

The endoreversible theory of solar energy conversion: a tutorial

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In the present tutorial, solar energy conversion is described in the framework of endoreversible thermodynamics, i.e. a recently developed subset of irreversible thermodynamics. From a general thermo-chemical endoreversible engine, we deduce the photovoltaic, the photothermal and the photochemical solar energy converter, besides of a few other, non-solar devices.

1. Introduction

The name *endoreversible thermodynamics* was introduced by Rubin [1]. It refers to a subset of irreversible thermodynamics. Modelling and calculations are easy, because all irreversibilities are restricted to transports. No irreversibilities are assumed to be related to conversions, mixings, etc. In the present paper, we will make matters even more transparent, as we will restrict our selves to stationary transports.

From a general framework, we will deduce various special cases, in particular those that can be applied to solar energy conversion. Thus we will follow the deductive approach: from the general model, the special cases will be derived. This is in contrast to previous publications [2,3], where an inductive line of reasoning was followed: from simple to more complicated examples, the general theory of endoreversible energy conversion was constructed.

2. Endoreversible engines

In the present section, we introduce endoreversible thermodynamics, a special class of irreversible thermodynamics. In an endoreversible system all irreversibilities are located in the transports from the source to the converter and from the converter to the sink. The inner part of the converter, however, is reversible. Hence the name endoreversible engine ($\epsilon\nu\delta\alpha$ meaning inner).

Fig. 1a shows a general endoreversible engine. It consists of four reservoirs. Their temperature T is constant, and so are their intensive quantities x , y , ...

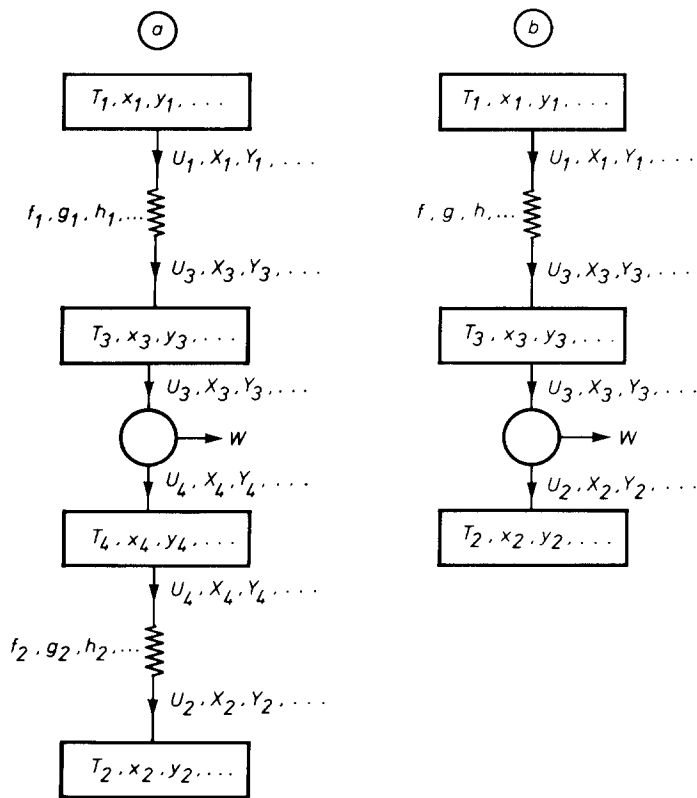


Fig. 1. Endoreversible engines. (a) Most general endoreversible engine, (b) endoreversible engine with only losses in the supply.

Each reservoir can supply an energy current U as well as extensive quantity currents $X, Y, \dots$, where the current X is associated to the parameter x , in such a way that the product xX is a work current. Some examples of intensive variables x and their associated extensive variables X are given in table 1.

The reservoirs #1 and #2 are the external reservoirs (source and sink, respectively) whereas the reservoirs #3 and #4 are the internal or intermediate reservoirs. Between reservoir #1 and reservoir #3 is an irreversible conductor, between reservoir #3 and reservoir #4 is a reversible engine and between reservoir #4 and

Table 1
Analogy between different thermodynamic quantities

Engine	x	X
chemical reactor	chemical potential μ	particle flow N
pneumatic engine	pressure p	volume flow v
electrical circuit	voltage V	current I

reservoir #2 is a second irreversible conductor. In each of these three parts the following axiom holds:

Axiom 1: conservation of energy:

$$U_3 = U_1, \quad U_4 = U_3 + W, \quad U_2 = U_4,$$

where the U 's denote the energy currents and W denotes the produced power, i.e. work per unit time.

The fact that the inner engine is reversible means that it satisfies the following second axiom:

Axiom 2: conservation of entropy:

$$S_4 = S_3,$$

where the S 's are the entropy currents associated with the energy currents U and the currents $X, Y, \dots$:

$$S = \frac{U - (xX + yY + \dots)}{T}.$$

The condition $S_4 = S_3$ thus expresses that no entropy is generated in the engine itself, in accordance with the name *endoreversible*: reversible in its internal parts. Thus all entropy generation takes place in the two conductors, i.e. in the communication between the engine and the external world, the latter consisting of reservoirs #1 and #2.

Note that we can also write

$$S = \frac{Q}{T},$$

where Q is $U - (xX + yY + \dots)$, the equality

$$U = Q + (xX + yY + \dots)$$

having to be interpreted as follows: the energy current U consists of two parts, i.e. a "high quality" part $xX + yY + \dots$ of power and a "low quality" part Q of heat.

The communication rate is assumed to be governed by transport equations of the form

$$\begin{aligned} U_1 &= f_1(T_1, x_1, y_1, \dots) - f_1(T_3, x_3, y_3, \dots), \\ X_1 &= g_1(T_1, x_1, y_1, \dots) - g_1(T_3, x_3, y_3, \dots), \\ Y_1 &= h_1(T_1, x_1, y_1, \dots) - h_1(T_3, x_3, y_3, \dots), \\ &\dots, \end{aligned}$$

for the communication between #1 and #3, and similarly by

$$\begin{aligned} U_2 &= f_2(T_4, x_4, y_4, \dots) - f_2(T_2, x_2, y_2, \dots), \\ X_2 &= g_2(T_4, x_4, y_4, \dots) - g_2(T_2, x_2, y_2, \dots), \\ Y_2 &= h_2(T_4, x_4, y_4, \dots) - h_2(T_2, x_2, y_2, \dots), \\ &\dots, \end{aligned}$$

for the communication between #4 and #2. Here $f_1, g_1, h_1, \dots, f_2, g_2, h_2, \dots$ are assumed to be known mathematical functions.

The total entropy creation rate is given by the entropy flow leaving the system minus the entropy flow entering it:

$$\sum S = S_2 - S_1 = \frac{Q_2}{T_2} - \frac{Q_1}{T_1},$$

of which the contribution

$$\frac{Q_3}{T_3} - \frac{Q_1}{T_1}$$

is generated in the conductor $f_1, g_1, h_1, \dots$ and the contribution

$$\frac{Q_2}{T_2} - \frac{Q_4}{T_4}$$

is generated in the conductor $f_2, g_2, h_2, \dots$.

For sake of simplicity, we will restrict ourselves almost exclusively to cases where rates are limited by the exchanges between reservoirs #1 and #3. Thus we assume no limitation in the communication between #4 and #2. We say that reservoirs #4 and #2 are short-circuited. Thus

$$T_4 = T_2, \quad x_4 = x_2, \quad y_4 = y_2, \quad \dots$$

See fig. 1b. Therefore we can simplify notations, by dropping subscripts for $f, g, h, \dots$:

$$\begin{aligned} U_1 &= f(T_1, x_1, y_1, \dots) - f(T_3, x_3, y_3, \dots), \\ X_1 &= g(T_1, x_1, y_1, \dots) - g(T_3, x_3, y_3, \dots), \\ Y_1 &= h(T_1, x_1, y_1, \dots) - h(T_3, x_3, y_3, \dots), \\ &\dots \end{aligned}$$

The only exception, where we will have to consider a finite conductance between reservoirs #4 and #2, will appear in section 5.3.

3. Endoreversible thermo-chemical engines

In thermo-chemical reservoirs we have only one intensive variable in addition to the temperature T , i.e. the chemical potential μ . The extensive variable, associated with it, is the particle current N . Thus $x = \mu$ and $X = N$. See fig. 2a.

To the two general axioms of section 2, i.e. to

$$U_3 = U_1, \quad U_2 = U_3 + W, \quad \frac{U_2 - \mu_2 N_2}{T_2} = \frac{U_3 - \mu_3 N_3}{T_3},$$

we add a new, specific, axiom:

Axiom 3: conservation of particles:

$$N_3 = N_1, \quad N_2 = N_3.$$

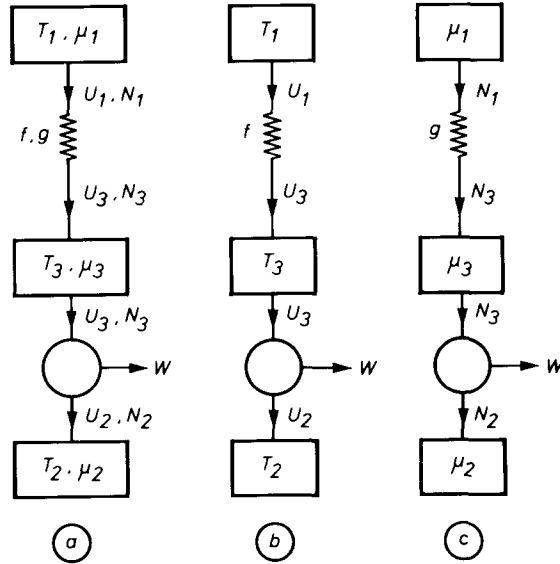


Fig. 2. Endoreversible engines. (a) Thermo-chemical engine, (b) thermal engine, (c) chemical engine.

The reader will easily verify that the three axioms together lead to

$$W = \left(1 - \frac{T_2}{T_3}\right) U_1 + \left(\frac{T_2}{T_3} \mu_3 - \mu_2\right) N_1,$$

a generalised Carnot law.

The conduction laws become simply

$$U_1 = f(T_1, \mu_1) - f(T_3, \mu_3), \quad N_1 = g(T_1, \mu_1) - g(T_3, \mu_3),$$

where the functions f and g are assumed to be two known mathematical expressions.

The extracted work W is thus given by

$$W = \left(1 - \frac{T_2}{T_3}\right) [f(T_1, \mu_1) - f(T_3, \mu_3)] \\ + \left(\frac{T_2}{T_3} \mu_3 - \mu_2\right) [g(T_1, \mu_1) - g(T_3, \mu_3)].$$

For fixed parameters of the “external” reservoirs, i.e. for fixed T_1 , μ_1 , T_2 and μ_2 , the extracted power W is thus a function of the two independent variables T_3 and μ_3 . This function $W(T_3, \mu_3)$ usually displays a maximum $W_{\max}$ for a particular set of coordinates (T_3, μ_3) , called the maximum-power point MPP.

The entropy creation rate is given by

$$\begin{aligned}\Sigma S &= \frac{Q_3}{T_3} - \frac{Q_1}{T_1} = \frac{U_1 - \mu_3 N_1}{T_3} - \frac{U_1 - \mu_1 N_1}{T_1} \\ &= \left(-\frac{1}{T_1} + \frac{1}{T_3} \right) [f(T_1, \mu_1) - f(T_3, \mu_3)] \\ &\quad + \left(\frac{\mu_1}{T_1} - \frac{\mu_3}{T_3} \right) [g(T_1, \mu_1) - g(T_3, \mu_3)].\end{aligned}$$

This $\Sigma S(T_3, \mu_3)$ displays a zero minimum for the coordinates (T_3, μ_3) equal to (T_1, μ_1) , a point called the reversible point RP.

3.1. Linear engines

The simplest functions f and g are

$$f(T, \mu) = AT + B\mu, \quad g(T, \mu) = CT + D\mu,$$

where A , B , C and D are constants. We can call A and D conductivities and B and C transconductivities. This linear model is often used to describe non-equilibrium thermodynamics not-far-from equilibrium.

The resulting function $W(T_3, \mu_3)$ is very simple:

$$\begin{aligned}W &= \left(1 - \frac{T_2}{T_3} \right) [A(T_1 - T_3) + B(\mu_1 - \mu_3)] \\ &\quad + \left(\frac{T_2}{T_3} \mu_3 - \mu_2 \right) [C(T_1 - T_3) + D(\mu_1 - \mu_3)],\end{aligned}$$

such that the maximum-power point can easily be calculated from

$$\frac{\partial W}{\partial T_3} = 0, \quad \frac{\partial W}{\partial \mu_3} = 0.$$

Calculations are straightforward, but involve some cumbersome square roots.

3.2. Radiative engines

In a radiative engine, the particles exchanged between reservoirs #1 and #3, are photons. After Planck's black-body spectrum, the functions f and g for radiative energy-and-particle exchange are given by

$$f(T, \mu) = A \int_{E_g}^{\infty} \frac{E^3 dE}{\exp\left(\frac{E - \mu}{kT}\right) - 1}, \quad g(T, \mu) = B \int_{E_g}^{\infty} \frac{E^2 dE}{\exp\left(\frac{E - \mu}{kT}\right) - 1},$$

where k is the Boltzmann constant, E is the photon energy and E_g is the bandgap of the radiative exchange (i.e. the larger of the bandgaps of the two materials #1

and #3). The constants A and B , we can call radiative conductivities. Besides physical constants, they contain emissivities, surface areas, etc.

The above expressions contain the Bose factor from Bose–Einstein statistics:

$$\frac{1}{\exp\left(\frac{E - \mu}{kT}\right) - 1},$$

where μ plays the role of a “quasi Bose level” [3,4], analogous to the quasi Fermi levels in Fermi–Dirac statistics. In real devices, an alternative approach is justified, using instead a combination

$$\exp\left(\frac{\mu}{kT}\right) \frac{1}{\exp\left(\frac{E}{kT}\right) - 1}$$

of a Boltzmann factor $\exp(\mu/kT)$ and a Bose factor $1/[\exp(E/kT) - 1]$:

$$f = A \exp\left(\frac{\mu}{kT}\right) \int_{E_g}^{\infty} \frac{E^3 dE}{\exp\left(\frac{E}{kT}\right) - 1}, \quad g = B \exp\left(\frac{\mu}{kT}\right) \int_{E_g}^{\infty} \frac{E^2 dE}{\exp\left(\frac{E}{kT}\right) - 1}.$$

3.3. Solar engines

A solar engine can be modelled as an endoreversible radiative engine, where $\mu_1 = 0$ (property of the Sun) and $\mu_2 = 0$ (property of the Earth), but μ_3 is non-zero [2,3]. The solar engine has two degrees of freedom: the temperature T_3 and the chemical potential μ_3 of the solar collector. Such engine is known as the hybrid solar converter or photothermal/photovoltaic converter or pt/pv converter [3,5].

3.4. Solar cells

When T_3 equals T_2 the solar engine is called a solar cell [2,3]. We have only one independent parameter left, i.e. μ_3 . This chemical potential is related to electrical quantities, simply by $\mu_3 = qV$, where V is the cell’s bias voltage. From

$$N_1 = g(T_1, 0) - g(T_2, \mu_3)$$

we deduce either

$$N_1 = B \left(\int_{E_g}^{\infty} \frac{E^2 dE}{\exp\left(\frac{E}{kT_1}\right) - 1} - \int_{E_g}^{\infty} \frac{E^2 dE}{\exp\left(\frac{E - \mu_3}{kT_2}\right) - 1} \right),$$

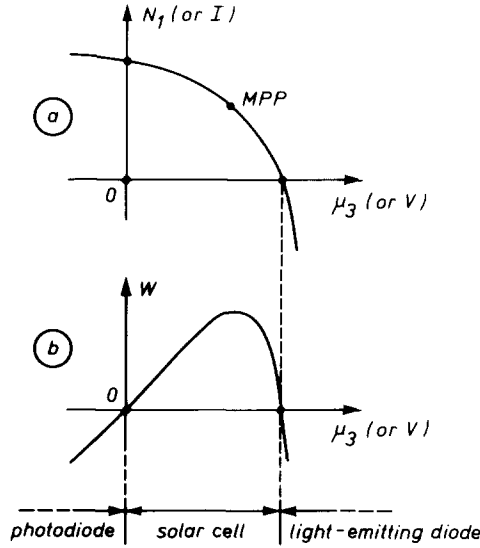


Fig. 3. Characteristics of a solar cell. (a) Current characteristic, (b) work characteristic.

or

$$N_1 = B \left(\int_{E_s}^{\infty} \frac{E^2 dE}{\exp\left(\frac{E}{kT_1}\right) - 1} - \exp\left(\frac{\mu_3}{kT}\right) \int_{E_s}^{\infty} \frac{E^2 dE}{\exp\left(\frac{E}{kT_2}\right) - 1} \right),$$

depending on which g -formula we choose. The former expression was introduced by De Vos and Pauwels [4], whereas the latter was proposed by Shockley and Queisser [6]. In both cases, the power produced is given by

$$W = \mu_3 N_1.$$

The functions $N_1(\mu_3)$ and $W(\mu_3)$ are shown in fig. 3. In particular, fig. 3a is to be interpreted as the I - V characteristic of the solar cell. Indeed, in ideal solar cells only radiative generation/recombination of carriers occurs, such that we have $I = qN_1$ for the cell's electric current. Together with $V = \mu_3/q$ this leads to $W = \mu_3 N_1 = (qV)(I/q) = VI$. The detailed form of the curves $I(V)$ and $W(V)$ depends on the function g . In particular the De Vos–Pauwels characteristics differ from the Shockley–Queisser characteristics in the V -range around and above open-circuit voltage. However, for both g 's, we have the following three modes of operation of an illuminated diode:

- for $V < 0$, we have $I > 0$ and $W < 0$: the diode works as a photodiode;
- for $0 < V < V_{oc}$, we have $I > 0$ and $W > 0$: the diode works as a true solar cell;
- for $V > V_{oc}$, we have $I < 0$ and $W < 0$: the diode works as a light-emitting diode.

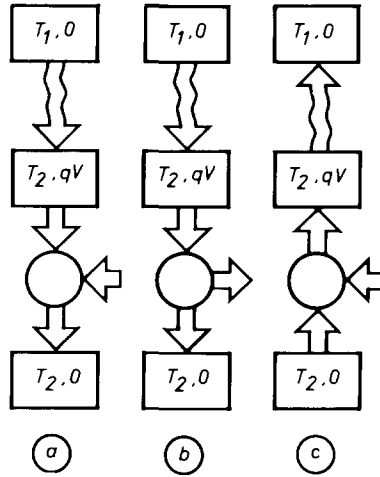


Fig. 4. Operational modes of a solar cell. (a) Photodiode, (b) true solar cell, (c) light-emitting diode.

Here V_{oc} is the open-circuit voltage, solution of the equation

$$N_1(V) = 0.$$

Fig. 4 shows the three operation modes (the arrows representing positive currents).

In real materials, also non-radiative processes contribute to the current I . Such generation/recombination processes (e.g. electron-phonon or Auger interactions) can be modelled into the endoreversible scheme, by adding the appropriate reservoirs and conductors. The result is a lower open-circuit voltage and a lower W_{max} .

4. Endoreversible thermal engines

In purely thermal engines, there are only temperature differences, thus no chemical potential differences:

$$\mu_1 = \mu_2 = \mu_3.$$

Fig. 2b shows an endoreversible thermal engine [2,3]: a heat source at constant temperature T_1 provides heat to a heat collector at temperature T_3 ; a Carnot engine converts the heat U_1 into work W and deposits waste heat U_2 to the surroundings at temperature T_2 . On the one hand, the rate of heat transport is governed by the temperatures T_1 and T_3 :

$$U_1 = f(T_1) - f(T_3),$$

where f is some function. On the other hand, the efficiency of the conversion of heat into work is determined by the temperatures T_3 and T_2 : it is given by the Carnot factor $1 - T_2/T_3$. Thus the rate of work production is given by

$$W = \left(1 - \frac{T_2}{T_3}\right) [f(T_1) - f(T_3)].$$

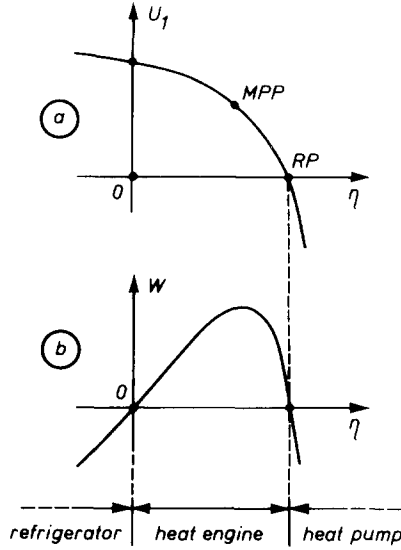


Fig. 5. Characteristics of thermal engine. (a) Current characteristic, (b) work characteristic.

For given values of T_1 and T_2 , the resulting rates U_1 and W are thus functions of the parameter T_3 , or equivalently of the dimensionless parameter $\eta = 1 - T_2/T_3$. Fig. 5 shows the functions $U_1(\eta)$ and $W(\eta)$. The detailed form of these curves depends on the particular function f . However, for any monotonously increasing function $f(T)$, we have the following properties:

- for $\eta < 0$, we have $U_1 > 0$ and $W < 0$: the engine works as a refrigerator;
 - for $0 < \eta < 1 - T_2/T_1$, we have $U_1 > 0$ and $W > 0$: the engine works as a true heat engine;
 - for $\eta > 1 - T_2/T_1$, we have $U_1 < 0$ and $W < 0$: the engine works as a heat pump.
- Fig. 6 shows the three operation modes (the arrows representing positive flows).

4.1. Linear thermal engines

For ordinary heat conduction, we have $f(T) = AT$. Thus

$$U_1 = A(T_1 - T_3), \quad W = A \left(1 - \frac{T_2}{T_3} \right) (T_1 - T_3).$$

The condition

$$\frac{dW}{dT_3} = 0$$

leads immediately to $T_3 = \sqrt{T_1 T_2}$ and to

$$W_{max} = A \left(\sqrt{T_1} - \sqrt{T_2} \right)^2.$$

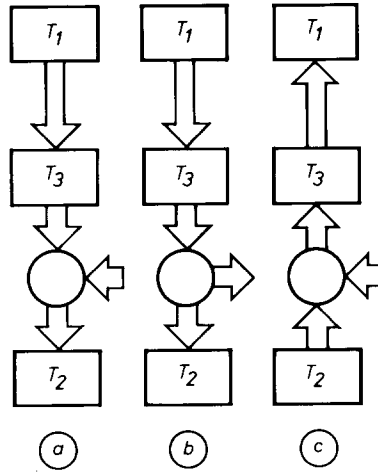


Fig. 6. Operational modes of endoreversible heat engine. (a) Refrigerator, (b) true heat engine, (c) heat pump.

Besides, we have the following simple property in the maximum-power point:

$$\eta = 1 - \sqrt{\frac{T_2}{T_1}}.$$

These results were discovered independently by Novikov [7] and by Curzon and Ahlborn [8].

4.2. Solar thermal engines

As mentioned above (section 3.3), solar engines work in the boundary conditions $\mu_1 = \mu_2 = 0$. If, besides, also μ_3 equals zero, then we talk of a thermal solar engine. Both the Shockley–Queisser and the De Vos–Pauwels transport laws become

$$f(T) = A \int_{E_g}^{\infty} \frac{E^3 dE}{\exp\left(\frac{E}{kT}\right) - 1}.$$

The transport law can successfully be applied to solar engines with a selectively black (or grey) absorber [2,3]. A special case is obtained for E_g equal zero, i.e. for a black-body (or grey-body) solar absorber. We can easily verify that this limit case gives rise to the Stefan–Boltzmann law: $f(T) = aT^4$, where a is proportional to A (i.e. equal to $\pi^4 k^4 A / 15$). The heat flow and the output power are thus

$$U_1 = a(T_1^4 - T_3^4), \quad W = a\left(1 - \frac{T_2}{T_3}\right)(T_1^4 - T_3^4),$$

such that $dW/dT_3 = 0$ leads to a 5th-degree equation in T_3 :

$$4T_3^5 - 3T_2T_3^4 - T_1^4T_2 = 0.$$

The equation was discovered independently by Müser [9], by Castaños [10] and by De Vos and Pauwels [4].

For the important case where $T_2 \ll T_1$ an approximate analytical solution exists:

$$T_3 \approx \left(\frac{T_1^4 T_2}{4} \right)^{1/5},$$

leading to

$$W_{max} \approx \left[1 - \frac{5}{4^{4/5}} \left(\frac{T_2}{T_1} \right)^{4/5} \right] a T_1^4.$$

5. Endoreversible chemical engines

In purely chemical engines, there are only potential differences, thus no temperature differences:

$$T_1 = T_2 = T_3.$$

Fig. 2c shows an endoreversible chemical reactor [3,11]: a particle source at constant chemical potential μ_1 provides particles to a collector at chemical potential μ_3 ; a reversible fuel cell converts the particle current N_3 (reactant or fuel) into the work flow W and deposits a waste particle current N_2 (reaction product or exhaust) to the surroundings at chemical potential μ_2 . On the one hand, the rate of particle transport is governed by the potentials μ_1 and μ_3 :

$$N_1 = g(\mu_1) - g(\mu_3),$$

where g is some function. On the other hand, the work generated per particle is $\mu_3 - \mu_2$. Thus the rate of work production is given by

$$W = (\mu_3 - \mu_2) [g(\mu_1) - g(\mu_3)].$$

For given values of μ_1 and μ_2 , the resulting rates N_1 and W are thus functions of the parameter μ_3 , or equivalently of the parameter $\zeta = \mu_3 - \mu_2$. Fig. 7 shows the functions $N_1(\zeta)$ and $W(\zeta)$. The detailed form of these curves depends on the particular function g . However, for any monotonously increasing function $g(\mu)$, we have the following properties:

- for $\zeta < 0$, we have $N_1 > 0$ and $W < 0$: the engine works as an exhaust pump;
- for $0 < \zeta < \mu_1 - \mu_2$, we have $N_1 > 0$ and $W > 0$: the engine works as a true fuel cell;
- for $\zeta > \mu_1 - \mu_2$, we have $N_1 < 0$ and $W < 0$: the engine works as a fuel pump (or fuel synthesizer).

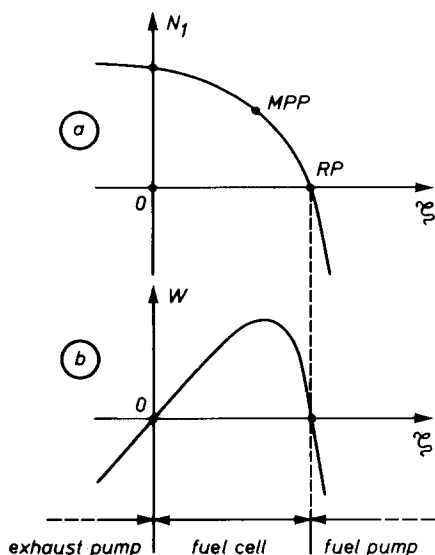


Fig. 7. Characteristics of a chemical engine. (a) Current characteristic, (b) work characteristic.

In fig. 7b, between short-circuit ($\zeta = 0$) and open-circuit ($N_1 = 0$), the delivered work W displays a maximum. In fig. 8, the three operational modes are shown. Note that in both figs. 8a and 8b, the reaction proceeds in the forward or spontaneous direction:

fuel $\rightarrow$ exhaust,

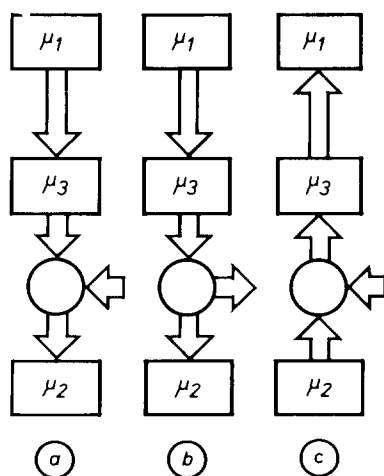


Fig. 8. Operational modes of endoreversible chemical engine. (a) Exhaust pump, (b) true chemical engine, (c) fuel pump.

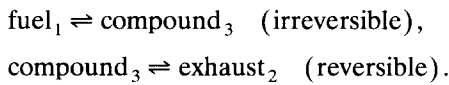
whereas in fig. 8c, the reaction proceeds in the reverse direction:
exhaust $\rightarrow$ fuel.

5.1. Linear chemical engines

The simplest g -function is the linear one [12]:

$$g(\mu) = D\mu.$$

The proportionality constant D can be interpreted as a “chemical ohmic conductance” [13,14]. The model is particularly useful if the fuel of the reversible reaction is to be produced by an irreversible reaction, such that the overall chemistry happens in two steps:



Note that compound #3 is an exhaust of the former reaction and a fuel of the latter reaction.

The mathematics look as follows:

$$N_1 = D(\mu_1 - \mu_3), \quad W = D(\mu_3 - \mu_2)(\mu_1 - \mu_3)$$

and the condition $dW/d\mu_3 = 0$ leads to

$$\mu_3 = (\mu_1 + \mu_2)/2$$

and to

$$W_{\max} = \frac{D}{4}(\mu_1 - \mu_2)^2.$$

The maximum-power condition can also be written as

$$\zeta = \frac{\mu_1 - \mu_2}{2},$$

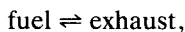
which will remind electrical engineers of the electrical load-matching problem. See figs. 9 and 10.

5.2. Diffusive chemical engines

An other function g is derived from Fick's diffusion law and Nernst's law:

$$g(\mu) = D \exp\left(\frac{\mu}{kT}\right),$$

where D contains, besides geometrical factors, a diffusion coefficient. This model is applicable to cases where the chemical transformation happens in one (reversible) step



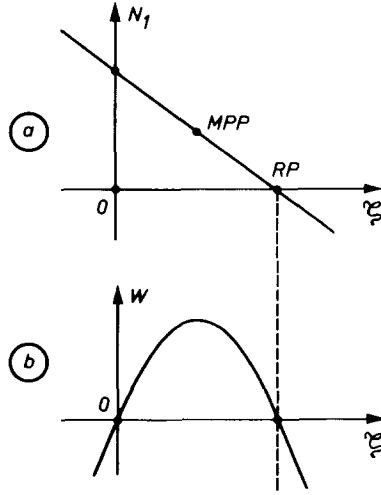


Fig. 9. Characteristics of a linear chemical engine. (a) Current characteristic, (b) work characteristic.

but where the supply of the fuel is limited by its transport towards the reversible reaction chamber (i.e. transport from reservoir #1 to reservoir #3). We have

$$N_1 = D \left[\exp\left(\frac{\mu_1}{kT}\right) - \exp\left(\frac{\mu_3}{kT}\right) \right], \quad W = D(\mu_3 - \mu_2) \left[\exp\left(\frac{\mu_1}{kT}\right) - \exp\left(\frac{\mu_3}{kT}\right) \right].$$

The maximum-power condition $dW/d\mu_3 = 0$ leads to a transcendental equation [3,11].

5.3. Photosynthetic engines

A photosynthetic engine can successfully be modelled as a diffusive chemical engine (section 5.2), powered by a photovoltaic engine (section 3.4) [3]. The (simplified) chemical reaction formula is

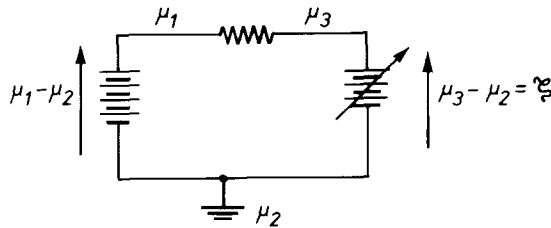
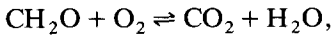


Fig. 10. Equivalent electrical circuit.

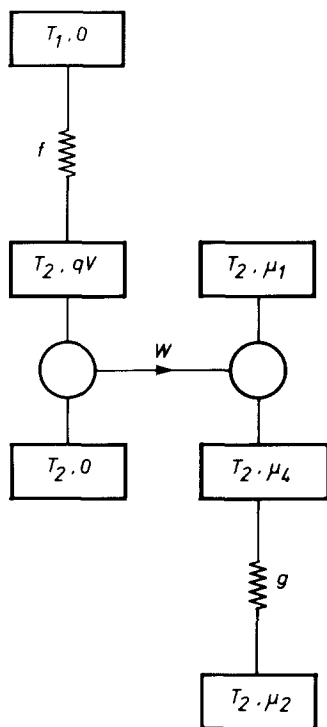


Fig. 11. Photosynthetic engine.

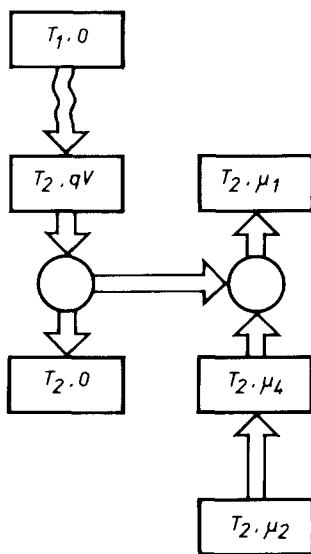


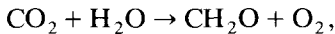
Fig. 12. Normal operational mode of photosynthetic engine.

i.e. the oxidation of a carbohydrate molecule (e.g. glucose). The chemical conductors associated with the chemical engine are [15,16]:

- g_1 , braking the supply of the fuels, consists of the plant's phloem, transporting the sugar, and
- g_2 , braking the drainage of the exhausts, consists of the plant's xylem tubules, transporting the water and the stomatal pores of the leaves, which control the transport of carbon dioxide.

The smallest g limits the kinetics of the reaction [3,11]. In the case of a plant, this role is performed by the g_2 of the stomata. This leads us to the scheme of fig. 11.

The three modes of operation of the diode (see fig. 4) and the three modes of operation of the chemical engine (see fig. 8) give rise to four combinations. Only four combinations are possible (instead of $3 \times 3 = 9$), as the signs of W (i.e. the sense of the W arrows) have to match. In normal conditions (i.e. in day-time), the diode functions in the mode of a true solar cell, whereas the chemical engine functions as a fuel pump, resulting in fig. 12, where once more arrows show positive flows. Note that in this circumstances, the reverse reaction takes place, i.e. the synthesis of sugar:



instead of the spontaneous reaction, i.e. the burning of sugar.

6. Conclusions

We demonstrated how various models of solar energy conversion can all be constructed by the use of

- thermodynamic reservoirs, labeled by a temperature T and/or a chemical potential μ , and
- thermodynamic resistors, limiting an energy flow U and/or a particle flow N .

Therefore solar energy is just one more interesting field of application of endoreversible thermodynamics, besides the many more fields, such as nuclear power [3,7], climatology [3,17], micro-electronics [18], economics, etc.

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Appendix: Onsager's restriction

In the present paper, we introduced f and g as two mathematical functions, which had merely to fulfil one, little restrictive, condition, i.e. had to be

monotonously increasing. For all above examples it leads to $A > 0$ and $D > 0$. The physical consequence is that we are guaranteed that heat flows spontaneously from a high temperature to a low temperature and that spontaneous particle flows happen from a high chemical potential towards a low one.

In reality, f and g have to obey some more physical restrictions, of which the most important is Onsager's reciprocity theorem. In the present appendix, we will look for its consequences.

In non-equilibrium thermodynamics often the two reservoir parameters T and μ are replaced by two equivalent ones: α and β , called affinities [19]:

$$\alpha = -\frac{1}{T}, \quad \beta = \frac{\mu}{T}.$$

This allows us to write Onsager's reciprocity theorem in a compact way:

$$\frac{\partial f}{\partial \beta} = \frac{\partial g}{\partial \alpha}.$$

As the transport equations of the linear thermo-chemical engine can be rewritten in terms of α and β as follows:

$$f = -A\frac{1}{\alpha} - B\frac{\beta}{\alpha}, \quad g = -C\frac{1}{\alpha} - D\frac{\beta}{\alpha},$$

this yields

$$B = -\frac{C}{\alpha},$$

or

$$B = CT.$$

This condition cannot be fulfilled for a constant B , a constant C and a range of T 's (unless $B = 0$ and $C = 0$). That is the reason why the linear model is only justified for cases not too far from equilibrium, i.e. when $\text{abs}(T_1 - T_3)$ is small compared to T_1 and T_3 themselves.

For the radiative engine, applying $\partial f/\partial \beta = \partial g/\partial \alpha$ to

$$f = A \int_{E_s}^{\infty} \frac{E^3 dE}{\exp\left(\frac{-E\alpha - \beta}{k}\right) - 1}, \quad g = B \int_{E_s}^{\infty} \frac{E^2 dE}{\exp\left(\frac{-E\alpha - \beta}{k}\right) - 1},$$

simply yields

$$A = B,$$

a condition that can be fulfilled without problems. This means this radiative model is applicable to any combination of T 's and μ 's. This is very fortunate, as the solar surface temperature (related to T_1) is about 6000 K and the earthly surface temperature (related to T_2) is about 300 K, such that T_1 and T_3 can be of different orders of magnitude.

The reader will easily verify that

$$f = A \exp\left(\frac{\beta}{k}\right) \int_{E_g}^{\infty} \frac{E^3 dE}{\exp\left(\frac{-E\alpha}{k}\right) - 1}, \quad g = B \exp\left(\frac{\beta}{k}\right) \int_{E_g}^{\infty} \frac{E^2 dE}{\exp\left(\frac{-E\alpha}{k}\right) - 1}$$

can fulfil Onsager's relation only if both

$$A = B$$

and

$$E_g \gg kT.$$

The latter condition leads to the serious restriction $E_g \gg kT_1$. This reminds us of the fact that the Shockley–Queisser model is somewhat “less fundamental” than the De Vos–Pauwels model [4].

References

- [1] M. Rubin, *Phys. Rev. A* 19 (1979) 1272.
- [2] A. De Vos, *Sol. Cells* 31 (1991) 181.
- [3] A. De Vos, *Endoreversible Thermodynamics of Solar Energy Conversion* (Oxford University Press, Oxford, 1992).
- [4] A. De Vos and H. Pauwels, *Appl. Phys.* 25 (1981) 119.
- [5] A. De Vos and J. Landries, *Endoreversible thermodynamics of hybrid photothermal–photovoltaic converters*, *Proc. 11th EC Photovoltaic Solar Energy Conference*, Montreux, 12–16 October 1992, pp. 363–366.
- [6] W. Shockley and H. Queisser, *J. Appl. Phys.* 32 (1961) 510.
- [7] I. Novikov, *Atomnaya Energiya* 3 (1957) 409 [English transl. *J. Nucl. Energy II* 7 (1958) 125].
- [8] F. Curzon and B. Ahlborn, *Am. J. Phys.* 43 (1975) 22.
- [9] H. Müser, *Z. Phys.* 148 (1957) 380.
- [10] M. Castañs, *Rev. Geofís.* 35 (1976) 227.
- [11] A. De Vos, *J. Phys. Chem.* 95 (1991) 4534.
- [12] J. Gordon, *J. Appl. Phys.* 73 (1993) 8.
- [13] J. Shiner, *J. Chem. Phys.* 87 (1987) 1089.
- [14] S. Sieniutycz and J. Shiner, *Open Systems and Information Dynamics in Physical and Life Sciences* 1 (1992) 149.
- [15] O. Björkman and J. Berry, *Sci. Am.* 229 (October 1973) 80.
- [16] R. McGilvery, *Biochemical Concepts* (Saunders, Philadelphia, 1975) pp. 267–292.
- [17] A. De Vos and P. van der Wel, *Theor. Appl. Climatol.* 46 (1993) 193.
- [18] A. De Vos, *Reversible and endoreversible computing*, to be published.
- [19] H. Callen, *Thermodynamics* (Wiley, New York, 1960) pp. 283–292.