ON THE MAXIMUM EFFICIENCY OF TRANSFORMATION OF RADIANT ENERGY INTO WORK

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The maximum energy efficiency (defined as the ratio of free energy increase to amount of radiant energy absorbed) is calculated for an arbitrary endoergic photoprocess by methods of classical thermodynamics as applied to irreversible processes. General formulas are derived from which η_m can be computed for incident radiation of arbitrary intensity and spectral composition and for various directivity. Concrete calculation formulas are derived for directed or diffuse monochromatic light. Values of η_m for monochromatic radiation from a number of sources are estimated.

THE question of the maximum attainable efficiency of conversion of radiant energy into work is of interest to physics and engineering (photocells, radiation thermocouples, solar energy sources), chemistry (endoergic photochemical reactions, i.e., accompanied by an increase in free energy), and biology (photosynthesis). In spite of the great significance of this question, its theory has not been extensively developed. The reason for it is apparently the widespread opinion that radiant energy can be completely converted into work (see, for example, [1,2]). In fact, however, thermodynamics imposes definite limitations on such a conversion.

Mortimer and Mazo [3] calculated by methods of the thermodynamics of irreversible processes the maximum energy efficiency η_m for photoendoergic chemical reactions. They used rather complicated derivations and arrived ultimately at a formula applicable only to a plane monochromatic wave, which therefore could not be used, strictly speaking, for real cases of nonmonochromatic and nonparallel light beams.

In the present paper we present a much simpler and more intuitive derivation of η_m, based on the principles of classical thermodynamics as applied to irreversible processes. The method which we use is similar in some respects to that used by Landau to determine the energy efficiency of photoluminescence [4] and by Weinstein [5] to determine the energy efficiency of thermoluminescence. The results obtained are suitable for radiation having an arbitrary spectral composition and varying directivity.

Since no assumptions are made with respect to the nature of the system absorbing the light, our results are applicable to all types of optical systems.

DERIVATION OF η_m FOR PHOTOENDOERGIC PROCESSES

We consider a system consisting of an object absorbing light and a surrounding medium which is in thermal contact with the object.

We are interested in a process whereby part of the light absorbed by the object is converted into internal energy of the object, and the remainder is degraded into heat and is transferred ultimately to the medium. The assumption that the internal energy (more accurately, the free energy, as will be shown below) of the object increases is merely a convenient stategem, which facilitates the arguments that follow, but does not change at all the physical gist of the question concerning the efficiency of conversion of radiation energy into work. Thus, for example, in the case of a photocell we can assume that it is connected to a storage battery which stores the electric energy with 100% efficiency. The work can subsequently be performed by the energy stored in the battery. In the case of a photochemical reaction, the object itself is the "storage battery."

Simultaneously with the energy conversion, a change in entropy takes place: the entropy of the absorbed radiation vanishes, the entropy of the object changes as a result of internal process, while that of the medium changes as the result of the heat produced through incomplete conversion of the absorbed radiation into internal energy.

The temperature of the object is assumed constant and equal to the temperature of the medium, that is, the processes are isothermal. Because of this, the energy efficiency should be defined as the ratio of the change (increase) in the free energy of the object to the total amount of energy absorbed by the object:

$$\eta = (U_c - TS_c)/F_a, \quad (1)$$

where η—efficiency, U_c—change in the internal energy of the object per unit time, T—its absolute temperature, and S_c—change per unit time in the entropy of the object, due to the internal processes which occur in the object (for example: formation of more complicated molecules from simpler ones and formation of ordered structures during photosynthesis); F_a denotes the radiation flux (power) absorbed by the object.

The laws of thermodynamics impose a definite limitation on the quantity $U_c - TS_c$ in (1). To demonstrate this, let us set up the energy balance with allowance for the change in entropy. We can exclude from consideration the radiation source (lamp or sun) and regard the expanded system, comprising the radiation plus object plus surrounding medium, as being adiabatically isolated. The possibility of such a procedure is based on the fact that because the velocity of light is finite, the radiation properties depend neither on the character of the source nor on the history of the rays. We can, for example, imagine that the experiment is carried out in the following manner: the source is situated at a very large distance from the object, and some time after the source is turned on, it is isolated from the object by a reflecting adiabatic shell.

Assuming that no work is done directly when the radiation is absorbed, we can write

$$F_a = U_c + Q, \quad (2)$$

where Q—amount of heat performed per unit time as a result of incomplete conversion of the absorbed radiation energy into internal energy. As was already noted, under stationary conditions Q is transferred to the medium.

According to the second law of thermodynamics we have for the expanded (closed) system

$$S_c + Q/T \geqslant S_a, \quad (3)$$

where S_a is the entropy of the absorbed radiant flux. This inequality includes only those changes in the entropy which are due to the absorption of the radiation. However, the radiation entropy can change also upon scattering, if the radiation has initially a definite direction. It is obvious that when diffuse light is incident we can neglect the foregoing change in entropy. On the other hand, if direct light is incident, we can neglect this change if the absorption is complete or if the scattering is weak. In the present article we consider precisely these cases and therefore we do not introduce into (3) the additional term that accounts for the increase in the entropy of the rays upon scattering.

Substituting $Q = F_a - U_c$ from (2) in (3) and taking (1) into account, we obtain

$$\eta \leqslant 1 - \frac{T}{F_a/S_a}. \quad (4)$$

The relation obtained shows that η_m depends on the ratio of the radiation flux absorbed by the object to the entropy of this radiation flux.

It is obvious that the flux of absorbed radiation is

$$F_a = F_0 - F_1, \quad (5)$$

where the subscript 0 pertains to the incident flux and the subscript 1 to the transmitted (nonabsorbed) flux. Analogously,

$$S_a = S_0 - S_1. \quad (6)$$

The quantities F_0, F_1, S_0, and S_1 can be expressed in terms of the transmission coefficient and the intensity of the radiation $I(\nu)$ incident on the vegetation, defined by the relation

$$dE(\nu) = I(\nu)\cos\theta\; d\nu\, d\sigma\, d\omega\, dt,$$

where $dE(\nu)$ is the radiant energy contained in a definite frequency interval $(\nu, \nu + d\nu)$ and in an elementary solid angle $d\omega$, transferred within a time interval dt through an area element $d\sigma$; θ is the angle between the considered direction of radiation and the outward normal to $d\sigma$ [6,7].

In the case in question, the intensity I_0 of the light incident on the object is made up of the intensity I_L of the radiation from the source and the intensity I_T of the thermal radiation of the medium, that is, $I_0(\nu) = I_L(\nu) + I_T(\nu)$. On the other hand, the intensity of the light which is not absorbed ("transmitted") consists of the intensity of the source radiation passing through the object [it is defined by means of a transmission coefficient $\tau(\nu)$], and the intensity of the thermal radiation of the object I_T, that is, $I_1(\nu) = I_L(\nu)\tau(\nu) + I_T(\nu)$.

From the definition of F and I it follows that

$$F_j = A\iint (I_L\tau_j + I_T)\cos\theta\; d\nu\, d\omega \qquad (j = 0, 1), \quad (7)$$

where A—effective area of the object and $\tau_0 = 1$, $\tau_1 = \tau(\nu)$.

We introduce analogously the concept of the intensity of the entropy of radiation $s(\nu) = s[I(\nu)]$ [6,8];

$$S_j = A\iint s(I_L\tau_j + I_T)\cos\theta\, d\nu\, d\omega. \quad (8)$$

for a ray (quasiparallel beam) or for completely diffuse light, of intensity $I(\nu)$, the explicit form of $s(\nu)$ is [6,8]

$$s[I(\nu)] = \frac{2k\nu^2}{c^2}\Big[\Big(1+\frac{c^2I(\nu)}{2h\nu^3}\Big)\ln\Big(1+\frac{c^2I(\nu)}{2h\nu^3}\Big) - \frac{c^2I(\nu)}{2h\nu^3}\ln\frac{c^2I(\nu)}{2h\nu^3}\Big], \quad (9)$$

where k—Boltzmann's constant, c—velocity of light, and h—Planck's constant. Formulas (4)—(9) solve our problem in principle.

PARTICULAR CASE OF INCIDENCE OF QUASIMONOCHROMATIC LIGHT

For practical calculations it is necessary to know the specific form of the functions $I_j(\nu, \theta, \tau_j)$. We shall consider a case when quasimonochromatic light of frequency ν, that is, light, whose intensity can be regarded as constant in the interval $(\nu, \nu + \Delta\nu)$, is incident on the vegetation. In addition, we consider the following limiting cases.

1) The intensity of the radiation from the source is: (a) appreciably larger than the intensity of the thermal radiation ($I_L \gg I_T$), or (b) considerably smaller ($I_L \ll I_T$).

2) The incident radiation is (a) completely absorbed ($\tau = 0$) or (b) weakly absorbed ($\tau \approx 1$).

3) The intensity I_0 of the incident radiation is (a) independent of θ (diffuse light) or (b) constant in a narrow angle interval θ, $\theta + \Delta\theta$ (directional or quasiparallel light beam).

We start with the case when $I_L \gg I_T$, which is practically always the case under real conditions. Since $s(I)$ is a monotonically increasing function of I, and since $S(I) \to 0$ as $I \to 0$, we can assume in this case [see (8)] that $S(I_L + I_T) \approx S(I_L)$ and $S(I_L + I_T) - S(I_T) \approx S(I_L)$.

1. Case of total absorption ($\tau = 0$). According to (5) and (7)

$$F_a = F_0 = A\iint I_L \cos\theta\, d\nu\, d\omega, \quad (10)$$

and according to (6) and (8)

$$S_a = S_0 = A\iint [s(I_L + I_T) - s(I_T)]\cos\theta\, d\nu\, d\omega = A\iint s(I_L)\cos\theta\, d\nu\, d\omega. \quad (11)$$

In the case of directed light we obtain from (10) and (11)

$$F_a = A\cos\theta\Delta\omega\iint I_L\, d\nu = A\cos\theta I_L\,\Delta\omega\,\Delta\nu,$$
$$S_a = A\cos\theta s(I_L)\,\Delta\omega\Delta\nu. \quad (10')$$

Consequently

$$F_a/S_a = I_L/s(I_L),$$

where $s(I_L)$ is given by (9).

We can analogously obtain a similar formula also for completely diffuse light.

2. Case of weak absorption. It is assumed that the intensity of the radiation changes only insignificantly when the light goes through the object; consequently

$$F_a = F_0 - F_1 \approx \Big(\frac{\partial F}{\partial I_L}\Big)_0 \Delta I_L,$$
$$S_a = S_0 - S_1 \approx \Big(\frac{\partial S}{\partial I_L}\Big)_0 \Delta I_L.$$

Hence

$$\frac{F_a}{S_a} = \Big(\frac{\partial F}{\partial I_L}\Big)_0 \Big/ \Big(\frac{\partial S}{\partial I_L}\Big)_0.$$

Differentiating (10′) with respect to I_L and differentiating the analogous formulas for the diffuse light, we find that for both directed and diffuse light we have

$$F_a/S_a = (\partial s/\partial I)^{-1}.$$

We can verify that (9) leads to

$$\frac{\partial s}{\partial I} = \frac{k}{h\nu}\ln\Big(1+\frac{2h\nu^3}{c^2I}\Big).$$

Summarizing, we arrive at the following result. When a sufficiently intense ($I_L \gg I_T$) directed or diffuse beam of quasimonochromatic radiation frequency ν is incident on an object, the maximum energy efficiency for the conversion of light energy into free energy is

$$\eta_m = 1 - T/T_e, \quad (12)$$

where in the case of total absorption of incident radiation the effective temperature is

$$T_e = \frac{c^2I_L}{2k\nu^2}\Big[\Big(1+\frac{c^2I_L}{2h\nu^3}\Big)\ln\Big(1+\frac{c^2I_L}{2h\nu^3}\Big) - \frac{c^2I_L}{2h\nu^3}\ln\frac{c^2I_L}{2h\nu^3}\Big]^{-1}, \quad (13)$$

and in the case of weak absorption

$$T_e = \frac{h\nu}{k\ln(1 + 2h\nu^3/c^2I_L)}. \quad (14)$$

Formulas (12) and (14) were derived in [3] for the case of a plane monochromatic wave.

It is easy to verify that as $I_L \to \infty$ formulas (12), (13), and (14) yield $\eta_m \to 1$. On the other hand, if $I_L \to 0$ we get $\eta_m \to -\infty$. The point is that (13), like (14), was derived under the assumption that $I_L \gg I_T$. To estimate η_m for very low values of I_L, we transform the general formulas (4)—(9), assuming that $I_L \ll I_T$.

For sufficiently small I_L we have

$$S\,(I_L + I_T) - S\,(I_T) \approx (\partial S/\partial I)_T I_L = I_L/T,$$

since for thermal radiation $\partial S/\partial I = 1/T$ [4].

Repeating the arguments which have led to (10′) and to the analogous formulas for the diffuse light, we find that, both in the case of total absorption and in the case of weak absorption of directional or diffused radiation we have $F_a/S_a = T$. Consequently, according to (4) we have $\eta_m \to 0$ as $I_L \to 0$, that is, very weak light intensity cannot give rise to processes in which the free energy increases.

In conclusion, we present some results of calculations of η_m by means of the formulas obtained. We assume the ambient temperature to be 20°C. For sunlight at sea level we obtain $\eta_m = 0.94$. For scattered sunlight at sea level $\eta_m = 0.78$. For an incandescent lamp with a color temperature 2800°K we have $\eta_m = 0.90$.

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