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Entropy Radiation and Negentropy Accumulation with Photocells, Chemical Reactions and Plant Growth

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IIASA Research Memorandum
March 1978

ENTROPY RADIATION AND NEGENTROPY ACCUMULATION WITH
PHOTOCELLS, CHEMICAL REACTIONS, AND PLANT GROWTH

Jean Thoma

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PREFACE

This Research Memorandum is an attempt to put the concept of negentropy accumulation in biomatter and capital equipment on a more complete physical basis. With phenomenological entropy as thermal charge, heat and solar radiation incorporate an entropy flow that is determined by Planck's theory of black-body radiation. Consequently, there is a Carnot factor limitation on the efficiency of solar power collection by photocells. In thermal machines, the notions of friction, efficiency, and reversibility are closely related and the concept of exergy efficiency replaces advantageously conventional efficiency.

Chemical reactions are similar to electric networks, but there is structural entropy associated with each chemical species. The structural entropy capacity can be compared to a vase that changes its width during reaction. The various flows in a chemical reaction are represented by arrows in networks with bond graph symbols in order to show clearly the similarity to and the difference from electric networks. Important is the stripping of structural entropy before the reaction and the unstripping after the reaction. Chemical reactions run from a higher to a lower chemical potential with corresponding dissipation and entropy generation unless they are pumped in reverse by special outside efforts.

Photosynthesis of biomatter is a chemical reaction in which the mass flow is pumped against a chemical potential difference by solar radiation or photon power. The ordered structure of biomatter contains less structural entropy than the oxides from which it is built, thus constituting negentropy accumulation. The difference between the structural entropies--indestructible like all entropies--is also pumped away and ultimately reradiated into space together with the entropy flow that arrives with the solar radiation and the entropy generated by various dissipations. Space as an entropy sink in this light is just as important for sustaining life as the incoming solar radiation.

Negentropy in biomatter is information in the sense of Shannon but its value is very high (one or more bits per molecule), and much higher than the amount of information in the specification of the difference between macro-information and micro-information of [1].

This Research Memorandum contains essentially the work done by the author during his visits to IIASA in August 1977 and January 1978. It is based on discussions with members of the Energy Systems Program, in particular with Wolf Häfele, Cesare Marchetti, and Hans-Richard Grümm.

ABSTRACT

The entropy flow in solar radiation is discussed on the basis of Planck's theory of blackbody radiation. It is 133 percent of the entropy flow in heat conduction (of the same power and temperature) and leads to a modified Carnot efficiency limit for photocells. Chemical reactions involve both entropy generation by dissipation and net stripping of structural entropy.

Photosynthesis of biomatter is a chemical reaction pumped against chemical potential differences by solar radiation or photon power. It reduces the structural entropy compared to the entropy of the reacting oxides and constitutes a negentropy accumulation. The structural entropy capacity of matter is compared to a vase that changes its width during reaction. Both the entropy flow of solar radiation and the removed structural entropy are reradiated into space; in this view space is as important as solar radiation for sustaining life.

In the beginning section, as a preparation to the above, the known exergy efficiency is shown to be less arbitrary than conventional efficiency and related to entropy generation or negentropy consumption.

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INTRODUCTION

This report deals with the thermodynamic foundation of
various life and energy conversion processes. It describes the
physical mechanisms of plant growth, photocells, and chemical
reactions on the basis of the entropy flow of solar and thermal
radiation. It applies both to normal combustion and to fuel
cells and endeavors to show directions for possible improve-
ments of such processes.

We use the viewpoint of network thermodynamics mentioned in
the IIASA Research Memorandum "Energy, Entropy, and Information"
[1]. The idea of network thermodynamics is to take entropy as
a thermal charge, visualized as gray paste, that is inseparably
connected to the flux of thermal energy or heat. This is the
phenomenological interpretation of entropy, in comparison to
which statistical entropy and information in the form of negative
entropy--or negentropy--constitute a theory of structure [1]. Net-
work thermodynamics also splits the real processes into simple
processes or, rather, elements. Such elements are either
frictionfree, i.e. entropy-conserving and reversible, or with
friction, i.e. they produce entropy and are irreversible.

LOSSES, ENTROPY GENERATION, AND EFFICIENCY

Exergy Efficiency

One central goal of machine construction is to keep losses
small and efficiencies high. In steady (i.e. time-independent)
operation, the sum of the outgoing power fluxes equals the in-
coming power flux. Hence the losses also produce an output
power flux that is presumably less useful. Efficiency η then is
the ratio of useful output flux, and its complement $1-\eta$ is the
ratio of "useless" output flux to input flux.

$$\eta = \frac{\dot{E}_{useful}}{\dot{E}_{in}} \quad , \quad 1 - \eta = \frac{\dot{E}_{useless}}{\dot{E}_{in}} \quad . \tag{1}$$

There is an interesting triangular relation between fric-
tion, efficiency, and reversibility symbolized by Figure 1.
Friction, as we know from network thermodynamics, is always
irreversible and reduces efficiency. A completely reversible
machine has an efficiency of 1 (100 percent), but the converse

is not necessarily true.   Such a machine is frictionless and generates no entropy.

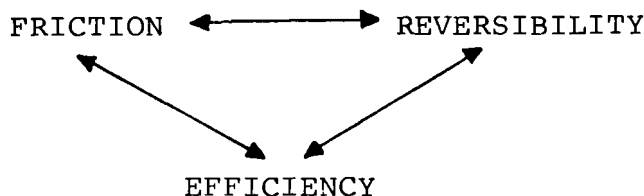$$\text{FRICTION} \longleftrightarrow \text{REVERSIBILITY}$$

EFFICIENCY

Figure 1.   Triangular relationship between friction, reversibility, and efficiency. A frictionless machine has 100 percent efficiency and is or can be made reversible.

All friction elements are power-conserving in the sense that output heat flux $\dot{T}S$ always equals the observed electric or mechanical power vi or $M\omega$. Heat conduction over a finite temperature difference is also a form of friction since it is irreversible and conserves power, but it generates entropy. The mixing of matter or diffusion is a similar case.

In the case of an electric generator, it is easy to separate the output into useful and useless (or lost) powers (Figure 2, right)[1]. Electric power $\eta\dot{E}_1$ is useful, and the friction power manifest as entropy flow and temperature or heat flow equaling $(1-\eta)\dot{E}_1$ is useless.
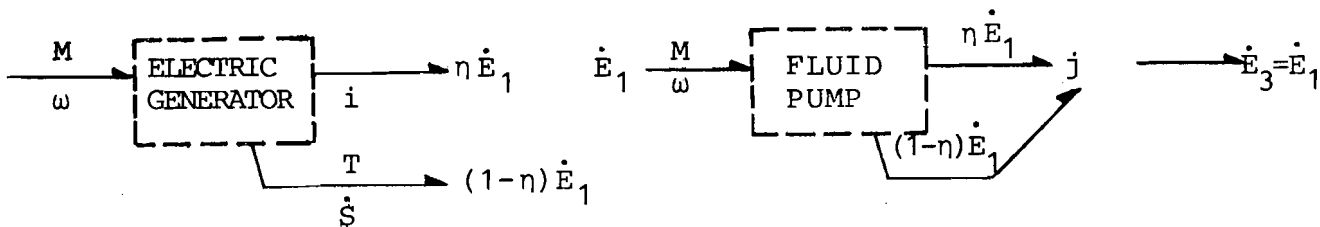
Figure 2.   Losses and efficiencies in an electric generator (left) and a fluid pump (right). The lost power is well separated and carried away by cooling air in the electric case, but is mixed with the fluid output in the hydraulic case. In the latter the output power $\dot{E}_3$ always equals the input power $\dot{E}_1$. (M = torque; ω = rotation frequency; v = voltage;   i = current; $\dot{S}$ = entropy flow;   T = absolute temperature; η = efficiency)

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[1]Figure 2 and several others in this paper use the bond graph method, where devices are not represented by pictures but by usually selfexplanatory words of one or several letters. This is especially suitable for chemical reactions which are difficult to depict.

Machines such as fluid pumps also have useful and friction power (Figure 2, right), but very often the friction power is injected into the fluid outflow, its direct heat transfer to the environment being negligible. Hence output power $\dot{E}_3$ equals the input power, since useful and useless parts are mixed in the fluid line or pipeline. The power ratio is therefore 1 and not an indicator of the efficiency of pump operation.

We solve the problem by noting that all inefficiencies are friction processes that generate entropy, which in the case of the pump enters the outlet line. As performance indicator we need a mixture of power and entropy, for which the term exergy flux (or available energy flux) has been introduced.

$$\dot{E}_x = \dot{E} - T_{env}\,\dot{S} \qquad \text{Exergy flux}$$
$$E_x = E - T_{env}\,S \qquad \text{Exergy}$$

(2)

Exergy then is the energy minus the entropy times the temperature of the environment. As mentioned in [1], the total power carried by fluids has several components the sum of which is called enthalpy flux $\dot{H}$. Hence

$$\dot{H}_x = \dot{H} - T_{env}\,\dot{S} \qquad (3)$$

represents the exergy flux of fluid lines. Nonthermal power carries no entropy, and consequently exergy and conventional power fluxes are equal.

In order to describe the operation of a machine, we can use its exergy efficiency, which is the sum of the exergy fluxes at the outlet divided by the exergy flux at the inlet. A frictionless machine has no entropy production, hence it is reversible and has an exergy efficiency of 1 (100 percent). This is what we would expect and, in fact, exergy efficiency is a very good indicator of how perfectly a machine operates:

$$\eta_x = \frac{\sum_i \dot{E}_i - T_{env}\,\dot{S}_i}{\dot{E}_1 - T_{env}\,\dot{S}_1} \quad ; \qquad (4)$$

the sum runs over all outlets i, where $\dot{E}_1$ and $\dot{S}_1$ are the energy and entropy flows, respectively, at the inlet. Exergy efficiency does not distinguish arbitrarily between useful and useless outputs. Instead there is some arbitrariness due to the choice of the temperature of the environment, but this is less arbitrary than the distinction of useful and useless power fluxes in Equation (1). This temperature, usually taken to be around 300 K, thereby assumes a more fundamental significance. It can be taken as the dividing line between entropy and negentropy if a zero entropy content is assigned to matter, especially to exhaust gases, at this temperature.

Some consequences of exergy efficiency are interesting. All thermal outputs contain some exergy if they leave the machine or system at a temperature higher than that of the environment, such as the cooling air of an automobile engine. Leaving such energy flux unused is then similar to not stopping a leak in a steam line: it is pure exergy dumping. This aspect should have useful implications on the design of cogeneration or total power systems.

Furthermore, heat exchangers have a definite exergy efficiency, but they always conserve power; if they are almost frictionless or reversible this efficiency can come close to 1 (100 percent). Here our interpretation of heat conduction at a finite temperature difference as friction and thus loss fits well. Similar relations presumably apply to the mixing of matter with friction, such as in the case of diffusion of different chemical species.

Steady and Unsteady Operation

Only in steady or time-independent operation are the output fluxes equal to the input fluxes--as used above for efficiency--because the various storages (C- and I-elements in the sense of bond graphs) remain constantly filled and absorb no flow or power.

In unsteady operation storages are filled or emptied and energy and other variables can be accumulated or released. In this sense combustion of a certain amount of fuel and plant growth are unsteady processes.

ENERGY AND ENTROPY IN SOLAR AND THERMAL RADIATION

Radiation in Thermally Excited Cavities

Solar radiation is essentially the output of a blackbody or a black cavity. Figure 3, a model of blackbody radiation, shows a cavity with a radiating hole. The radiated power is supplied by a conduction line or bond from a temperature source on the left. This source supplies as much entropy (and heat) as is needed to keep the temperature constant. Otherwise the walls of the spherical cavity in Figure 3 are perfectly insulated.

Such a cavity as a source of thermal radiation was discussed many years ago by Max Planck [2], using both thermodynamics and Maxwell's electromagnetic theory. In Figure 3, thermal radiation leaves from the hole on the right, which is small enough as not to disturb appreciably the radiation field inside. This field has been described by Max Planck and others as photon gas.
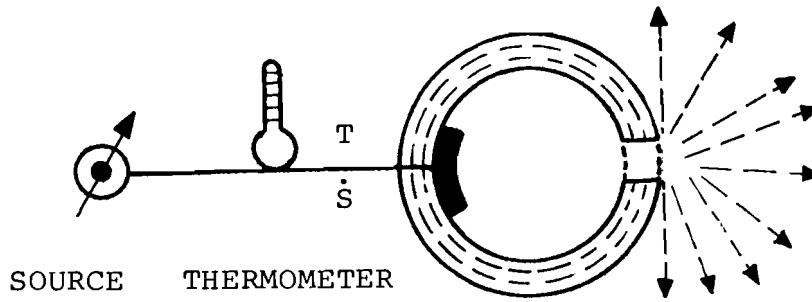
T

$\dot{S}$

SOURCE   THERMOMETER

Figure 3.   Schematic representation of a cavity with thermal
(blackbody) radiation. Thermal power T$\dot{S}$ is supplied
from the temperature source (right), passes a thermo-
meter, and enters the cavity into a kind of hot-plate.
The spherical cavity is perfectly insulated but ther-
mal radiation escapes through the hole on the right,
which is small compared to the cavity in order not to
disturb the radiation field but large compared to the
wavelength to allow for radiation.

With a radiation pressure equaling one third of the energy
density of the radiation field, p = u/3, the cavity has the
following energy and entropy densities [2, 3]:

$$u = a\ T^4 \quad ; \qquad s = \frac{4}{3}\ a\ T^3 \quad . \tag{5}$$

Radiation through the hole is a convection process with the
velocity of light c. Therefore, according to Max Planck, the
power and entropy radiation are [1]

$$\dot{Q} = \frac{ac}{4}\ T^4 \quad ; \qquad \dot{S} = \frac{ac}{3}\ T^3 \quad . \tag{6}$$

Consequently power flux and entropy flow are related by

$$\dot{Q} = \frac{3}{4}\ \dot{S}T \quad ; \qquad \dot{S} = \frac{4}{3}\ \frac{\dot{Q}}{T} \quad . \tag{7}$$

The form factor in Equation (14) of [1] equals 0.75 or, in other
words, solar and thermal radiation carry four thirds, i.e. 133
percent, of the entropy transported in a conduction process of
the same power (heat flow) and temperature.

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[1]With u = energy/volume ratio or density, s = entropy/volume
ratio and a = $7.6 \cdot 10^{-16}$ J/m^{3}K^4, a constant related to the
Stephan-Boltzmann radiation constant σ by σ = ac/4.

This high relative entropy content of 133 percent applies to the completely random and incoherent radiation that can be induced by a temperature (heat) source according to Figure 3. One may visualize this source as a hot-plate in a modern kitchen that is fed through the line from the left. Focusing the radiation or excluding part of the 2π space angle into which the hole radiates does not change the relative entropy content. It can be reduced, however

- by polarization, as mentioned by Planck; and
- by obtaining coherence of the radiation,

until for a monochromatic, coherent ray with definite polarization the radiated entropy is zero ([2], page 116).

The relative entropy content appears to be a convenient scale to describe radiation. This content seems to depend essentially on the coherence of the radiation field. Simple spectral filtering in non-dissipative devices, such as the classical prisma with dispersion but without absorption, or interference filters, will conserve entropy.

Further work on the relation of spectral distribution and the relative entropy content of electromagnetic radiation is desirable. It would also be important for microwave transmission of electric power from orbital solar collecting stations.

As detailed in [2], each spectral part of the blackbody radiation acts independently. Hence the ratio of energy to entropy increment equals the temperature and is the same over the entire spectrum

$$\frac{\delta \bar{u}}{\delta \bar{s}} = T \quad , \tag{8}$$

where $\bar{u}$ and $\bar{s}$ are the volume densities per unit interval of frequency of energy and entropy, respectively.

Equation (8) is analogous to the expression $\delta U = T\delta S$ of thermal C-fields, as are gases in frictionless heating. This is an indication that blackbody radiation behaves like a photon gas, as will be seen more clearly in the case of cavities with variable volume.

Cavities with Variable Volume

For illustration of the properties of solar radiation, Figure 4 shows a cavity whose volume is variable by means of a cylinder and a piston that is subject to radiation pressure. The energy and entropy densities are given by Equation (5); multiplication by the volume yields the energy and entropy contents of the cavity. When the volume is increased by outward

movememt of the piston, the required entropy is taken from the
temperature source. Consequently an entropy flow of

$$\dot{S} = -s\dot{V} = \frac{4}{3} aT^3 V = \frac{4}{3} u\dot{V}/T$$

runs from the temperature source to the cavity (compare Equa-
tion 5). The corresponding power is

$$\dot{E}_1 = \frac{4}{3} u\dot{V} = \frac{4}{3} aT^4 \dot{V} \quad , \tag{9}$$

of which $aT^4 \dot{V}$ increases the energy density, and of which
$1/3 \, aT^4 \, \dot{V} = p\dot{V}$ leaves through the piston to the environment.
This process is frictionless and reversible. Hence, when the
piston is pushed inwards the thermal power $4/3 \, u\dot{V}$ returns to
the temperature source; $u\dot{V}$ originates from the disappearing
radiation field, and $1/3 \, u\dot{V}$ from the mechanical power supplied
by the piston.
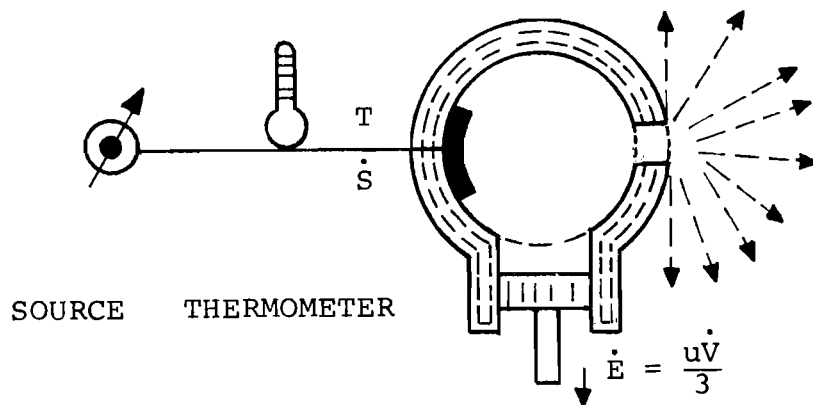

Figure 4. Cavity whose volume is variable by use of the piston
           below which is subject to radiation pressure. Chang-
           ing the volume by operation of the piston is a fric-
           tionless process; upon volume reduction the entropy
           in the cavity is returned to the temperature source
           on the right, together with the energy in the cavity
           and the energy supplied by the piston against the
           radiation pressure. Only the radiation through the
           hole is an (irreversible) friction process.
           (u = energy/volume ratio; $\dot{V}$ = rate of change of
           volume)

     Since the expansion and compression of the radiation field
is similar to that of an ideal gas in classical thermodynamics,
the cavity radiation has been described as a photon gas. The
exception is that there is no equivalent to mass conservation

in this case since the number of photons can decrease and the pressure only depends on the temperature but is independent of the volume.

The cavity behaves as a C-field in the sense of bond graphs as is shown in Figure 5. The emission process itself involves friction since it produces new entropy to raise the relative entropy content of the emitted radiation to 133 percent, and is irreversible. Consequently absorption, the basis of solar thermal collectors, cannot take place alone but must be accompanied by the reemission of the excess entropy at the lower temperature of the solar collector [2]. This requires power and results in a kind of Carnot factor limitation for thermal solar collectors.
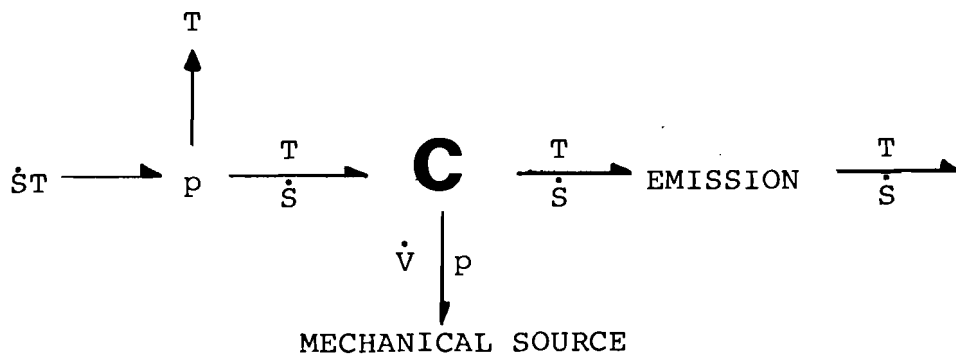

Figure 5. Bond graph corresponding to Figure 4, representing the cavity as a C-field, the thermometer as a p-junction, and the emission by EMISSION. The letter C represents a generalized capacitor network, the letter p a parallel junction; both are standard bond graph symbols.

POWER AND ENTROPY COLLECTION BY PHOTOCELLS

Carnot Factor for Photocells

Among the various devices for solar energy collection are photocells, which absorb thermal radiation and produce electric power. Being nonthermal electric power carries no entropy and the incoming entropy flow of the blackbody radiation must be removed by other channels. This requires power proportional to the sink temperature T_2 and leads to an efficiency limitation similar to that of heat engines described in [1] (Figure 1, Equation 2). If the entropy is removed to the sink by conduction (instead of reradiation into space) the power is $\dot{S} T_2$, and efficiency η_{cT} becomes

$$\eta_{cT} = \frac{3/4 \ \dot{S}T_1 - \dot{S}T_2}{3/4 \ \dot{S}T_1} = 1 - \frac{4}{3} \frac{T_2}{T_1} \tag{10}$$

(see Figure 6). In spite of the aggravating factor of 133 percent, the Carnot factor η_{CT} remains high because of the high source temperature. With

$$T_1 = 5760 \text{ K and } T_2 = 310 \text{ K } (37^{\circ}\text{C}) \text{ ,}$$

one obtains

$$\eta_{CT} = 92.8\% \text{ ,}$$

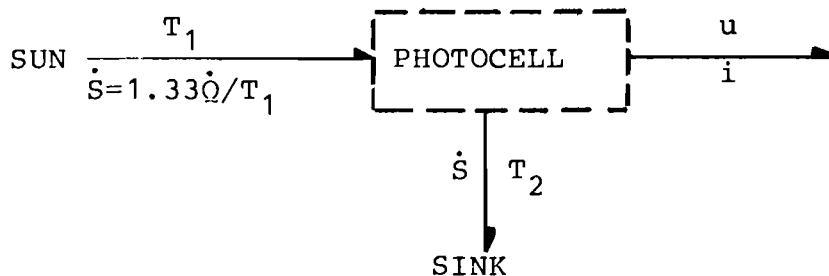which could be considered a zero-order approximation to photocell efficiency.

Figure 6. Global representation of a photocell. The incoming entropy flow of solar radiation must be removed by the low-temperature sink, which poses a Carnot factor efficiency limit of about 93 percent.

Available photocells have efficiencies far below the Carnot factor of the order of 10 to 15 percent. Hence about 90 percent of the incoming power must be removed, and 310 K seems to be the lowest feasible operating temperature. The performance of photocells deteriorates rapidly with increasing temperature, much more than is indicated by the reduction of the Carnot factor [4].

The efficiency of available photocells is further below the Carnot factor than the efficiency of steam power plants and Diesel engines. There seems to be more room for improvement, therefore, and it is of interest to look into the conversion process with its various loss mechanisms.

Bond Graph Representation of Photocells

Figure 7 shows a photocell with the various effects and elements represented by letter symbols and interconnected by lines or bonds numbered consecutively 1 to 11. The powers are denoted $\dot{E}_1$ to $\dot{E}_{11}$. The symbols stand for the following:

RFL   between bonds 1, 2, and 3 denotes the reflection of the incoming solar radiation to the sky from the surface of the cell. This reflection is power- and entropy-conserving.

PHOTEF is the photoeffect itself, where photons kick or push electrons out and across the PN-junction in semiconductors. The electric power represented by $ev\dot{n}$ enters bond 9 ($\dot{n}_9$ = kicked particle flux), while the excess energy of the photon appears as kinetic energy in bond 8. The kinetic energy that originates from kicking can be called "football energy".

RS   describes the various loss mechanisms, each consisting of a friction element or resistor R directly connected to an entropy source S. They are numbered according to the bond that leads into them:

RS 4   represents the photons below threshold $h\nu < ev_{11}$ which cannot kick and dissipate their energy to the lattice or ion structure and thus produce new entropy.

RS 6   represents the photons above the threshold which do not kick because of the finite quantum photoefficiency.

RS 8   shows the dissipation of the excess kinetic energy ("football energy"), of the electrons that have been kicked, by collision with the lattice or structure of the material.

RS 10 shows the electric leakage current of the PN-junction. Its value is given as the resistance of a reversed biased diode.

j   is a general conserving connection or junction, and

p   is a parallel junction that is also power-conserving.

Figure 7 contains at the bottom representative values of the losses which are expressed in percentages of the power influx after reflection $\dot{E}_3$. With the quantum collection efficiency being arbitrarily set to 1 ($\dot{E}_6$ = zero) they indicate the power contained in the photons below threshold $\dot{E}_4$ and the excess kinetic energy of the kicking photons $\dot{E}_8$. They are based on Planck's formula of black cavity radiation. The values of Figure 7 correspond to 0.45 volt operating voltage and yield an efficiency of 29.6 percent.

Table 1 describes loss and efficiency values on the same basis but with different operating voltages. It is seen that with increasing voltage the losses below threshold increase and the "football" losses decrease, the optimum being close to one volt.
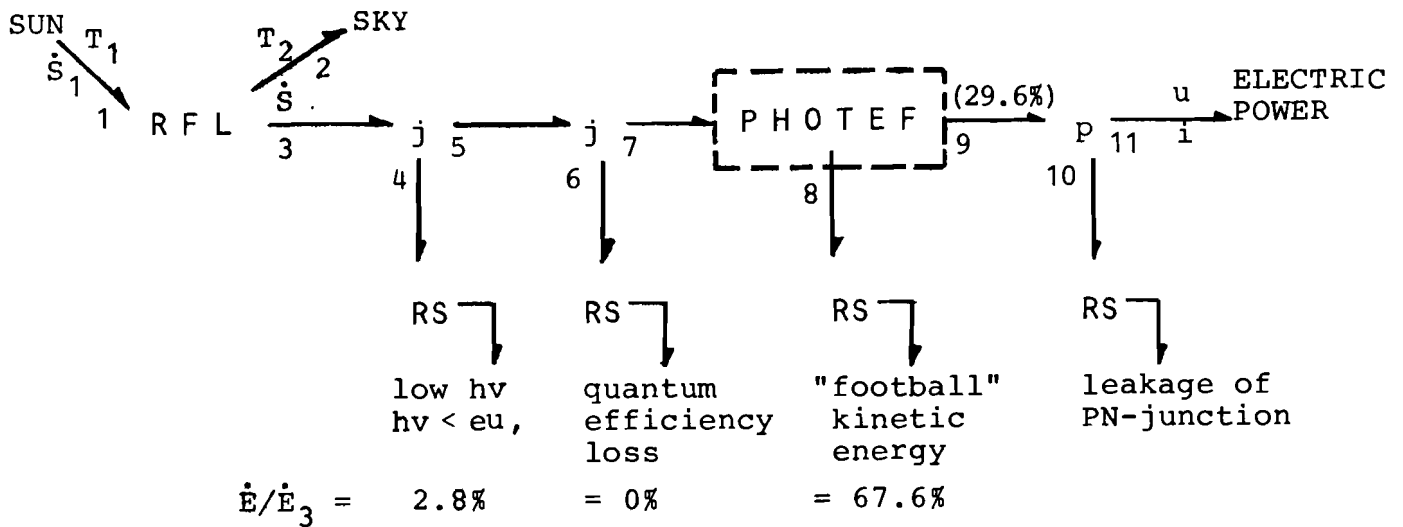
Figure 7. More detailed representation of a photocell with
various loss mechanisms as RS-fields. The per-
centages below refer to a second approximation to
efficiency. (RFL is the frictionless reflection of
the photocell surface; for other abbreviations see
text).

Table 1: First order approximation to photocell efficiency
and various losses according to Figure 7 as a func-
tion of operating voltage v_{11}[1].

v_{11} (volt)	0.4	0.45	0.5	0.6	0.8	1.0	2.0
$\dot{E}_1$ (%)	100	100	100	100	100	100	100
$\dot{E}_4$ (%)	2.7	2.8	3.7	5.8	11.5	18.9	61.1
$\dot{E}_8$ (%)	70.9	67.6	64.4	58.2	47.0	37.4	10.2
$\dot{E}_9$ (%)	26.4	29.6	31.9	36.0	41.5	43.7	28.7

[1] H.-R. Grümm of IIASA compiled the formulae and executed
the necessary integrations of Planck's formula on an HP 9830
desk calculator.

As regards the entropy flow from the photocell, since entropy is proportional to the spectral energy density according to Equation (8), the below-threshold losses simply absorb a corresponding part of the incoming entropy flux. The same applies to the photons that do not kick in bond 6 in Figure 7. They generate new entropy depending on the temperature at which the loss power is removed from the photocell. The entropy of the kicking photons and their friction power are removed via bond 8.

When a photocell is run with monochromatic light and with matching operating voltage, the excess kinetic energy could become small. Further clarification is desirable, therefore, regarding the efficiency of photocells with monochromatic light in connection to the entropy content of the incoming radiation, be it coherent or not.

The solar entropy flow is contained in the incoherence of blackbody radiation [5]. This follows both from classical and from quantum-mechanical considerations.

ENTROPY PRODUCTION IN COMBUSTION AND ENTROPY CONTENT OF EXHAUST GASES

Combustion and Oxidizing Reactions

Combustion is a reaction between fuel and oxygen to produce oxides, while inert substances, such as nitrogen, during the reaction travel to the outlet without much change. The relations between the variables are more complex than in photocells and are based on concepts such as free energy of chemical thermodynamics. The following is a short account of these relations based on network thermodynamics, which is much simpler because it explicitly uses the concept of phenomenological entropy as thermal charge or gray paste. Discussion will include both ordinary combustion and oxidizing reactions in fuel cells.

Batch Representation of Combustion and Chemical Reactions

Matter with constant mass behaves like a C-field with two ports, which means that there is a functional relation between the four variables pressure, volume, temperature, and entropy. This behavior is frictionless and reversible, but any friction of a real process must be accounted for by separate RS-fields. A variable mass, as in a chemical reaction, appears in a third bond with the chemical potential represented as effort and the molar mass flow as flow [6].

As an introduction to the bond graph representation, Figure 8 on the left shows an electric network with two capacitors connected by a resistor. An electric current flows if the voltages u_1 and u_2 are unequal, its value depends on

the resistance. The power that is dissipated and that equals
the voltage drop times current appears as heat flow, i.e. is
generated entropy flow times temperature at the resistor, as
indicated.

Figure 8 on the right contains an equivalent bond graph
with C-elements for the capacitors, and the resistor in between
in series, as shown by the s-junction. Its symbol is RS, the
usual R together with an S indicating that it is a source of
thermal power (heat flow). It is the dissipation that is
irreversible since it generates entropy.
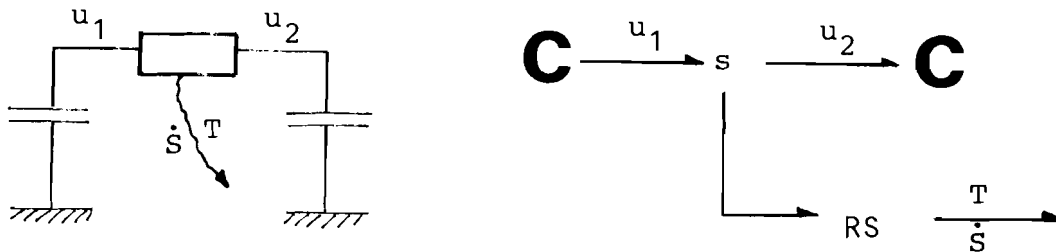
Figure 8. Electric network with two capacitors and one resistor
           in between, represented by circuit symbols (left) and
           as bond graph (right). The symbol RS represents a
           resistor (or friction) with an entropy source.

Chemical reactions are exemplified by Figure 9, which is a
basic representation or reticulation of a chemical reaction in
an arrangement similar to that of Figure 8. The reactants are
contained in the C-element on the left, the products in the C-
element on the right. If desired, one can draw a C-element for
each of the reactions and products (chemical species), which are
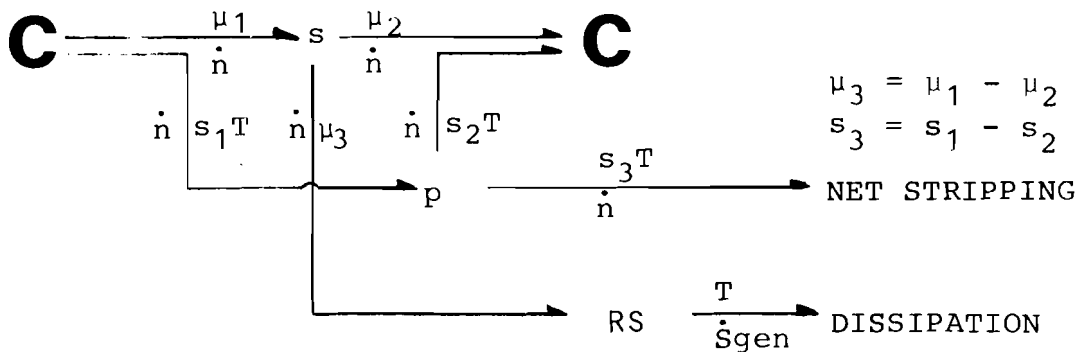connected in series via transformers ([6] and Figure 11 further
below).

Figure 9. Basic reticulation of a chemical reaction with entropy
           stripping. In addition to dissipation $\dot{S}$gen, there is
           a reversible, net stripping entropy flow. μ = chemical
           potential, $\dot{n}$ = molar mass flow, sT = effort in the
           stripping bond (equal to entropy/mass ratio times ab-
           solute temperature).

New compared to the electric case is the stripping (strip-
tease) of entropy. The mass flowing out from the reactants
carries structural entropy as indicated by the double line. This
entropy must be stripped off in order to determine the effort
(voltage like variable) responsible for the flow, as shown by the
well known Gibbs formula

$$\mu = \frac{G}{n} = G = U - TS + pV \quad , \tag{11}$$

where

G = free enthalpy (Gibbs free energy),
n = molar mass,
μ = chemical potential,
U = internal energy.

Here -TS represents entropy stripping, but the term pV gives a
pressure/volume ratio that is less important in the present con-
text ([6] and Figure 11 further below). Nature simply requires
the stripping of entropy, which is the fundamental reason why
the ratio (or derivative) of free enthalpy to molar mass is the
chemical potential (driving effort) and not the derivative of
internal energy as in mechanics.

Putting together the products in Figure 9 on the right,
the necessary structural entropy is taken unstripped from the
parallel junction (p-junction), while the net stripped entropy
flow appears on the right. Contrary to dissipation, net strip-
ping or structural entropy change is reversible and its
value depends on the structure of the molecules (see, for in-
stance, [7]).

Both the dissipated and the net stripped entropy appear at
the thermal interface. If the unstripped entropy (structural
entropy of the products) is much larger than the stripped one,
it may exceed the dissipation. Then the reaction requires
entropy from outside to keep its temperature constant or,
in other words, it is endothermic.

Representations such as Figure 9 are also called reticula-
tions, the term being derived from chemical networks in the
spirit of network thermodynamics. All variables in Figure 9,
in particular the chemical potentials, depend on the temperature
(see Equation (12) below).

Figure 10 is a reaction with added electrochemical ion coup-
ling such as in batteries and fuel cells. The coupling is in-
dicated by the transformer TF connected in series with the other
chemical power flows $\mu\dot{n}$. Here the reaction rate, at given
chemical potentials of reactants and products, depends not only
on the chemical resistance but also on the transformed electric
voltage. With a suitable external voltage u the reaction can

be made to run slowly and with an (almost) vanishing chemical
potential to drop at the chemical resistance. Then the dissi-
pation also disappears and the reaction becomes reversible.
In order to arrive at this ideal situation it is all-important
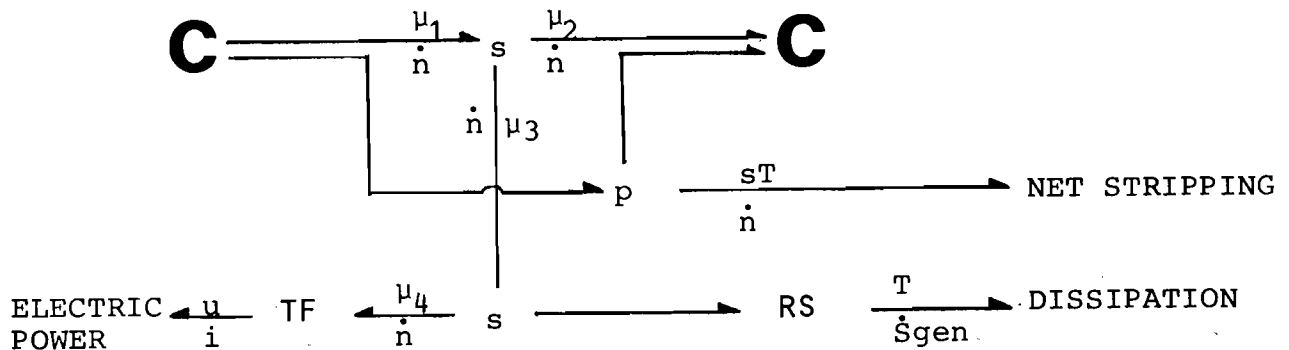to reduce the chemical resistance, which is an important part of
fuel cell research[1].

Figure 10. Reticulation of a chemical reaction with ion coup-
            ling as in batteries and fuel cells. The letters
            TF represent a generalized power-conserving trans-
            former.

In summary the power fluxes in chemical reactions are:

(1)   the net stripping power $T\dot{S}_{str}$ as the difference of struc-
      tural entropy of reactants and products. This is a revers-
      ible thermal power flux.

(2)   The irreversible dissipation $T\dot{S}_{gen}$; and

(3)   The electric power that is removed by ion coupling ui
      (shown only in Figure 10).

      Figure 11 is a slightly more complete chemical reaction
with two reactants and one product, such as $C + \frac{1}{2}O_2 = CO$. Apart
from the two C-elements for the two reactants, Figure 11 has
the following new features:

(a)   A transformer TF for the stoichiometric coefficients ($\frac{1}{2}$ in
      the above example). It transfers the chemical potential
      into affinity and the molar mass flow into an "advancement
      (rate) of chemical reaction";

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[1]For "well stirred reactions", RS is only the chemical re-
sistance. In the case of spatial variations of C-concentration
gradients, additional RS have to be introduced for the inter-
diffusion of chemical species.

(b)   The hydraulic bonds on top of the C-elements. They indi-
cate the volume changes.

In Figure 11 there is an additional power flow:

(4)   The hydraulic power given by the volume rate of change
times the external pressure.

The simple Figure 9 is used in this paper to describe plant
growth and biomatter since it contains the essentials of such
chemical reactions. This figure should also be the starting
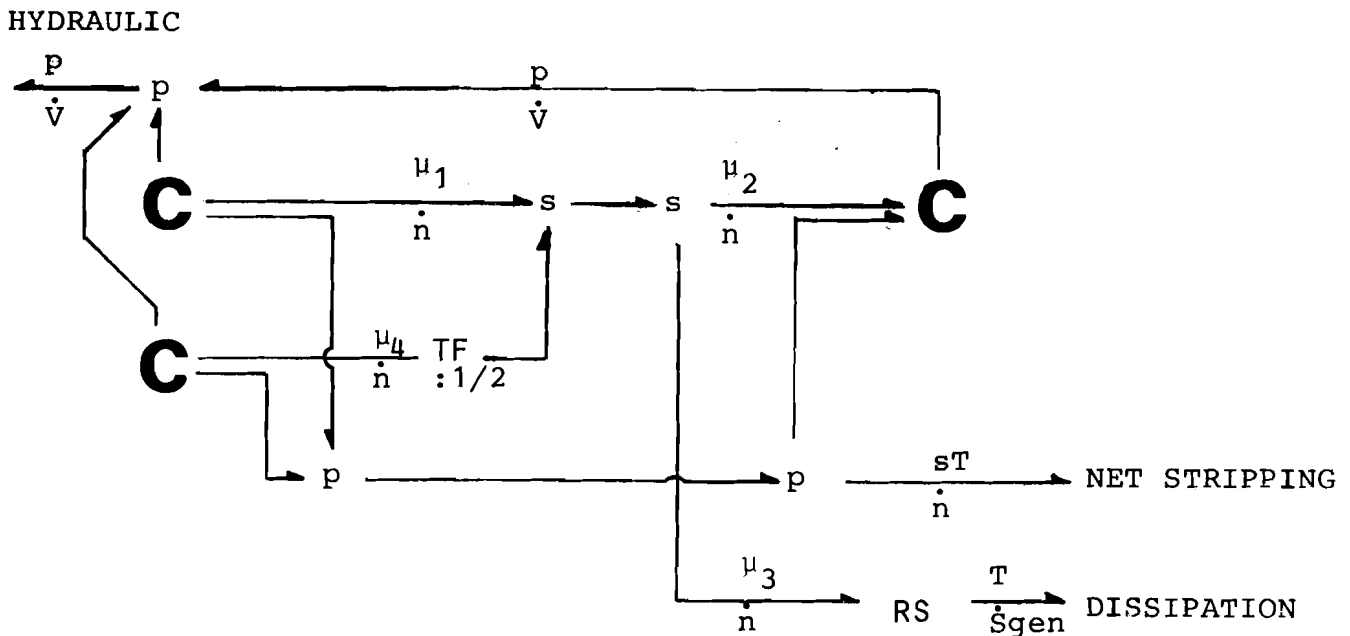point for work on relations or analogies with economic capital
and human labor.

HYDRAULIC

Figure 11.   Chemical reaction with two reactants and one product.
The transformer TF represents the stoichiometric co-
efficient.

Quantitative Relations or Constitutive Equations

We have seen that the chemical potential represents the
tendency of matter of one chemical species to change to others,
much like the voltage for the electric charge in a capacitor.
The chemical potential depends mainly on the temperature and
concentration, for which one uses the following constitutive
equation in chemistry

$$\mu = \mu_o(T) + RT \ln ac \quad , \tag{12}$$

with

        c = n/N concentration;
        R = universal gas constant;
        a = activity coefficient;

(the latter tends to 1 at low concentration). μ_o is the con-
centration-independent (temperature-dependent) part of the
chemical potential.

We have discussed the change of structural entropy during
a reaction. Actually this entropy depends on the temperature.
One can imagine the structural entropy capacity as a vase filled
with entropy to a certain level (temperature) after Wiberg [7].
As shown in Figure 12, the vase changes its width (capacity)
with the reaction and requires external entropy to maintain its
level. This corresponds to the net stripping flows of Figures
9 to 11. In Figure 12 the width increases, the vase absorbs
external entropy, and the chemical reaction is endothermic if
the dissipation is not too high. If the reaction is run in ther-
mal insulation (adiabatically), the level in the vase tends to
decrease. With negligible dissipation, the decrease of tempera-
ture will be such as to maintain the stored entropy constant.

The tables for entropies and chemical potentials are al-
ways given for certain temperatures and pressures, usually at
298 K and 1 bar absolute (matters under these conditions are
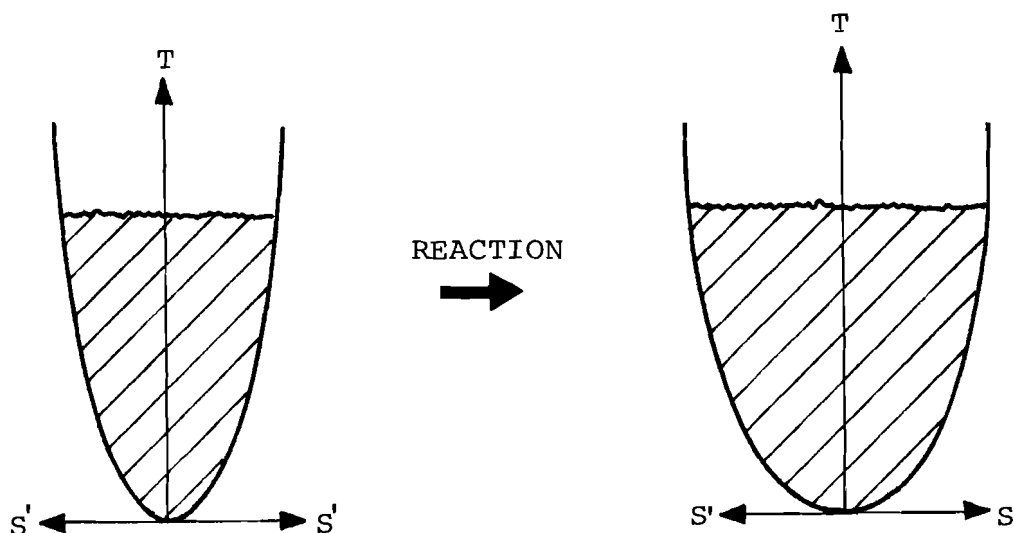

Figure 12.   Structural entropy capacity of a chemical species
             represented as a vase that changes its width
             (diameter) during the reaction. Keeping the level
             (temperature) constant requires entropy from the
             environment.

said to be in the standard state). Values for other temperatures can be calculated [7]. It should be noted that the observable heat of the reaction is the sum of net stripping and dissipation (with $\Delta\mu n = \Delta G$)

$$\dot{Q}_{obs} = \Delta\mu\dot{n} + T\,\dot{S}_{str} = \Delta\dot{H} \,, \tag{13}$$

with the enthalpy flux

$$\dot{H} = \dot{G} + T\dot{S} \ .$$

Finally it should be noted that the batch representation of the chemical reactions in Figures 9 to 11 corresponds to the Lagrangian viewpoint in fluid mechanics.

Eulerian Representation of Combustion

Figure 13 is an Eulerian representation of a chemical reaction with the fuel and the oxidant entering from the left. The net-stripped and the generated entropy flows are injected into the combustor output through the general power-conserving junction j. The mixture of fuel and oxidant then goes into a heat exchanger HEX, which is like a steam boiler, where it delivers entropy before it goes to the outlet.

In Figure 13 the entire chemical potential is dissipated, but the entropy generation depends on the temperature at the combustor outlet. It is chosen according to the technological limits of the material, such as its high-temperature strength, and can be controlled by bypassing a mass flow or by running
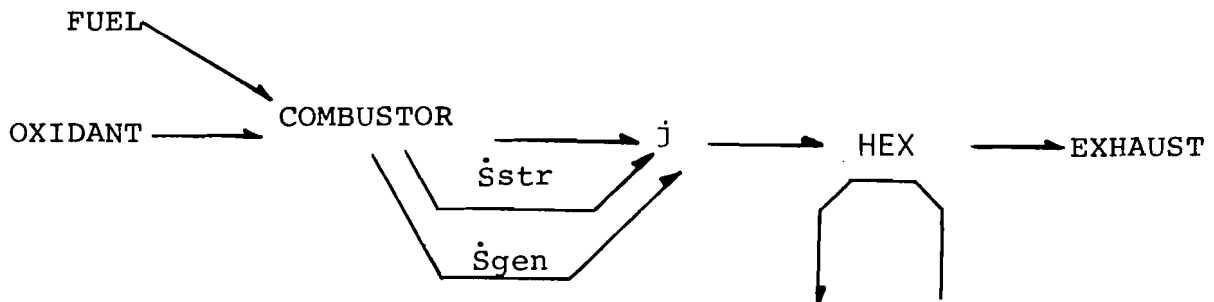

Figure 13.   Eulerian representation of combustion with heat exchanger HEX before exhaust. The net-stripped entropy flow $\dot{S}_{str}$ and the entropy flow $\dot{S}_{gen}$ generated by dissipation are shown separately although they are physically in the combustor and its outlet pipe.

through the combustor an inert gas such as nitrogen. Much
entropy is generated in the process, the more the lower the
temperature is at the inlet of the heat exchanger. The hydrau-
lic bond of Figure 10 is not shown separately in Figure 13
since it is part of a combustion gas flow and of less importance
for entropy relations.

The various bonds of Figure 13 are fluid lines and have
several power components. In particular, the stripped and dis-
sipating entropy flows are physically always contained in the
combustor outflow. Nevertheless, the conceptual separation of
Figure 13 underscores these basically different flows.

Figure 14 is another representation of the combustion
reaction. It shows explicitly that the reactants are brought
from their standard state to combustion pressure and tempera-
ture by supply of mechanical and thermal power in the prepara-
tor before the reaction. Thereafter this power is similarly
taken out again in decompressors. In practice various steps
of preparation are taken, such as compression in internal com-
bustion engines and gas turbines, and air preheating from
exhaust gases in steam boilers. The Figure also stresses the
importance of the change of state of the reactants and products
for the efficiency, the dissipation, and the speed of the
reaction. This is connected with the general reduction of the
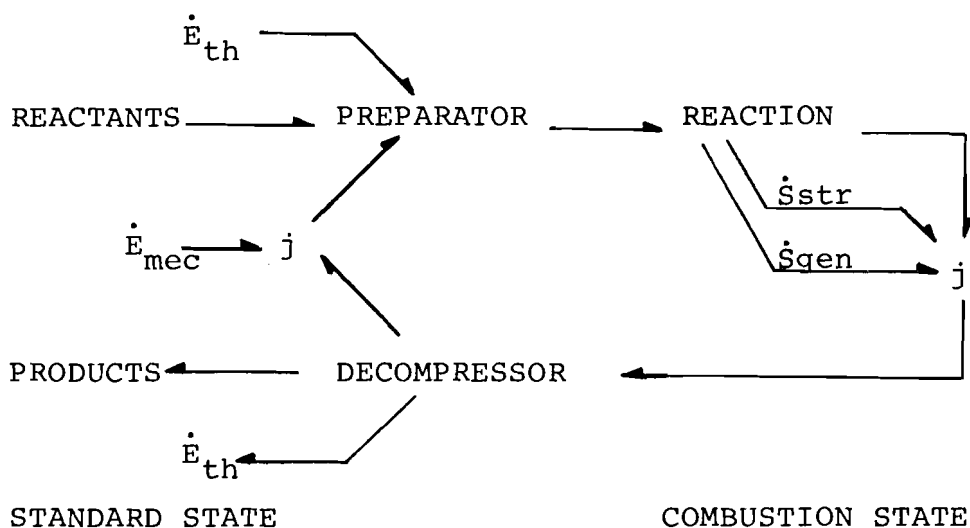chemical resistance at a high temperature.

Figure 14. Representation of combustion or other chemical
reactions showing the preparation of the reactants
from their standard (environmental) state to ob-
tain the appropriate reaction pressure and tempera-
ture by addition of mechanical and thermal power in
a preparator. This process can be frictionless.
Similarly the products are returned to their stan-
dard state by the decompressor.

PHOTOSYNTHESIS OF BIOMATTER

Plant growth by photosynthesis is essentially an oxidation reaction driven in reverse by the incoming blackbody radiation of the sun. Its description therefore is a combination of the photocell and the bond graphs of a chemical reaction.

Figure 15 is a global bond graph for plant growth, where the biomatter accumulation takes place in the big C-field. Re-radiation to the sky serves to carry away not only the incoming entropy flow but also the stripped entropy flow of the oxides (minus the smaller unstripped entropy flow entering the biomatter structure), and the various dissipations.
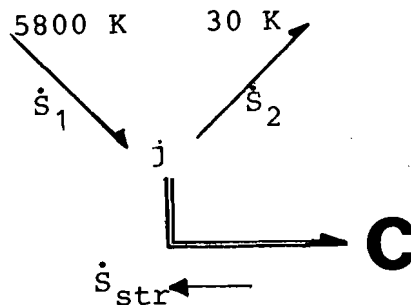

Figure 15.   Global representation of plant growth as C-field with a mass bond. Structural entropy is removed by the incoming radiation and reradiated to the sky.

Figure 16 contains more detail and is similar to Figures 7 and 10. Here the photosynthesis is driven or pumped against the chemical potential by photon power. This allows to move the excess stripping or structural entropy back to the re-radiation surface, together with the chemical dissipation of the RS-field, from which it is returned into space. Naturally there are many more dissipations that all produce entropy to be radiated into space. The term biomatter in Figure 16 includes oxygen and other products of photosynthesis.

When sunlight disappears in the dark there is no photon pumping. Then the reaction runs in the direction of oxidation and, generally, plants consume again at night a definite percentage of the oxygen and biomatter they produce by day.

In global terms plant growth is a reverse combustion and results in an accumulation of energy and negentropy (reduction of structural entropy) in biomatter. This state basically corresponds to the average temperature and pressure of our environment.
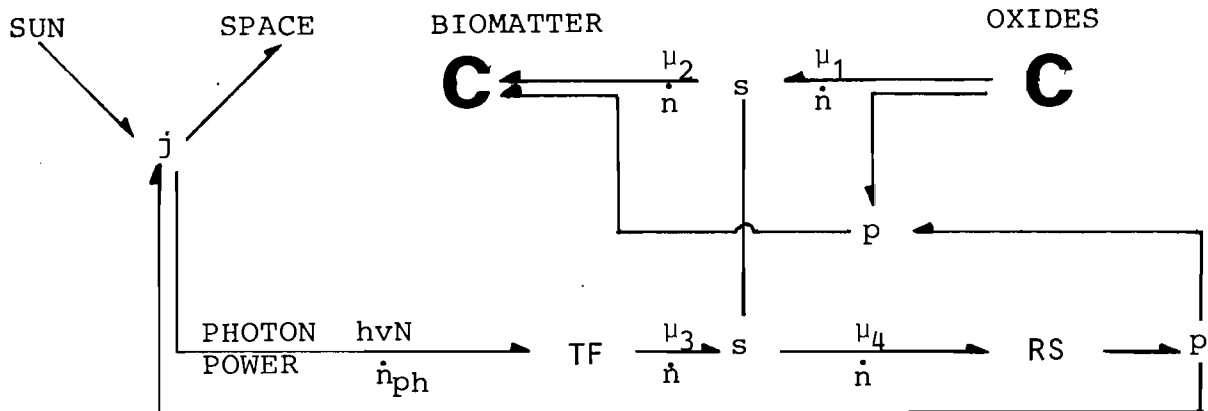
Figure 16. Detailed representation of plant growth as a combination of photocells and chemical reaction. The reaction is driven by the photon power against the chemical potential differences, and, together with the dissipations, the structural entropy is returned to the sky.

Looking at Figures 10 to 16 one might be tempted to say that the transport of structural and dissipation entropy into space by re-radiation is more important for life than the incoming thermal power of the sun. In practice, of course, life would not be possible without both sustaining effects.

The importance of storage effects or C-fields in Figures 15 and 16 is derived from the fact that plant growth is essentially an unsteady process. It appears to be globally steady (time-independent) if one also considers plant decay or oxidation. There the stored energy is released and the structural entropy of the standard state recovered or the corresponding negentropy expelled. However, the dissipations are irreversible and the generated gray paste will always exist somewhere in our universe. The corresponding negentropy is permanently consumed.

ENERGY AND NEGENTROPY ACCUMULATION AND INFORMATION

With respect to W. Häfele's view that the consumption of negentropy is an essential aspect of the process of life [8] one may certainly hold that biomatter contains less entropy than their constituant oxidants (H_2O and CO_2). Therefore negentropy is stored. At the same time there is also storage of chemical energy with respect to the standard state.

When stored negentropy is released by combustion or a similar reaction, both the stored entropy and the structural negentropy become available. It would therefore be possible in principle to use that energy in industry and for private

consumption. It will ultimately dissipate, and the entropy that is generated could be partly redeposited as structural entropy in the combustion products or oxides. Environmentally this would be an excellent way to provide for human needs.

Unfortunately, all oxidations involve much dissipation, which is especially true for combustion. In this case, entropy is generated and put into water to drive a steam turbine and is rejected thereafter to the environment while heating rivers or the atmosphere. Oxidation in a fuel cell is fundamentally much better since it does not require entropy generation by dissipation.

The description of the sun as an negentropy source is actually an oversimplification. Rather the entropy flow at a high temperature represents much power and allows to pump the entropy of the standard state oxides away to produce structural negentropy by re-radiation of the entropy into the sky.

The pumping action of the incoming solar entropy flow can be compared to the draining of a building excavation, where a pump is driven not electrically but by a high-pressure water motor (Figure 17). The water leaving the motor mixes with the water in the excavation and must also be moved by the pump. Globally a small water flow at a high pressure is transformed into a larger flow at a lower pressure that drains the excavation including the motor output. High-pressure water motors were often used in the nineteenth century before the development of electric power transmissions. An interesting variation of that time was the hydraulic ram, where an unsteady flow and valves replaced moving shafts, wheels, and pistons.
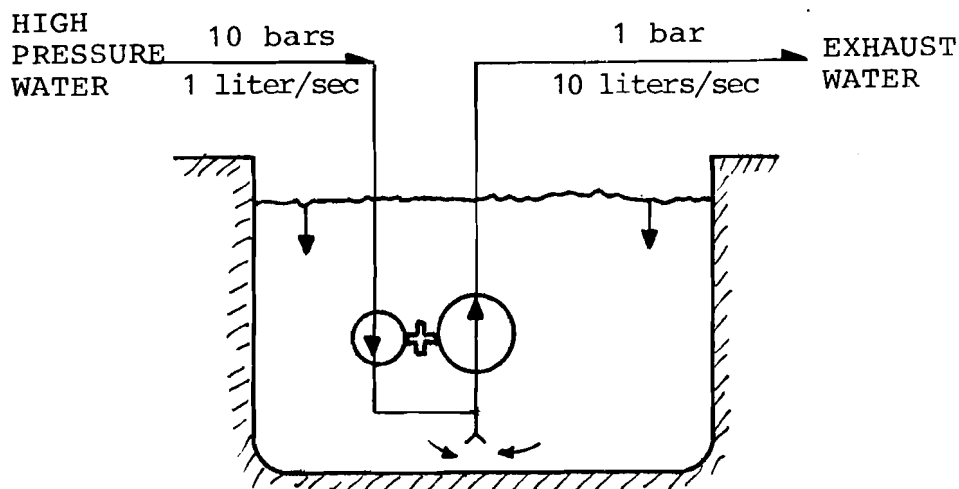

Figure 17. Building excavation as an analogy to plant growth of Figures 15 and 16. The water level is lowered by a draining pump that is driven by a high pressure water motor. The pump must also remove the water flow leaving the motor.

Concerning the relation between information as statistical negentropy and information in physical capital, one may say that the negentropy in the structure of matter certainly contains information. But its information value is high (several bits per molecule), and much higher than the amount of information in the numerical specification of capital equipment ([1], Section 3). The ratio of the two is the difference of macro- and micro-information that is described in [1]. For further work in this direction not much accuracy can be expected, but even orders of magnitude are most interesting.

The concept of negentropy as being equivalent to order and information is very persuasive. Only in nature there exists no negative entropy, and the zero point of all entropy in matter is given by the Nernst theorem or third law of thermodynamics: At the zero level on the Kelvin scale all matter contains no entropy (unless some entropy is frozen in). Negentropy is always counted from a certain reference or standard state for which the environmental or standard values can be taken, just as this is usually done for exergy.

An interesting effect is Häfele's entropy buffer [8], which is needed to separate flows and to extract entropy by processes such as the combination in oceans of high-temperature water from the surface and low-temperature water from the depth. Presumably one will find a similar redundancy as between macro- and micro-information.

One may conclude that the present description of the various processes indicates that there is much room for improvement of technological devices and processes and provides incentives for research. There is no natural law against economizing a great amount of negentropy or one that helps to protect the environment from excessive entropy rejection. There are of course many technological obstacles to progress, but they could be removed by new breakthroughs and inventions.

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