united nations educational, scientific and cultural organization

international atomic energy agency

the **abdus salam** international centre for theoretical physics

H4.SMR/1202-29

"Fifth Course on Mathematical Ecology including and introduction to Ecological Economics"

28 February - 24 March 2000

THERMODYNAMIC GOAL FUNCTIONS IN ECOYSTEM ANALYSIS

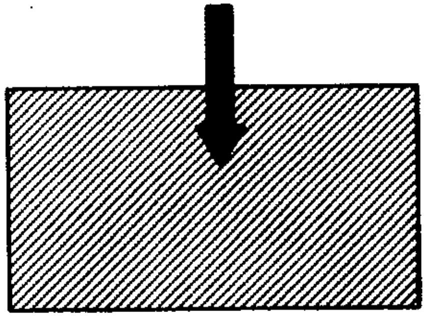
Claudio Rossi

Department Chemical & Biosytem Sciences
University of Siena
Pian dei Mantellini 44
53100 Siena, Italy

Phone: 0577 232022
Fax: 0577 232004
e-mail: rossi@unisi.it

Basic Thermodynamic Definitions

- Thermodynamic System

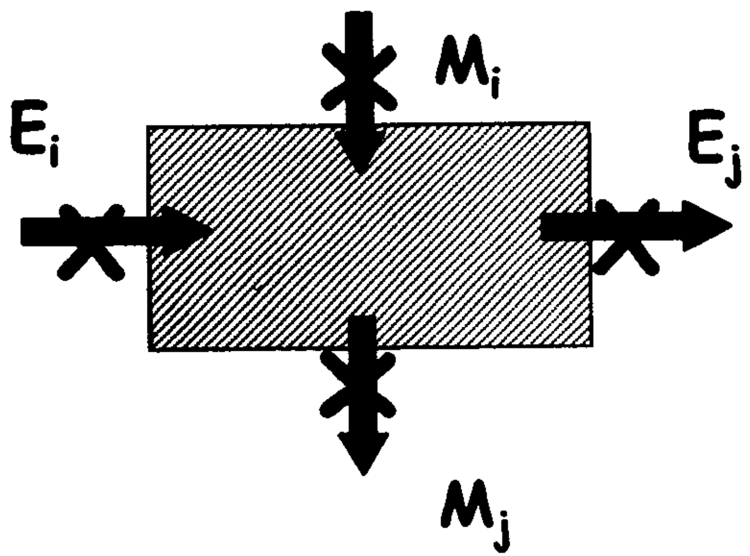


Space region defined by a physical or mathematic surface which includ a statistically sufficient number of structures (molecules atoms, elementar particles, etc)

- Environment

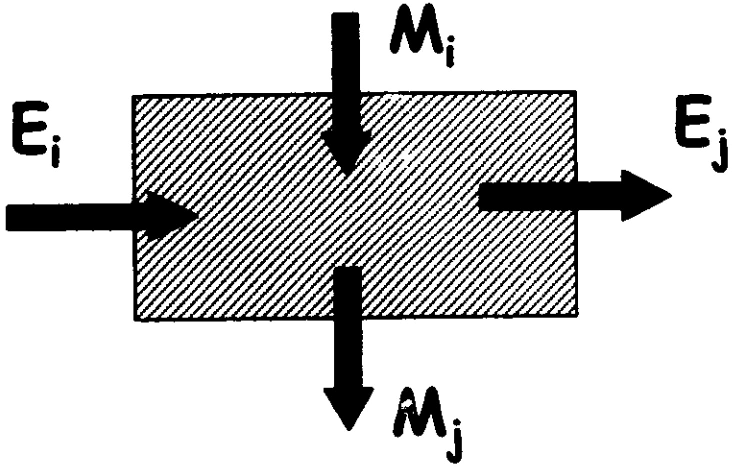
Isolated Thermodynamic Systems

Systems which do not exchange energy or matter with the environment



Open Thermodynamic Systems

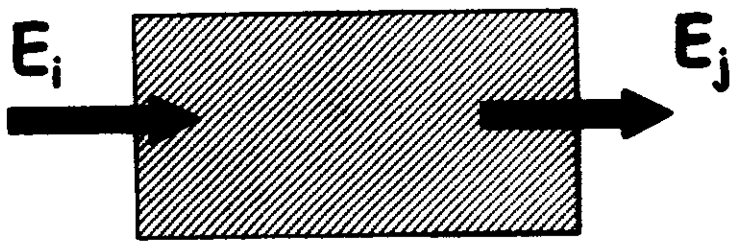
Systems which exchange both energy and matter with the environment



Cells and Ecosystems are open systems

Closed Thermodynamic Systems

Systems which exchange only energy with the environment



Thermodynamic Equilibrium

is the lower energy (Free Energy) state reached by irreversible path.
This state does not allow any oscillation behaviour.

Thermodynamic Steady-State

is a far from the equilibrium condition, mainteined by energy and/or matter fluxes.

A thermodynamic state is defined by *thermodynamic observables* (pressure, volume, temperature, chemical potential, etc.)

Thermodynamic functions of state identify a thermodynamic state and their values depend on the values assumed by the thermodynamic observables

U = Internal energy $\quad U\ f(T)$

Enthalpy $\quad H=U+PV$

Free Energy, Helmotz $\quad F=U-TS$

Free Energy, Gibbs $\quad G=H-TS$

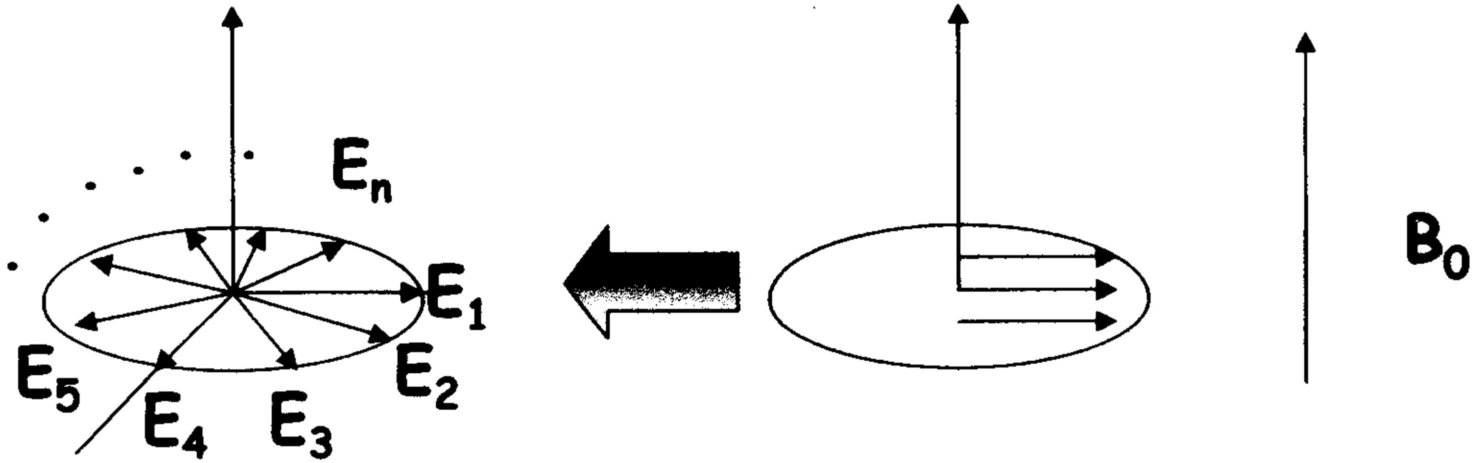
Entropy

$$dS = \frac{\delta Q}{T}$$ Thermodynamic view

$$S = K \ln K$$ Statistical view

Entropy in natural systems increases as a consequence of:

- an increase of disorder
- an increase of more probable states



$$E_1 = E_2 = \ldots. = E_n$$

$$dS = dS_i + dS_e$$

dS_i = Internal Entropy Variation alway >0

dS_e = Entropy Variation induced by energy and/or matter flux >, <, =0

$$\frac{dS}{dt} = \frac{dS_i}{dt} + \frac{dS_e}{dt}$$

$$\frac{dS_i}{dt} \rightarrow \sigma \qquad \frac{dS_e}{dt} \rightarrow \varphi$$

$$\frac{dS}{dt} = \sigma + \varphi$$

In steady-state

$$0 = \sigma + \varphi$$

$$\sigma = -\varphi$$

Proposed goal functions for dynamic systems

Proposed for	Goal functions	References
Several system	Maximum useful power of energy flow	Lotka (1924), Odum and Pinkerton (1955)
	Minimum entropy	Glansdorff and Prigogine (1971)
	Maximum retention time	Cheslak and Lamarra (1981)
Ecological system	Maximum ascendency	Ulanowicz (1986)
	Maximum biomass	Margalef (1968)
	Maximum persistent organic matter	Whittaker and Woodwell (1971), O' Neill et al. (1975)
	Maximum emergy	Odum (1983)
	Maximum exergy stored	Mejer and Jørgensen (1979)
	Maximum energy dissipation	Schneider and Kay (1993)
	Maximum indirect effects	Patten (1995)
Economic systems	Maximum profit	Various authors

Structure of Goal Functions

$GF = K \Sigma Q C$ Currently used

example

$E_{x\ spe} = K \sum_i \beta_1 \chi_i$

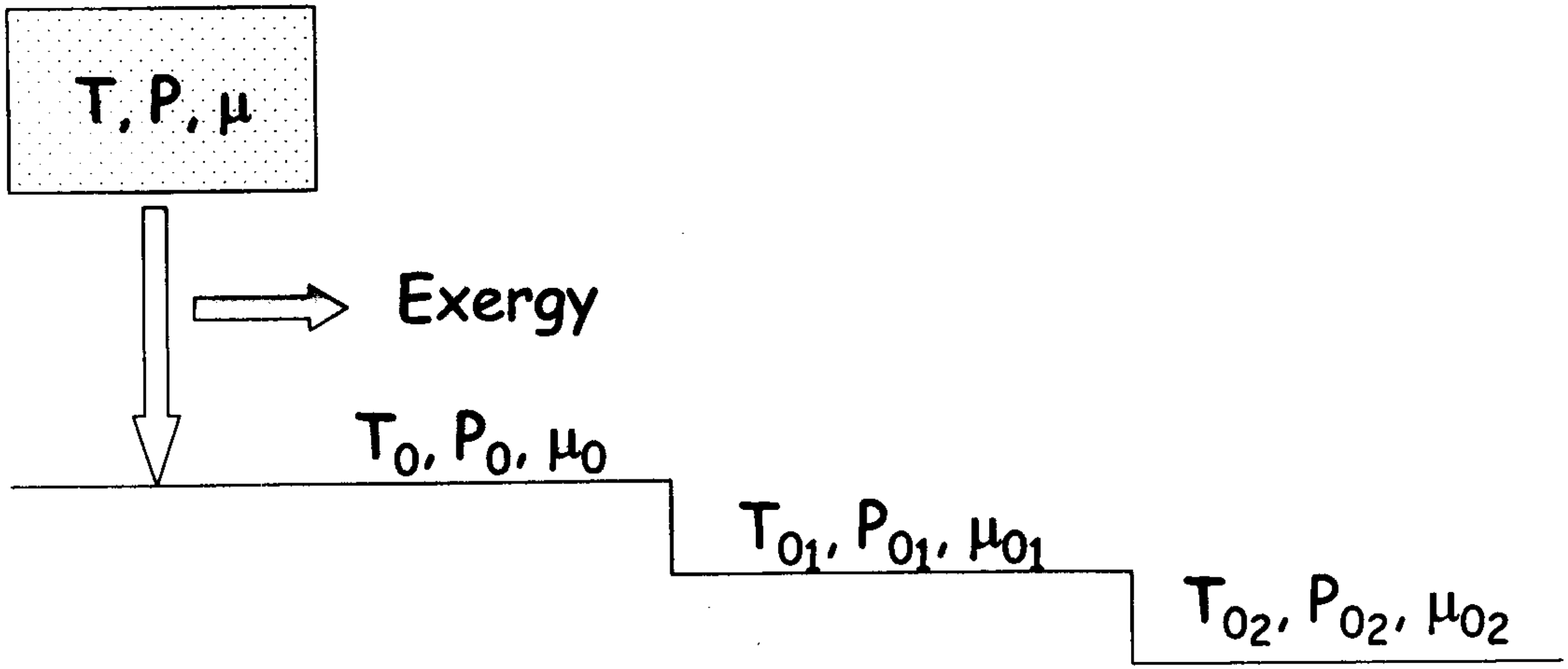
β = quality factor n. genes
χ = biomass concentration of the i species

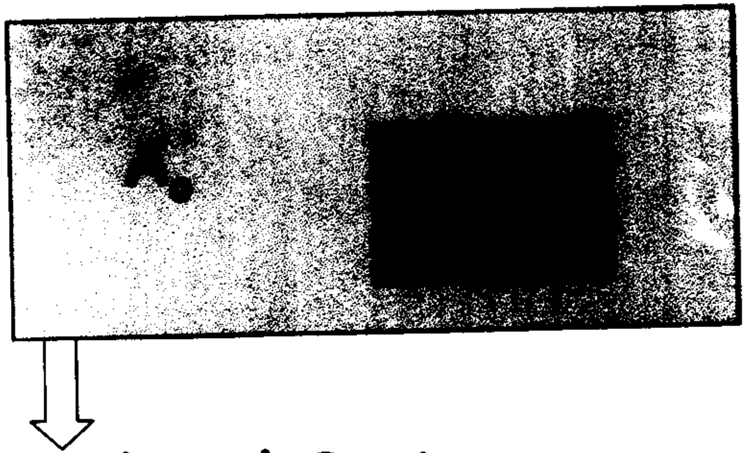
Future Perspective:

$MGF = K \Sigma Q C X_i$ X_i = interaction

Exergy is a system property which identify the "free energy" obtained when the thermal equilibrium "dead-state" with the environment is reached.

R. Evans (1969 Ph.D. Thesis Dartmouth College, Hannover USA)





Isolated System

A_o = Environment

A = System

$A_o >> A$

Extensive proprieties:

U_0	U
V_0	V
S_0	S
N_{0i}	N_i

Intensive variables:

T_0	T
P_0	P
μ_0	μ

If certain amount of work can be exchanged by A_0 and A

$$dU + dU_0 = 0 \longrightarrow dU = -dU_0$$

$$dV + dV_0 = 0 \longrightarrow dV = -dV_0$$

$$dN_i + dN_{0i} = 0 \longrightarrow dN_i = -dN_{0i}$$

If $A_0 \gg A$ $\quad d\mu_0 \div dT_0 \div dP_{0i} \cong 0$

From the Gibbs equation the entropy variation of the Environment can be definite as:

(A_0)

$$dS_0 = \frac{dU_0 + P_0 dV_0 - \sum \mu_{oi} dN_{oi}}{T_0} =$$

$$= -\frac{+dU + P_0 dV - \sum \mu_{oi} dN_{oi}}{T_0}$$

The total Entropy variation is then:

$$dS_{tot} = dS + dS_0 = dS - \frac{dU + P_0 dV + \Sigma \mu_{0i} dN_{0i}}{T_0}$$

$$dS_{tot} = \frac{dU + P_0 dV - T_0 dS + \Sigma \mu_{0i} dN_{0i}}{T_0}$$

$$dS_{tot} = -\frac{dEx}{T_0}$$

Ex = Exergy

$$Ex = U + P_0 dV - T_0 dS + \Sigma \mu_{0i} dN_{0i}$$

If dS is calculated for the A system, then:

$$dS = \frac{dU + PdV - \Sigma\mu_i dN_i}{T}$$

by integration: $TS = U + PV - \Sigma\mu_i N_i$

$$U = TS - PV + \Sigma\mu_i N_i$$

$$dN_i = -dN_{0i}$$

$$Ex = U + P_0 dV - T_0 dS + \Sigma\mu_{0i} dN_{0i}$$

$$Ex = TS - PV + \Sigma\mu_i N_i + P_0 V - T_0 S + \Sigma\mu_0 dN_0$$

$$\Downarrow$$

$$Ex = S(T - T_0) - V(P - P_0) + \Sigma N_i(\mu_i - \mu_{0i})$$

Exergy: $$Ex = S(T-T_0)-V(p-p_0)+\Sigma N_0(\mu_i - \mu_{i0})$$

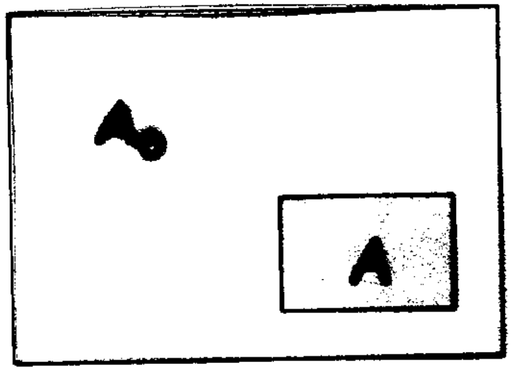
$$dS_{tot} = -\frac{dEx}{T_0}$$

$$\int_S^{S_{equ}} dS_{tot} = -\frac{1}{T_0}\int_{Ex}^{0} dx$$

$$Ex = T_0(S_{equ}-S)$$

Exergy attempts to account for the actual free energy of the biomass including the free energy stored in the information.

S.E. Jorgensen, Ecol. Mod. 102, 5 (1997)



A_0 = Environment

A = Microsystem

$A_0 >> A$

Intensive variables: T_0 T

p_0 p

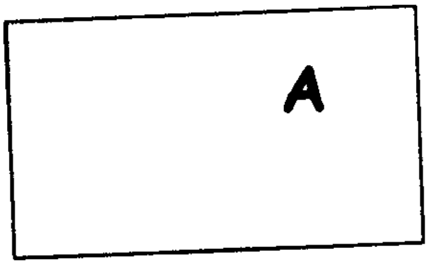
μ_0 μ

$$Ex = S(T - T_0) - V(p - p_0) + \Sigma N_0(\mu_i - \mu_{i0})$$

Exergy is the amount of work the system can perform by being brought into equilibrium with its environment.

Exergy and Ecosystems

A= acquatic ecosystem



Pression, Temperature, Volume } = K

Δ Ex ⇨ Change in the distribution of the system components

Phosphorus { Solution (P_s), Algae (P_a)

$$P_{tot} = P_s + P_a$$

$$P_a = P_a^{eq} + \delta$$

$$P_s = P_s^{eq} - \delta$$

$$dP_a = -dP_s = d\delta$$

$$dEx = d\delta(\mu_a - \mu_s) = \mu_s dP_s + \mu_a dP_a$$

$$\mu_a = \mu_a^{eq} + RT\ln\frac{P_a}{P_a^{eq}} = RT\ln\frac{P_a^{eq} + \delta}{P_a^{eq}}$$

$$\mu_s = \mu_s^{eq} + RT\ln\frac{P_s}{P_s^{eq}} = RT\ln\frac{P_s^{eq} + \delta}{P_s^{eq}}$$

$$\frac{dEx}{d\delta} = RT\ln\frac{(P_a^{eq} + \delta)P_s^{eq}}{(P_s^{eq} - \delta)P_a^{eq}}$$

by integration:

$$Ex = RT\left[(P_a^{eq} + \delta)\ln\frac{P_a^{eq} + \delta}{P_a^{eq}} + \right.$$

$$\left. + (P_s^{eq} - \delta)\ln\frac{P_s^{eq} - \delta}{P_s^{eq}}\right]$$

Assuming that:

$$P_s^{eq} \cong P_{tot} \qquad \delta \ll P_s^{eq} \qquad \delta \gg P_a^{eq}$$

$$Ex = RT\delta \ln \frac{\delta}{P_a^{eq}}$$

If we consider algae and zooplankton, assuming:

$$P_a^{eq} \ll P_{tot} \qquad P_z^{eq} \ll P_{tot} \qquad \delta_a \gg P_a^{eq} \qquad \delta_z \gg P_z^{eq}$$

$$Ex = RT\left[\delta_a \ln \frac{\delta_a}{P_a^{eq}} + \delta_z \ln \frac{\delta_z}{P_z^{eq}}\right]$$

$$\boxed{Ex = RT\sum_{i=1}^{n} C_i \ln \frac{C_i}{C_i^{eq}}}$$

In case of a matter flux:

$$Ex = RT\sum_{i=0}^{n}\left[C_i \ln \frac{C_i}{C_i^{eq}} - (C_i - C_i^{eq})\right]$$

where the index 0 is assigned to the inorganic components in the ecosystem

Exergy and Organisms

$$Ex = RT \sum_{i=0}^{i=n} C_i \ln \frac{C_i}{C_i^{eq}}$$

i=0 inorganic components
i=1 detritus
i>1 bacteria, algae, yeast, fishes, birds....humans

For detritus:

$$\mu_1 = \mu_1^{eq} + RT \ln \frac{C_1}{C_1^{eq}}$$

$\mu_1 - \mu_1^{eq}$ is known

In general the C_i component can be determined by:

$$P_i = \frac{C_i^{eq}}{\sum_{i=0}^{n} C_i^{eq}} \cong \frac{C_i^{eq}}{C_0^{eq}}$$

P_i= is the probability to find the i component in the equilibrium conditions

$$P_1 = \frac{C_1^{eq}}{C_0^{eq}}$$

$$P_1 = \frac{C_1}{C_0^{eq}} \exp\left[-(\mu_1 - \mu_1^{eq})/RT\right]$$

$$E_x = RT \sum_{i=1}^{n} c_i \ln P_i$$

S.E. JORGENSEN et al

Ecol. Mod. **102**, 5 (1997).

For $i > 1$ $\qquad P_i = P_1 P_{ia}$

Where P_{ia} is the term which account the complexity of each organism

20 = number of different amino acids present in proteins

700 = average number of amino acids in proteins

γ = number of genes in each organism

[redacted]
i=1

$$Ex = (\mu_i - \mu_1^{eq})\sum_{i=1}^{n}\frac{C_i}{RT} - \sum_{i=2}^{n} C_i \ln P_{ia}$$

For multicellular organisms

e.g. zoo plankton (about 10^5 cells) :

$$\ln P_{i200} = -\ln(20^{-50000 \times 700} \times 10^5) = 1048.5 \times 10^5$$

$$Ex/RT = (1.79 \times 10^6)P + (31.5 \times 10^6)Z + (2.58 \times 10^8)F +$$
$$+ (D + P + Z + F) \times 7.42 \times 10^5$$

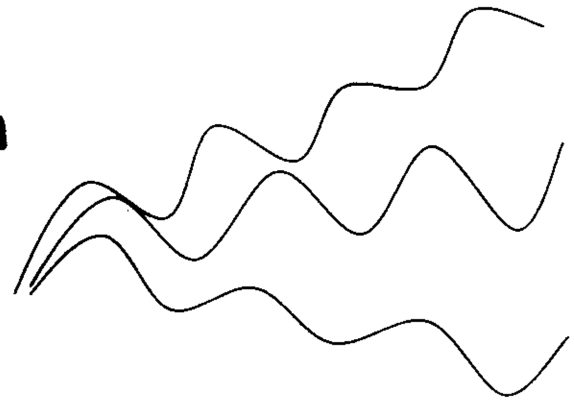
[redacted]
i=1

Genes and Weigthing factors

Organism	Number of information genes	Weigthing factor W_i
Bacteria	600	2×10^6
Algae	850	2.5×10^6
Yeast	2000	4×10^6
Fungi	3000	7×10^6
Plants, trees	10000 - 30000	4.3×10^7
Zooplankton	10000 - 50000	1.2×10^8
Insects	10000 - 15000	2.7×10^7
Worms	10000 - 100000	2.7×10^7
Crustaceans	100000	2.1×10^8
Fish	100000 - 120000	2.3×10^8
Birds	120000	2.3×10^8
Amphibians	120000	2.3×10^8
Reptiles	120000	2.7×10^8
Mammals	140000	3×10^8
Human	250000	5.3×10^8

Exergy as Goal Function

Monitoring the evolution of natural ecosystems if the experimental parameters are known



To be used during modelling development to compare the effects induced by a change in the value of different parameters and for comparison of different models