_{th}} = 1 - \sqrt{\frac{T_2}{T_1}}$$
Typical dependance efficiency on the power

Comparison of the Carnot efficiency with the minimum entropy production (usually called endoreversible) and actual efficiencies.

<table>
<thead>
<tr>
<th>Power plant</th>
<th>$T_L$ [°C]</th>
<th>$T_H$ [°C]</th>
<th>$\eta_{\text{Carnot}}$</th>
<th>$\eta_{\text{endo}}$</th>
<th>$\eta_{\text{observe}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Thurrock (UK) coal-fired power plant</td>
<td>25</td>
<td>565</td>
<td>0.54</td>
<td>0.4</td>
<td>0.36</td>
</tr>
<tr>
<td>CANDU (Canada) nuclear power plant</td>
<td>25</td>
<td>300</td>
<td>0.48</td>
<td>0.28</td>
<td>0.3</td>
</tr>
<tr>
<td>Larderello (Italy) geothermal power plant</td>
<td>80</td>
<td>250</td>
<td>0.33</td>
<td>0.178</td>
<td>0.16</td>
</tr>
</tbody>
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HFC structure and corresponding relevant processes.

Chemical energy transformation

Fuel and waste transfer
The energy balance for non-expansion work $\dot{W}_{\text{nexp}}$ is formulated by the enthalpy $H$

$$\mathcal{J}_q + \mathcal{J}_{Dh} = \dot{H} + \dot{W}_{\text{nexp}},$$

where $\mathcal{J}_q$ is the heat flux and $\mathcal{J}_{Dh}$ is the enthalpy flux. For steady state is total enthalpy in the system constant, i.e., $\dot{H} = 0$.

The entropy balance is

$$\dot{S} - \mathcal{J}(S) = \mathcal{P}(S) \geq 0,$$

for $\mathcal{J}(S) = \mathcal{J}_q(S) + \mathcal{J}_{Dh}(S) - \mathcal{J}_{Dg}(S)$.

The global entropy production $\mathcal{P}(S) = \int_V \sigma(s) d\nu \geq 0$ is always positive and corresponding heat is continuously removed from the system by the heat flux $-\mathcal{J}_q(S)$. The entropy production $\mathcal{P}(S) \geq 0$ is compensated by the flux of the negative entropy (fuel delivery) which is composed from the enthalpy flux $\mathcal{J}_{Dh}(S) \geq 0$, and especially from the Gibbs free energy flux $\mathcal{J}_{Dg}(S) \sim \frac{\Delta G}{T} < 0$...outer normal. The change of the Gibbs free energy is $\Delta G < 0$; when the Gibbs free energy decreases, a spontaneous chemical reaction take place.
Energy conversion in the closed cycle at constant enthalpy.

**Electrolyser** – the incoming energy flux contains the energy $\dot{W}_{1\text{ nexp}}$ needed for the chemical reactions (e.g., water decomposition) and corresponding heat loss is $\dot{Q}_{1\text{ out}}$, so that $\dot{Q}_{1\text{ in}} = \dot{Q}_{1\text{ out}} + \dot{W}_{1\text{ nexp}}$.

**FC** – the outgoing energy $\dot{W}_{2\text{ e}}$ contains the electric power accompanied by the heat $\dot{Q}_{2\text{ out}}$, so that $\dot{Q}_{2\text{ in}} = \dot{Q}_{2\text{ out}} + \dot{W}_{2\text{ nexp}}$. 
Definitions of efficiencies I

For the $\Delta S_{ir} = 0$ the maximum efficiency of a chemical transformation is

$$
\eta_{th} = \frac{-W_e}{\Delta H} = \frac{\Delta G}{\Delta H} + \frac{S_{eq}\Delta T}{\Delta H} \bigg|_{T=\text{const}} = \frac{\Delta G}{\Delta H}.
$$

The incoming power is $\dot{\Delta H}_{in} = V_{eq\ T,\ p} z_e F \dot{N}_{H_2\ in}$ and measured outgoing power is $\dot{W}_{act} = V_{cell} I$. The measured actual efficiency by means of the polarization curve is

$$
\eta = \frac{-\dot{W}_{e\ act}}{\dot{\Delta H}_{in}} = \frac{\dot{\Delta G}_{in}}{\dot{\Delta H}_{in}} \left(1 + \frac{\dot{T}\dot{\Delta S}_{ir}}{\dot{\Delta G}_{in}}\right) = \frac{-\dot{W}_{nexp}}{\dot{\Delta H}_{in}} + \frac{\dot{W}_{e\ act}}{\dot{W}_{nexp}}
$$

polarization losses membrane losses

$$
= \eta_0 \eta_{II} = \frac{V_{cell}}{V_{eq\ T,\ p}} \frac{\dot{N}_{H_2\ in}}{\dot{N}_{H_2\ act}} = \frac{V_{cell}}{V_{eq\ T,\ p}} \frac{I}{Z_{e\ F} \dot{N}_{H_2\ act}}.
$$

fuel utilization

$V_{eq\ T,\ p} = -\frac{\Delta G}{2F} = 1.184$  $V$ is equilibrium cell potential at temperature $T = 353$ K, pressure $p = 101.3$ kPa for pure hydrogen and air. Theoretical efficiency $\eta_{th} = \frac{V_{eq\ T,\ p}}{1.482} \approx 0.7989 \approx 0.8$. 
Definitions of efficiencies II – efficiency splitting

Fuel transport efficiency defined as

\[ \eta_0 = \frac{\dot{W}_{\text{nexp}}}{\Delta H_{\text{in}}} = \frac{\dot{\Delta G}_{\text{in}}}{\Delta H_{\text{in}}} \] …dissociation-polarization losses

We consider that hypothetical FC (PEM especially) convert all incoming Gibbs free energy into electric power \( \dot{W}_e \), i.e., \( \dot{W}_{\text{nexp}} = \Delta G_{\text{in}} = -\dot{W}_e \) and is connected with the reactants delivery and products outflow and does not depend on the actual chemical energy transformation.

The membrane efficiency is

\[ \eta_{\text{III}} = -\frac{\dot{W}_{e\text{ act}}}{\dot{W}_{\text{nexp}}} = -\frac{\dot{W}_{e\text{ act}}}{\Delta G_{\text{in}}} = 1 + \frac{T\dot{\Delta S}_{\text{ir}}}{\Delta G_{\text{in}}} \leq 1 \]

and describes the transformation of the chemical energy \( \Delta G_{\text{in}} \) into electric energy through the dissipation \( T\Delta S_{\text{ir}} \).
Efficiency – minimum entropy production concept

We suppose the closed cycle, it means that the change of the total enthalpy is zero ($\dot{H} = 0$) and the energy balance becomes

$$\dot{Q}_{in} - \dot{Q}_{out} = \dot{W}_{nexp} = - T \Delta S + \overline{\Delta H} = - \dot{W}_e,$$

for efficiency

$$\eta = \frac{\dot{W}_{nexp}}{\dot{Q}_{in}} = \frac{- \dot{W}_e act}{\Delta H_{in}}$$

heat fluxes are

$$\dot{Q}_{in} = \frac{\dot{W}_{nexp}}{\eta}, \quad \dot{Q}_{out} = \frac{1 - \eta}{\eta} \dot{W}_{nexp}.$$

For minimum entropy production concept are needed three assumptions

- Minimum of entropy production
  $$\delta \mathcal{P}(S_0) = 0$$

- Additional condition for internal entropy flux
  $$\delta^2 \mathcal{J}(S_0) = 0 \quad \text{so called stability of minimum entropy production state}$$

- Attenuation of the fluctuations
  $$\frac{1}{2} \delta^2 S_0 = \sum \delta J_\alpha \delta X_\alpha \geq 0$$

The final form of the entropy balance for the electrochemical device is

$$\frac{\dot{Q}_{in}}{T_3} - \frac{\dot{Q}_{in}}{T_4} + \frac{\dot{W}_{nexp}}{T_4} - \frac{\dot{G}_{in}}{T_4} = 0 \quad \equiv \quad \delta^2 \mathcal{J}(S_0) = 0$$
The heat and enthalpy fluxes between the different temperatures are driven by the temperature gradients

\[
\int_{\partial V} (j_q + \sum_\alpha j_{D\alpha} h_\alpha) \text{d}a = J \sim \nabla T,
\]

\[\dot{Q}_{\text{in}} = \mathcal{J}_{q3} + \mathcal{J}_{Dh3} = -\gamma_H (T_1 - T_3), \quad \dot{Q}_{\text{out}} = \mathcal{J}_{q2} + \mathcal{J}_{Dh2} = \gamma_L (T_4 - T_2),\]

for \( \gamma_H = \alpha_H + \beta_H, \quad \gamma_L = \alpha_L + \beta_L. \)

The relation between the total efficiency \( \eta = \dot{W}_{\text{e,act}} / \dot{Q}_{\text{in}} \) and the actual electric power is the relation between the total efficiency \( \eta \) and the actual electric power is

\[
\dot{w}_{\text{nexp}} = \frac{\eta[(1 - \eta_{II})\eta - \tau\eta_{II}]}{(\gamma - 1)(1 - \eta)\eta_{II} - \eta} = \frac{\eta_0\eta_{II}[(1 - \eta_{II})\eta_0 - \tau]}{(\gamma - 1)(1 - \eta_0\eta_{II}) - \eta_0}
\]

for \( \dot{w}_{\text{nexp}} = \frac{\dot{W}_{\text{nexp}}}{\dot{W}_{\text{nexp, ref}}} = -\frac{\dot{W}_e}{\gamma_H T_1} \left( = \frac{\dot{W}_e}{\dot{H}_{\text{in}}} \right) \)

and \( \gamma = \frac{\gamma_H}{\gamma_L} \geq 1 \)

If non-expansion power is taken as the electric power, i.e. \( \dot{W}_{\text{nexp}} = -\dot{W}_e \), equation it will be valid for fuel cells, electrolyzers, batteries, etc. Moreover, the positive power output is ensured by

\[
\tau = \frac{T_2}{T_1} - 1 > \eta_0(1 - \eta_{II})
\]
Typical form of the efficiencies

\[
\eta_{\text{th}} = 0.798, \quad \eta_0, \min = 0.513, \quad \eta_{\text{II},0} = 0.89, \quad \dot{W}_{\text{nexp,ref}} = \gamma_H T_1 = -\dot{G}_{\text{in}} = -\Delta G \dot{m}_{\text{H}_2} = 0.723 \text{ Wcm}^{-2}, \quad T_1 = 353 \text{ K}, \quad \gamma_H = 0.00205 \text{ Wcm}^{-2} \text{K}^{-1}, \quad \gamma = 1.95, \quad \tau = 0.074.
\]
Minimum of entropy production

The abbreviated form of the constitutive relations

\[
\begin{align*}
\mathbf{j}_{Dw} &= -\frac{\rho_w M_w D_w}{R} \cdot \frac{R}{M_w a_w} \nabla a_w \\
\mathbf{J}_w &= -L_{ww} \cdot \mathbf{X}_w \\
\mathbf{J}_e &= -L_{H+w} \cdot \mathbf{X}_w \\
\mathbf{J}_{H^+} &= -\hat{L}_{wH^+} \cdot \frac{F}{T M_{H^+}} \nabla \phi \\
\mathbf{J}_{H^+} &= -L_{wH^+} \cdot \mathbf{X}_e \quad \text{water flux} \\
\mathbf{J}_{H^+} &= \frac{\sigma_{H^+} T M_{H^+}^2}{F^2} \cdot \frac{F}{T M_{H^+}} \nabla \phi \\
\mathbf{J}_{H^+} &= -L_{H^+H^+} \cdot \mathbf{X}_e \quad \text{proton flux}
\end{align*}
\]

The entropy production of the whole FC with the volume \( V_m \) is equal

\[
\mathcal{P}(S) = \sigma_m(S) V_m = -(\mathbf{J}_e \mathbf{X}_e + \mathbf{J}_w \mathbf{X}_w) V_m = \frac{\Delta S_{ir}}{\Delta t} \geq 0 \quad \left[ \frac{W}{K} \right]
\]

and as it is always positive and is continuously generated in the system in the steady state.
Minimum subject to constrains – given electric output

The value of entropy production of the FC generating the given electric power density $\dot{W}_e = -i_e \nabla \phi = - T J_e X_e$ [W m$^3$]. Applying the method of Lagrangian multipliers $-\lambda_T$ the minimum of the density entropy production has to fulfill the extremum condition

$$\delta(\sigma_m(S)) - \lambda(\dot{W}_e + T J_e X_e)) = -\delta[(J_e X_e + J_w X_w) + \lambda_T(\dot{W}_{eT} + J_e X_e)] = 0$$

for $\lambda_T = \lambda T$ and $\dot{W}_{eT} = \dot{W}_e / T$.

For the forces $X_w, X_e$ we find that this equation is fulfilled for $\dot{W}_e \neq 0$ when $\lambda_T = (-1 \pm \sqrt{13})/3$ only.

These two solutions are related to the coupling coefficient

$$q^2 = \frac{4(1 - \lambda_T)}{(\lambda_T - 2)^2} \quad \text{for} \quad q \in (0, 1)$$

which has direct relation to the unknown "cross coefficient"

$$\hat{L}_{H_3O^+ w} = q \frac{M_{H_3O^+}}{F} \sqrt{\frac{\rho_w M_w T}{R}} D_w \sigma_p$$

and connects the material properties of the electrolytic membrane, i.e., water diffusivity $D_w$ and proton conductivity $\sigma_p$. $q$ express the **electro-osmotic coupling**.
The lower value of the minimum entropy density production is \( \sigma(q = 0.901) = 3.5 \cdot 10^3 [\text{Jm}^{-3}\text{K}^{-1}] \). For the second value of \( \lambda_T = 0.8685 \), \( q = 0.6409 \) is \( \sigma(q = 0.6409) = 1.472 \cdot 10^4 [\text{Jm}^{-3}\text{K}^{-1}] \) and it is greater. So that the FC performance with the coupling coefficient \( q = 0.901 \) is probably more stable. Moreover, the shape of the surface \( \sigma(X_w, X_e) \) for \( q = 0.6409 \) is more flat.
Negative entropy flux

Total entropy flux is

\[ J_{\text{tot}}(S) = \frac{\dot{Q}}{T} \left\{ \int_{\partial V} -\frac{q}{T} \, da \right\} + \frac{\dot{G}}{T} \left\{ \int_{\partial V} \sum_\alpha j_{D\alpha} \mu_\alpha \, da \right\} \]

\( \dot{Q} < 0 \) cooling  \( \dot{G} < 0 \) spontaneous chemical reactions

\[ = J_q(S) + J_{Dh}(S) - J_{Dg}(S) = \frac{\dot{Q}_{\text{in}}}{T_1} - \frac{\dot{Q}_{\text{out}}}{T_2} \]

\[ = -\frac{\dot{W}_e}{\eta T_1} \left[ 1 - \frac{(1 - \eta) T_1}{T_2} \right] = -P(S) \leq 0 \]

This relationship combines the processes inside the system with the magnitude of its interaction with the environment.
Two operation states of FC

For the same electric output $\dot{W}_e$ and external (anode) temperature $T_1$ the ratio of the entropy production ratio is

$$\frac{\sigma_{up}(q = 0.901)}{\sigma_{low}(q = 0.6409)} = \frac{P_{up}(q = 0.901)}{P_{low}(q = 0.6409)} = \frac{J_{low}(S)}{J_{up}(S)}$$

$$= \frac{\eta_{low}(\eta_{up} + \tau_{up})(1 + \tau_{low})}{\eta_{up}(\eta_{low} + \tau_{low})(1 + \tau_{up})} = \frac{\eta_{low}}{\eta_{up}} \left( \frac{V_{low}}{V_{up}} \right) = \frac{3.5 \cdot 10^3}{14.7 \cdot 10^3} = 0.239$$

The higher entropy production corresponds to the lower part of the curve and therefore to the lower efficiency (lower voltage). For a sufficiently large domain of performance $\dot{W}_e \in (0.01, 0.2) \text{Wcm}^{-2}$, this ratio is approximately equal to 0.24.
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Population growth can be written as an analogy to auto catalysis in chemistry

\[ E_{I} + N \xrightleftarrows^{k_{+1}}_{k_{-1}} gN + E_{I} - J(X) \]

where $E_{I}$ is surrounding interaction of individual $N$ before reproduction and $E_{I}'$ is surrounding interaction of individual $N$ after reproduction.

Rate of reproduction characterizes rate constant $k_{+1}$ and rate of cessation characterizes rate constant $k_{-1}$. Migration flux is $J(N) = \frac{N}{R}$. Here $R$ is the resistance of the surroundings

- $g = 2$ proliferation-e.g., cells division
- $g \geq 3, 4, \ldots$ number of descendants, e.g., sex reproduction.
Energetic of population growth II

According to the **mass action law** the time change of a number of individuals is given as

\[
\frac{dN}{dt} = k_{+1} N_{EI} N - k_{-1} N_{E^1} N - \mathcal{J}(X)
\]

\(N_{EI}\) and \(N_{E^1}\) are the factors determining the influence of the environment on the reproduction of the biological species \(N\). Equilibrium constant of this reaction \(K_N\) is connected with the enthalpy of the reaction \(\Delta H_N\) and with the change of entropy \(\Delta S_N\)

\[
K_N = \frac{k_{+1}}{k_{-1}} = \exp \left( \frac{-\Delta G_N}{RT} \right) = \exp \left( \frac{\Delta S_N}{R} - \frac{\Delta H_N}{RT} \right)
\]

Stationary state of the system is

\[
N_0^{g-1} = K_N \frac{N_{EI}}{N_{E^1}} - \frac{K_N}{k_{+1} N_{E^1} R}
\]
Energetic of population growth II

For two systems, where there is no migration, where is the same number of individuals \( N_{0p} = N_{0s} \), i.e. \( N_{0p} \) for proliferation with \( g = 2 \) and \( N_{0s} \) for the sex reproduction with \( g \geq 4 \), the following condition is satisfied

\[
\ln N_{0p} = \frac{-\Delta G_{Np}}{RT} \quad \text{and} \quad (g - 1) \ln N_{0s} = \frac{-\Delta G_{Ns}}{RT}
\]

or

\[
(g - 1)\Delta G_{Np} = \Delta G_{Ns}
\]

and for \( \Delta G_N < 0 \) – spontaneous reaction

\[
\Delta G_{Np} > \Delta G_{Ns}
\]

Sex reproduction has lower Gibbs free enthalpy
Energetic of population growth III

From thermodynamic point of view, sex reproduction is more advantageous for $g > 4$ (more than 2 descendants). $\Delta G_{Np}$ is the Gibbs free enthalpy of proliferation (e.g., cell division) and $\Delta G_{Ns}$ is the Gibbs free enthalpy of sex reproduction. $\Delta G_{Np}, \Delta G_{Ns}$ are negative (processes are spontaneous), therefore

$$\Delta G_{Np} > \Delta G_{Ns} \text{ or } \Delta G_{Np} \text{ has for } g > 4 \text{ higher value than } \Delta G_{Ns}$$

The same number of descendants produced by sex reproduction is reached by the lower Gibbs free enthalpy and it is probably the reason why sex reproduction is evolutionarily advantageous.
Human population

Two population models applied to evolution of the Earth.

Supposed stationary state is 10 billions. Sex reproduction curve is fitted to data from World population prospects.
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Dynamics of predator $N_3$-prey $N_2$ system: Lotka-Volterra model

Two competitive ecological systems (in general two auto catalytic reactions) of type predator $N_3$ and prey $N_2$.

\[
\begin{align*}
&\text{EI} + N_2 \xleftrightarrow[k_{+1}]{k_{-1}} g_1 N_2 - J(X_2) \quad (\rho = 1) \\
&N_2 + N_3 \xleftrightarrow[k_{+2}]{k_{-2}} g_2 N_3 - J(N_3) \quad (\rho = 2) \\
&N_3 \xleftrightarrow[k_{+3}]{k_{-3}} + \text{EI} \quad (\rho = 3)
\end{align*}
\]

where EI is surrounding interaction before reproduction and $\text{EI}'$ is surrounding interaction after reproduction.

Rate of reproduction characterizes rate constant $k_{+\rho}$ and rate of cessation constant $k_{-\rho} \to 0$.

Parameter $g$ complies condition $g_1, g_2 \geq 3, 4, ...$ and depends on number of descendants. Migration fluxes are $J(N_2)$ and $J(N_3)$. 
Dynamics of the system

Assuming rates of reversed reactions equal to zero. i.e., $k_{-\rho} = 0$ (it is just reproduction) the rate of the origin of individuals is

\[
\frac{\partial N_2}{\partial t} = k_{+1} N_{E1} N_2 - k_{+2} N_2 N_3 - \mathcal{J}(N_2)
\]

\[
\frac{\partial N_3}{\partial t} = k_{+2} N_2 N_3 - k_{+3} N_3 - \mathcal{J}(N_3)
\]

Stability of system can be studied by fluctuation dynamics of stationary state in form of traveling wave in direction $r$ from center

\[
N_2(r, t) = N_{20}(r) + \delta N_2(r, t) \exp(\omega t - ikr)
\]

\[
N_3(r, t) = N_{30}(r) + \delta N_3(r, t) \exp(\omega t - ikr), \quad \omega = \omega_r + \omega_{im}
\]
Dynamics of predator-prey competition: Lotka-Volterra model without migration

Dynamics of ecological model predators $N_3$, preys $N_2$, for stationary values $N_{30} = 10$, $N_{20} = 20$, with rate constant $k_{+1}N_{EI} = 70$, $k_{+2} = 7$ and time period $\tau = 0.064$. Thermodynamically correct evolution is in direction of arrow because just evolution in this direction produces positive entropy.
Dynamics of predator-prey system: Lotka-Volterra model with migration

Migration is a consequence their over-concentration in a place expressed by distance $r$ from a center

$$J(N_2) = -\frac{D_2}{r} \frac{\partial}{\partial r} \left( r \frac{\partial N_2}{\partial r} \right) \quad \text{prey migration}$$

$$J(N_3) = -\frac{D_3}{r} \frac{\partial}{\partial r} \left( r \frac{\partial N_3}{\partial r} \right) \quad \text{predator migration}$$

Stability of this system is determined by the frequency

$$\omega = \omega_{re} + i \omega_{im} \quad \text{of state oscillation}$$

$$\omega^2 - \omega(D_2 + D_3)k^2 + D_2 D_3 k^4 + k_2 N_{20} N_{30} = 0$$

Usually, the stationary state is maintained by permanent leaving of preys $D_2 > 0$ and by permanent leaving of predators $D_3 > 0$. We suppose the specific situation, where $D_3 = m D_2$ migration of predators depends on parameter $m$

- i) $m > 0$ ... migration predators $N_3$ out
- ii) $m < 0$ ... migration into (penetration of predators $N_3$)
Dynamics of predator-prey system: Lotka-Voltera model with migration

\[
\omega = \omega_r + \omega_{im} = \omega_D \pm i\omega_D \sqrt{\left(\frac{\omega_0}{\omega_D}\right)^2 - 1}
\]

\[
\omega_D = \frac{(1 + m)D_2k^2}{2}, \quad \omega_0 = \sqrt{k+2N_2N_{30}}
\]

diffusion frequency for \( D_3 = mD_2 \)
predator-prey frequency for \( D_2 = D_3 = 0 \)

Distribution of population (concentration) e.g., of specie \( N_2 \)

\[
N_2 = N_{20} + \delta N_2 \exp(\omega_D t) \exp \left\{ i \left[ \pm \omega_D \left( \sqrt{\left(\frac{\omega_0}{\omega_D}\right)^2 - 1} \right) t - kr \right] \right\}
\]

close-up change in time traveling wave

The traveling wave stops for \( \omega_0 = \omega_D \) and periodic strips appear. Wave vector \( k = 2\pi/\lambda \), where \( \lambda \) is the wavelength.

\[
\lambda = \pi \sqrt{\frac{2(1 + m)D_2}{\omega_0}} = \pi \sqrt{\frac{2(1 + m)D_2}{\sqrt{k+2N_2N_{30}M_0}}} \quad m \in (-\infty, \infty)
\]
An example of reaction-diffusion processes in biological systems

\[ \lambda \sim \sqrt{\tau_0 D} \]

\[ \tau_0 \text{ ...time of one cycle} \]

\[ D \text{ ...diffusivity} \]

Two component reaction-diffusion system of Fitzhugh-Nagumo type

...propagation of el. potential in the heart ventricles

see, e.g. Wikipedia
Influence of migration

Population of preys grows in living area of dimension $L^2$ in $[m^2]$

$$N_2 \approx \exp(\omega_D t) = \exp\left[\frac{4\pi^2(1+m)D_2}{L^2} t\right]$$

only for $m > -1$ and $m \geq \frac{L^2}{\pi \tau_0 D_2} - 1$

$$\tau_0 = \frac{2\pi}{\omega_0} = \frac{2\pi}{\sqrt{k_{+2} N_{20} N_{30}}} = \frac{2\pi}{\sqrt{k_{+1} k_{+3} N_{EI}}}$$

time of one cycle

Prey populations decrease when $m < -1$ as a result of predator penetration
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The heat power (approximately 75 W) determines amount of consumed energy (glucose)

\[ \dot{\Delta Q}(-75W) = -\dot{\Delta G} \text{ up to } 45 \text{ mgs}^{-1} \text{ of glucose} \]

\[ \rightarrow \text{ basal metabolism } 6347 \text{ kJ day per day} \]

\[ \rightarrow \text{ equiv. } 4 \text{ Liters of bier } 10^\circ \text{ per day} \]

Value of basal metabolism 6347 kJ per day is used as an assumed limit value. The entropy production of a human being in basal metabolism state at ambient temperature 18$^\circ$C is given from the stability condition of the dynamical equilibrium.

\[ P(S_0) \sim -\frac{\dot{\Delta Q}}{273 + 18} - \frac{\dot{\Delta G}}{273 + 37} = 0.5\text{WK}^{-1} < -\int_{t_1}^{t_2} \mathcal{J}(S_0)dt \]

This minimal entropy production needs to be maintained by negative entropy flux for keeping the thermodynamic non-equilibrium (figuratively "preservation of life") and depends strongly on temperature of surroundings.
Evolution of the open systems

- The system exists only when it is stable. Stability is assured by its growth.
- The driving force of evolution is a competition for space and resources.

Stability condition for open system

\[ \dot{S}_0 = \dot{J}(S_o) + \dot{P}(S_o) \quad < 0 – \text{stable evolution (or} > 0 – \text{unstable evolution)} \]

\[ 0 \leq \dot{P}(S_o) \leq -\dot{J}(S_o) \]

\( \dot{P}_\alpha \) – stable evolution, \( \dot{P}_\beta \) – dynamic evolution, \( \dot{P}_\gamma \) – unstable evolution.


Maršík F, Dvořák I.: Biotermodynamika, Academia, Praha 1998
