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Thermodynamic Limitations on the Conversion of Radiant Energy into Work*

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The fraction of radiant energy incident on an absorber which may appear as work is limited by the radiation entropy, and entropy gained in irreversible transfer from the radiation field to an absorber. Irreversibility may result from directionality of the radiation field, and some irreversibility is necessary to cause a net flow of energy from a radiation absorber into work or free energy storage. Impedance in the conversion apparatus may further limit the efficiency. Maximization of power storage under these constraints is discussed, and the general arguments are then applied to photoelectrical and photochemical systems; in these systems non-resonant decay of the excited state represents a major source of inefficiency, which may be minimized by appropriate choices for the Boltzmann temperature and optical density of the absorber. The relationships are developed for narrow band absorption, but application to broad band photochemical systems is discussed.

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I. INTRODUCTION

In the past few years interest has intensified in biological photosynthesis, and in photochemical and photoelectrical devices for the conversion of solar energy into work. This interest has stimulated theoretical derivations[1,2] of the fraction of monochromatic radiation energy which may appear as work, or the thermodynamic work equivalent, which is the Helmholtz free energy, A = E-TS.

Related derivations have considered the conversion of heat into light,[3] and thermodynamic limitations on the performance of a polarizer.[4]

In theory developed specifically for p-n junction photovoltaic cells, Shockley and Queissar[5] have considered a number of the additional efficiency limitations treated more generally in this paper.

The transformation of light energy into work may be divided into two stages: (1) interaction of an absorber with the radiation field, and (2) the conversion of net absorbed energy into work (see Fig. 1). Any operation performed on the absorbed energy before its appearance as work, or its storage as free energy, we consider to occur in an engine. Such an engine might be of the conventional piston variety, or the engine may be present more abstractly as, e.g., a pair of thermocouple junctions with wires connecting them to a locus of electrical work, or even a sequence of chemical reactions leading to a stable, energetic product.

The fraction of net absorbed energy which may appear as work is restricted by the Carnot limitation of classical thermodynamics: $1 - T_L/T_H$, where T_H is the temperature of the absorber, and T_L is the ambient temperature. The Carnot efficiency is frequently described as a restriction on the engine; this is a convenient and meaningful terminology for

conventional engines, but it has at times given the false impression that the Carnot factor may be circumvented by using apparatus which does not employ macroscopic heat reservoirs. Actually, the term $(1 - T_L/T_H)$ represents only the fraction of free energy in an energy increment at T_H, relative to a standard state at T_L. The heat engine formalism is simply a convenient manner of representing the entropy associated with net absorbed energy.

The term absorber must be defined rather carefully if our discussion is to apply to all light capturing systems: An absorber is an assembly of states, within an absorbing material, which interact directly with a radiation field, and which are characterized by a common temperature regardless of the nature of the radiation field. Thus the absorber may constitute the whole of the absorbing material, or it may constitute as little as a single degree of freedom.

The next section of this paper shows how the interaction of the radiation field with the absorber limits the maximum possible T_H. Section III considers the irreversibility necessary for net absorption of energy, and shows how power storage may be maximized by an appropriate choice of T_H. The steady-state effect of impedance is treated briefly in Section IV.

In Section V we consider some additional features present in photochemical and photoelectrical systems, and consider the effect of absorber optical density on optimum efficiency.

Section VI extends the narrow band treatment to the broad band absorption situation of photochemical and photoelectrical devices.

II. ABSORBER TEMPERATURE

Material located in the cavity of a blackbody will equilibrate at the temperature of this blackbody. Similarly, an absorber illuminated by a blackbody will, if not cooled by interactions with other surroundings, reach the temperature of the blackbody.

The radiation flux emitted by a blackbody of temperature T is[6]

$$I_\nu = (2\nu^2/c^2)\,[\exp(h\nu/kT) - 1]^{-1} \qquad (1)$$

photons per unit solid angle, per unit bandwidth, per unit area, per unit time. Convenient units for this specific intensity are photons/sr$(sec^{-1})cm^2$sec.

This equation may be rearranged to describe the temperature of a blackbody in terms of the specific intensity of the radiation which it emits:

$$T^{-1} = (k/h\nu)\,\ln(1 + 2\nu^2/c^2 I_\nu) \qquad (2)$$

Equation (2) will also define the temperature of an absorber illuminated solely by a blackbody, and not coupled to any other system.

Now suppose that a very narrow bandpass filter is placed between the blackbody source and the absorber, so that the frequency and specific intensity are effectively constant across the pass band. If the absorber is sensitive (i.e., has non-zero absorptance) only for radiation within the band passed by the filter, then it will be unaffected by the elimination of other frequencies, and its temperature will continue to be defined by (2).

Such a narrow band, essentially monochromatic, absorber will be unable to distinguish between radiation produced by a blackbody and radiation produced by any unpolarized source which has the same specific intensity at the absorption frequency of the absorber. Consequently,

equation (2) defines the temperature of radiation from any source as a function of frequency.

A monochromatic absorber will be raised to the temperature specified by (2) only if the absorber is sensitive exclusively to radiation in the direction of the source. As seen from the absorber, most high temperature sources are highly directional, so that the absorber must be quite directional if it is to attain the temperature of the source.

An absorber may be intrinsically directional, perhaps because it consists of an ordered array, or it may be made effectively directional through optical magnification of the source, as with the parabolic mirrors used in solar furnaces. But most absorbers are not highly directional.

An absorber will average the incident intensities over all the directions in which it is sensitive to radiation, and the temperature of the absorber will be determined from (2) with an average specific intensity. If an absorber is spherically symmetric with respect to its interaction with a radiation field, then the effective intensity is reduced to $I_\nu\ (\text{eff}) = \int I_\nu\, d\Omega/4\pi$.

For lower absorption symmetries, one must consider in detail the steady-state relationship between an absorber and a radiation field of intensity distribution $I(\nu,\Omega)$. Assume that the absorber has a probability of emitting or absorbing light which is dependent on angle, $P(\Omega)$, and define the <u>effective radiation temperature</u>, T_R, as the temperature of an absorber which interacts exclusively with the radiation field.

By requiring equality between the intensity emitted and the intensity absorbed, T_R is defined in the integral equation

$$(2\nu^2/c^2)\,[\exp(h\nu/kT) - 1]^{-1} \int P(\Omega)\, d\Omega = \int I(\nu,\Omega)\, P(\Omega)\, d\Omega \qquad (3)$$

If the radiation as seen by the absorber falls in a range of solid angle in which the variation of $P(\Omega)$ from $P(\Omega_o)$ is small, then the right-hand side of (3) simplifies to

$$P(\Omega_o) \int I(\nu,\Omega)\, d\Omega \qquad (4)$$

As most radiation sources subtend a small solid angle, and most absorbers are not sharply directional, (4) will hold in most cases; it holds exactly for unidirectional light and for non-directional absorbers.

We may relate the effective intensity of radiation (relative to a given absorber) to the radiation temperature by a modification of (2):

$$T_R^{-1} = (k/h\nu) \ln[1 + 2\nu^2/c^2 I_\nu(\text{eff})] \qquad (2')$$

By solving (3) with (4) for T_R, we find the effective radiation intensity to be

$$I_\nu\ (\text{eff}) = P(\Omega_o) \int I(\nu,\Omega)\, d\Omega \Big/ \int P(\Omega)\, d\Omega \qquad (5)$$

The temperature varies as the logarithm of intensity, so only sharply directional absorbers can have an effective radiation temperature which is significantly greater than that for non-directional absorbers.

The radiation temperature is a steeper function of intensity at lower frequencies. Consequently, reduction of the effective intensity, such as by dilution over solid angle, causes the most variation in radiation temperature at lower frequencies. Consider an absorber which

is sensitive over a range of directions which is D times the solid angle subtended by a blackbody source of temperature T_S, i.e., $D = I_\nu(T_S)/I_\nu$ (eff). By substitution of (1) into (2') we find that

$$T_R^{-1} = (k/h\nu) \ln \{D[\exp(h\nu/kT_S)-1]+1\} \quad (6)$$

For $h\nu/kT_S$ greater than 3, this simplifies to

$$T_R^{-1} \approx (k/h\nu) \ln D + T_S^{-1} \quad (7)$$

Fig. 2 shows T_R as a function of frequency for a source temperature of 6000° K and a reduction of intensity by 10^5; this corresponds to the effective radiation temperature of the sun as seen by a non-directional absorber on Earth,[7] uncorrected for atmospheric absorption.

The appearance of absorbed energy as work is limited by the Carnot factor, $1 - T_L/T_R$, where T_L is the ambient temperature. Fig. 3 plots this efficiency as a function of wavelength for $T_L = 300°$ K conversion of energy from a narrow band absorber illuminated by a 6000° blackbody source. Curves are shown for an absorber which sees the full blackbody intensity, the 10^5 reduction of intensity characteristic of unfocused solar radiation on Earth, and a 10^{10} reduction.

The Carnot limitation may be applied to a broad band of frequencies by averaging $T_R^{-1}(\nu)$, weighted by the frequency distribution of incident energy. To attain this efficiency for an arbitrary distribution of T_R over frequency, it appears that a conversion system would have to be composed of a large number of sub-systems, each of which was designed to optimize the conversion of a narrow band of frequencies. This is technically difficult, and any real conversion apparatus has no more than a few such sub-systems. Understanding this sub-structure of a broad band absorber may permit a limit on the efficiency which is significantly below the band averaged Carnot limit (see Sec. VI).

III. RERADIATION LOSSES

Until now we have ignored a major consequence of the fact that an absorber at T_R emits (as resonant fluorescence) a photon flux equal to the flux absorbed: Energy may be withdrawn for doing work (or free energy storage) at only an infinitesimal rate if the absorber is to remain at T_R.

If energy reradiated by the absorber is not considered, and if there are no other energy leaks, then the Carnot limit of $1 - T_L/T_R$ can apply.

When there are losses from the absorber, however, then total efficiency is limited by the product of a Carnot efficiency, and the fraction of the absorbed quanta which are used for work or free energy storage:

$$\eta = (1 - T_L/T_H)(1 - I_{out}/I_{in}) \quad , \qquad (8)$$

where I_{in} is the input intensity, I_{out} is the loss intensity, and T_H is the absorber temperature.

When losses are present, the conditions for optimal efficiency may be found by determining the dependence of I_{out} on T_H, and setting the differential of (8) to zero.

The efficiency of most practical interest is the ratio of power storage to incident energy flux; in this case I_{in} is the incident intensity, and I_{out} includes losses from reflection, transmission, absorber emission, and any energy leaks from the absorber. We will not consider reflection; transmission is considered for photochemical systems in Section V.

If the absorber is a leak-free ideal (narrow band) blackbody, so that the only loss is the reradiation, then

$$I_{out}/I_{in} = (e^R - 1)/(e^H - 1) \qquad (9)$$

where $R = h\nu/kT_R$ and $H = h\nu/kT_H$.

For wavelengths $\gtrsim 1\mu$, the ones in (9) may be neglected except under conditions of extraordinarily high light intensity; we shall neglect them from now on, so that the efficiency becomes

$$\eta = (1 - H/L)(1 - e^{R-H}) \quad , \tag{10}$$

where $L = h\nu/kT_L$.

The condition on the absorber temperature for optimal power storage is that

$$H_{opt} = R + \ln X \tag{11}$$

where

$$X = 1 + L - H_{opt} \tag{12a}$$

$$= 1 + L-R - \ln[1 + L-R - \ln(1 + L-R-...)] \quad , \tag{12b}$$

which converges quite rapidly.

The resulting optimum efficiency is

$$\eta = (1 - (R + \ln X)/L)\ (1 - 1/X) \tag{13}$$

The expression within the brackets is the Carnot term, and $1/X$ represents the fraction of quanta reradiated under optimum conditions.

As was true of decreased efficiency due to reduced incident intensity, the losses due to the presence of reradiation are largest at the long wavelength end of the spectrum. Fig. 4 demonstrates the effect of reradiation as a function of wavelength for a narrow band absorber illuminated by a 6000° blackbody sun (i.e., blackbody intensity reduced by 10^5). The difference between the highest and middle curves represents the decrease in Carnot efficiency necessary for maximum power storage; the gap between the middle and lowest curves shows the loss due to actual reradiation.

If T_H is not maintained at or near the optimal value, then the efficiency may be markedly lower than the maximum set by (13) (see, e.g., Fig. 6).

IV. INTERNAL IMPEDANCE LOSSES

Any real transfer of energy from one place to another encounters some resistance, or impedance, to the transfer. Similarly, an apparatus, or engine, which transfers absorber energy to a locus of free energy storage must have some impedance. Work must be expended to cause a flow through this impedance, and the work used reduces the amount of work available for storage.

As a result of this power dissipation, the maximum efficiency for conversion of radiant energy into work becomes

$$\eta = (1 - I_{out}/I_{in})(1 - T_L/T_H - W/h\nu) \quad , \qquad (14)$$

where W represents the average work required to move the energetic products of one photon through the engine.

W will be a function of the energy flow from the absorber into the engine: $W = W(I_{eng})$, where $I_{eng} = I_{in} - I_{out}$. The form of this function will depend on the system which it describes, but it cannot be negative. If the function has continuous derivatives, then it may be expanded in a Maclaurin series:

$$W = w_0 + w_1 I_{eng} + w_2 (I_{eng})^2 + \cdots \qquad (15)$$

If w_0 is zero, then W equals $w_1 I_{eng}$ in the limit of small flux. This linear relationship between flux and thermodynamic potential difference holds with good accuracy for many transfer processes which operate at the molecular level; a familiar example is Ohm's law for electrical conduction. Diffusion and heat conduction are also typically linear.[8]

The notable exception to linearity occurs in chemical reactions, in which the rate has an inverse hyperbolic dependence on the potential drop. Because of this dependence, chemical reactions are sure to be linear only for $W \ll kT$. If a chemical reaction may be considered as a sum of several

elementary reactions, then the condition for linearity is relaxed to require only that the free energy change across each of the partial reactions be small with respect to thermal energies.[9] This may be the case in biological systems.

In linear systems equation (15) becomes

$$\eta = (1 - H/L)(1 - e^{R-H}) - f(1 - e^{R-H})^2 \quad , \tag{16}$$

where $f = I_{in} w_1/h\nu$. H may be adjusted for maximum power storage.

The dependence of power stored on light intensity under optimal conditions is shown in Figure 5. The curve with impedance is for $f = 10$ at intensity I_0. At intensities where f is very small, the effect of the resistance is negligible. For large f (e.g., high light intensities) the impedance places a ceiling on the power stored of

$$P = (h\nu/4w_1)(1 - T_L/T_R)^2 \quad , \tag{17}$$

which is shown as a dotted line on the figure.

The parameters used for this figure are equivalent to 300° K conversion of 1 μ radiation which at I_0 has the effective intensity of an unfocused 6000° blackbody sun on Earth. The assumption of a relatively long wavelength serves to accentuate the slopes of the assymptotic curves, but the shape of the power curve is not strongly dependent on the parameters used.

V. PHOTOCHEMICAL SYSTEMS

We define an energy conversion system to be photochemical if the absorber consists of a restricted number of degrees of freedom within the spatial bounds of the absorbing material. Any radiation conversion system which does not employ heat reservoirs in the usual macroscopic sense fits this definition, so that photoelectrical devices, as well as conventional photochemicals, are considered to be photochemical.

The temperature of the absorber, T_H, is represented by the relative populations of the ground and excited states resonant with the radiation.

A characteristic feature of photochemical systems is the transfer of energy from the degree(s) of freedom resonant with the radiation to a degree of freedom which does not interact significantly with radiation and otherwise equilibrates with the surroundings only slowly. This transfer may be partially or wholly by processes such as ionization, molecular rearrangement, chemical reaction, intersystem crossing to another spin state, migration of the excitation to a physically distinct "trap" species, or simply relaxation within an excited electronic state to a sub-state which has relatively less overlap with the ground state.

The total transfer process may frequently be described as involving several such steps, each of which has a progressively slower interaction with the surroundings: e.g., vibrational relaxation, intersystem crossing to a triplet state, then chemical reaction.

The final locus of free energy storage is usually in reactable chemicals: Energy stored from a photovoltaic cell is likely to be in a battery of electrochemical cells; photosynthesis leads indirectly to firewood. This storage may be viewed as a metastable excitation of the degree of

freedom represented by a chemical reaction coordinate.

By definition, energy transfer to non-useful degrees of freedom (e.g., vibrational) represents a heat leak which is unique to photochemical systems. This transfer may be completely non-radiative, or it may involve a combination of radiative and non-radiative processes. The rate of these losses is usually directly proportional to the excited state population, and thus a constant proportion of the radiative loss at the absorption frequency (the resonant fluorescence). The total rate of non-resonant loss may thus be represented as an absorber relaxation coefficient, ξ, times the rate of resonant fluorescence.

If I_{out} in (8) is multiplied by $(\xi + 1)$, this is mathematically equivalent to reduction of the input intensity by the same factor. Consequently, the effect of absorber relaxation on optimal T_H and efficiency is precisely that of an external reduction in the effective thermodynamic intensity. Equations (6) and (7) hold with $(\xi + 1)$ multiplying D, and Figure 3 demonstrates the effect of absorber relaxation on efficiency as a function of wavelength. The efficiency continues to be specified by (10) and (13), providing that

$$R_\xi = R + \ln(\xi + 1) \qquad (18)$$

is substituted for R in (10) through (13). The fraction, 1/X, representing loss from the absorber now includes losses from non-resonant decay.

This non-resonant absorber relaxation is caused by a coupling between the absorbing degrees of freedom and their surroundings. If a constant temperature is maintained throughout the absorber--which is required by our definition of a single absorber--then the rate of absorber heat leak due to non-resonant relaxation increases when more absorbing sites (degrees of freedom) are added to an absorber.

This introduces a question as to the optimum number of absorbing sites for maximum power storage. If the number of sites is quite large, then virtually all incident radiation may be absorbed, but the non-resonant losses will be relatively high. If the number of sites is small, then non-resonant losses are small, but a significant fraction of the incident radiation will pass through the absorber. When the number of absorbing sites, or--equivalently--the optical density, is controllable, then (8) may be optimized with respect to this variable also.

Consider unidirectional irradiation normal to a planar absorber which is made up of an ensemble of absorption sites, each of which has a site relaxation coefficient defined analogously to ξ. If different sites have different relaxation coefficients, then the accuracy of our treatment requires that the mean site relaxation coefficient, α, be essentially constant when averaged over the mean free path of a photon having the absorption frequency.

The fraction of light passing completely through the absorber is e^{-S}, where S is the thickness of the absorber in units of the photon mean free path.

The fraction of incident intensity, I_{in}, lost due to resonant radiative decay is $\frac{1}{2}(1-t)e^{R-H}$, where R is defined for a spherical absorber, and $\ln\frac{1}{2}$ corrects this to the flat plate value. The mean transparency averaged over solid angle, t, is the order of e^{-S}/S for large S; this correction is so small that we shall neglect it.

Assuming that any directionality in the absorption of individual sites is eliminated by averaging, the fraction of I_{in} lost by non-resonant absorber relaxation is $\alpha S e^{R-H}$.

Substituting these expressions into (8), we find that

$$\eta = (1 - H/L)\{1 - e^{-S} - (\alpha S + 1/2)e^{R-H}\} . \tag{19}$$

Differentiating with respect to S, we find that for maximum efficiency,

$$S_{opt} = H - R - \ln\alpha . \tag{20}$$

Substituting this into (19), the efficiency becomes

$$\eta = (1 - H/L)\{1 - (\alpha S_{opt} + \alpha + 1/2)e^{R-H}\} . \tag{21}$$

By comparison with (10) and (18), we note that this expression is that of an absorber with

$$\xi + 1 = \alpha S_{opt} + \alpha + 1/2 \tag{22}$$

Accordingly, from (11), (18), and (22) we have that

$$H_{opt} = R + \ln(\alpha S_{opt} + \alpha + 1/2) + \ln X . \tag{23}$$

By combining (20) and (23), and recalling (12a), one obtains a convenient set of coupled equations for maximum power storage:

$$H = R + S + \ln\alpha \tag{24a}$$

$$X = 1 + L - H \tag{24b}$$

$$S = \ln X + \ln(1 + S + 1/2\alpha) . \tag{24c}$$

If α, R, and L are known, then H, X, and S for maximum efficiency may be determined accurately by a few cyclic iterations of (24).

Maintaining T_H at the optimum in photochemical systems corresponds to keeping the relative population of the excited state(s) at a proper value. Raising the population above this level results in increased losses from absorber relaxation. If the population of the excited state is below the optimum value, then the free energy gain in the energy storage process is less than optimal.

T_H is controlled by the sum of the thermodynamic potential at the locus of free energy storage and the potential drop across any impedance. Figure 6 plots the efficiency as a function of the storage potential, ΔA, for no impedance and also for a linear impedance with $f = 0.3$. The curves shown are for parameters equivalent to 300° K conversion of 1 μ radiation from a 6000° source with dilution by 10^8. For radiation of higher intensity and/or shorter wavelength, the impedance free curve would peak even more closely to the right edge.

For photovoltaic devices Figure 6 represents power delivered as a function of load voltage, without and with an internal resistance.

During the course of a typical photochemical reaction, the thermodynamic activities of the reactants will vary, altering the free energy of reaction. Usually the reaction starts at equilibrium and progresses to a photostationary state by depleting the supply of reactants and increasing the concentration of products. This is equivalent to moving along Figure 6 from the left to the right edge. The mapping of time onto the horizontal axis of the figure will depend on the reaction considered. A significant free energy of reaction builds up rather readily, so that motion away from the left edge will be relatively rapid. The rate of approach to the right-hand edge will be slow, and assymptotic to zero, as the quantum yield goes to zero.

The inefficiencies we have discussed do not include any effects due to a finite rate of transfer from an excited state, from which losses occur, to more stable species further along the storage pathway. Attainment of good efficiency requires that the gross forward rate of any transfer step be very much faster than the rate of energy leakage from

the state preceding the step. The intrinsic quantum yield for a transfer is $k_t/(k_t + k_l)$, where k_t is the forward transfer rate, and k_l is the loss rate. This effect is independent of the thermodynamic losses discussed, and is quite significant in many photochemical and photoelectrical systems.[10]

VI. BROAD BAND ABSORPTION

Few radiant energy sources are anywhere near being monochromatic, making it necessary for practical energy converters to utilize radiation in a broad band of frequencies. Many photochemical and photoelectrical systems have an appropriately broad absorption band, extending above some threshold excitation energy, $h\nu_0$. Excitation energies in excess of this minimum are usually quickly dissipated as heat, and hence of no use for energy storage, so that the effective photon energy is $h\nu_0$. (The problem of an optimum threshold energy for maximum energy storage has been considered elsewhere.[11] The wavelength and intensity dependence of the efficiencies discussed in this paper should be considered in such an optimization.)

The relaxation within the excited state may increase the population of the lower sub-states markedly, increasing the effective absorber temperature. This decrease in entropy represents a fractional saving of the energy lost by relaxation from more energetic levels.

A broad excited electronic state--giving broad band absorption--is frequently associated with a broad ground electronic state. Such a broad ground state gives rise to significant absorber relaxation by non-resonant fluorescence, which lowers the effective absorber temperature.

If one has little or no experimental information on a system of interest, then this fluorescence may be lumped into the site relaxation coefficient, and the monochromatic absorber formalism may be retained.

Assuming that equilibrium within the excited band is much more

rapid than the loss processes, then reradiation is predominantly from the bottom of the band. If it is assumed that the sub-levels of the excited state are populated according to a thermal distribution for a temperature T_p, then an effective T_R may be calculated by requiring equal numbers of absorbed and emitted photons. For a thermal distribution obeying Boltzmann statistics in a broad band, T_R is generally about the same as if all the intensity were incident in a band of width kT_p on a narrow band absorber operating at ν_0.

If the data are available, a more straightforward approach is to use the absorption spectrum and fluorescence lifetime to calculate an absorber temperature directly:

The rate of excitation into the excited state is

$$P \int i(\nu)A(\nu)d\nu, \tag{25}$$

where P is the ground state population, i is the incident light intensity (in units such as quanta/cm^2 sec per unit band width), and A is the absorption cross section. The rate of decay of the excited state is simply

$$P^*/\tau \tag{26}$$

where P^* is the excited state population, and τ is the fluorescence lifetime. By equating these two rates, we may determine P/P^*.

The free energy increment per photon at the absorber is

$$h\nu_0 - kT_L \ln(PQ^*/P^*Q), \tag{27}$$

where Q and Q^* are the partition functions of the ground and excited states. For atomic and most molecular systems, Q^*/Q is given accurately by the ratio of the spin multiplicities.[12]

The thermodynamic potential at the absorber in the absence of

energy storage may be defined as

$$h\nu_0 \left(1 - T_L/T_M\right), \tag{28}$$

where T_M is the maximum absorber temperature.

Equating (27) and (28), we find that

$$M = \ln(PQ^*/P^*Q), \tag{29}$$

where $M = h\nu_0/kT_M$, and when the population ratio is measured in the absence of energy storage.

By using (P/P^*) from (25) and (26), we find that

$$M = -\ln[(Q/Q^*)\tau \int i(\nu)A(\nu)\, d\nu],$$

where τ is measured in the absence of energy storage.

As M contains many of the effects of site relaxation internally, the equations for the optical density problem must be modified slightly. If it is assumed that fluorescence emitted by one site cannot be used by another, then the basic efficiency relation is

$$\eta = (1 - H/L)\{1 - e^{-S} - Se^{M-H}) \tag{19'}$$

By steps analogous to equations (20) through (23), it is easily determined that for maximum power storage:

$$H = M + S \tag{24a'}$$

$$S = \ln(1 + S) + \ln X\ . \tag{24c'}$$

VII. CONCLUSIONS

There are several sources of inefficiency in the transformation of light into work which may be considered in thermodynamic terms: (1) directional radiation incident on a non-directional absorber; (2) irreversibility necessary to get a directional flow of energy into work or free energy storage; (3) internal resistance losses; and (4) energy leaks from the absorber.

Efficiency, as defined by the amount of power stored, is most significantly affected by control of the thermodynamic potential at the locus of free energy storage; indirectly, this means control of the absorber temperature. The latitude in this control for good efficiency in a photochemical system is indicated in Fig. 6.

As shown in Fig. 3, absorber directionality and absorber relaxation rate must change by at least an order of magnitude to significantly affect the thermodynamically limited maximum efficiency. The loss due to absorber relaxation in a given chemical system may be minimized by an appropriate choice of optical density for the absorber.

Internal resistance losses may be reduced by removing some of the resistance, but the significance of such a reduction depends on the degree of saturation (see Fig. 5).

An understanding of these sources of inefficiency may be useful in the design of radiation converters, such as in efforts to devise a simple photochemical system for the effective capture of solar energy.

The process may also be reversed: Information can be obtained about a radiation conversion system by studying its efficiency, or parameters such as chemical potential or fluorescence yield, as a

function of the variables considered in this paper. Biological photosynthesis is the system which originally motivated this work, and we hope that an understanding of the thermodynamics of radiation conversion may be particularly useful in this area.

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[12] This is demonstrated in molecular systems by agreement between the experimental fluorescence lifetime and that calculated from the absorption and fluorescence spectra. See (a) G. N. Lewis and M. Kasha, J. Am. Chem. Soc. 67, 994 (1945); (b) S. J. Strickler and R. A. Berg, J. Chem. Phys. 37, 814 (1962).

Fig. 1. Schematic diagram for the conversion of radiant energy into work.

Fig. 2. Maximum temperature for a non-directional narrow band absorber on Earth illuminated by a 6000° K blackbody sun.

Fig. 3. Maximum efficiency from a narrow band absorber illuminated by a 6000° blackbody source, with efficiency calculated on the basis of net absorbed light intensity. Curves from top for full blackbody intensity; intensity reduced by 10^5 (solar equivalent); reduction by 10^{10}.

Fig. 4. Effect of reradiation on the efficiency from a narrow band absorber on Earth illuminated by a 6000° blackbody sun. $1 - T_L/T_R$: maximum Carnot efficiency; $1 - T_L/T_H$: Carnot efficiency for maximum power storage; η: maximum efficiency calculated on the basis of incident light intensity.

Fig. 5. Maximum stored power as a function of incident light intensity. Upper curve: no impedance; lower curve: $f = 10$ at I_0. Parameters are discussed in Sec. IV.

Fig. 6. Dependence of efficiency on the thermodynamic potential at the locus of free energy storage. Upper curve: no impedance; lower curve: $f = 0.3$. Parameters are discussed in Sec. V.

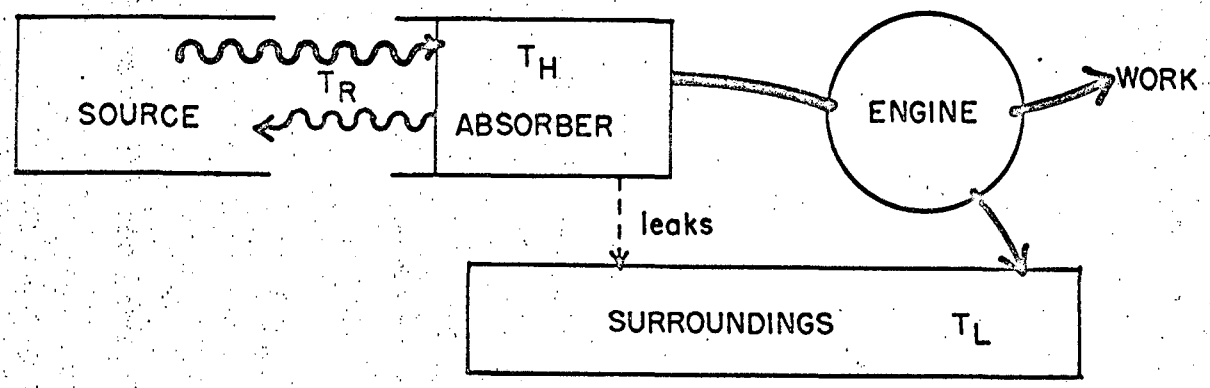

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Fig. 1

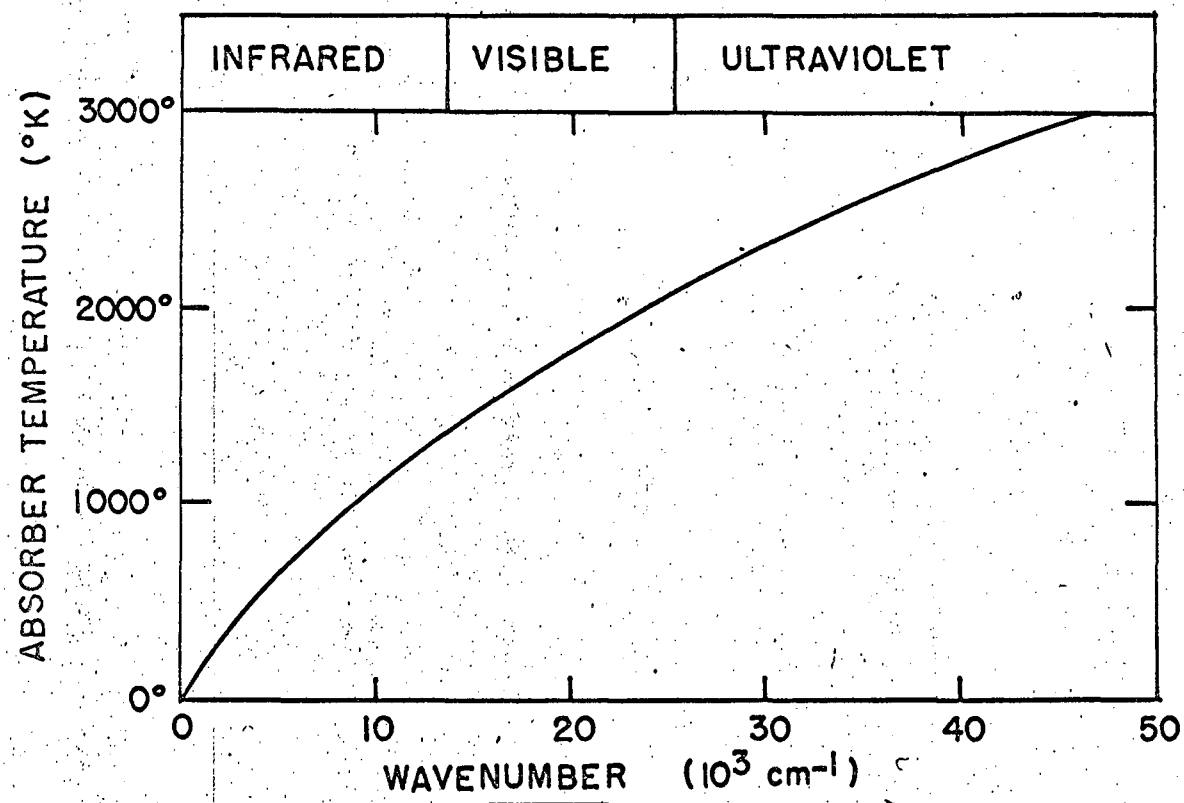

Fig. 2

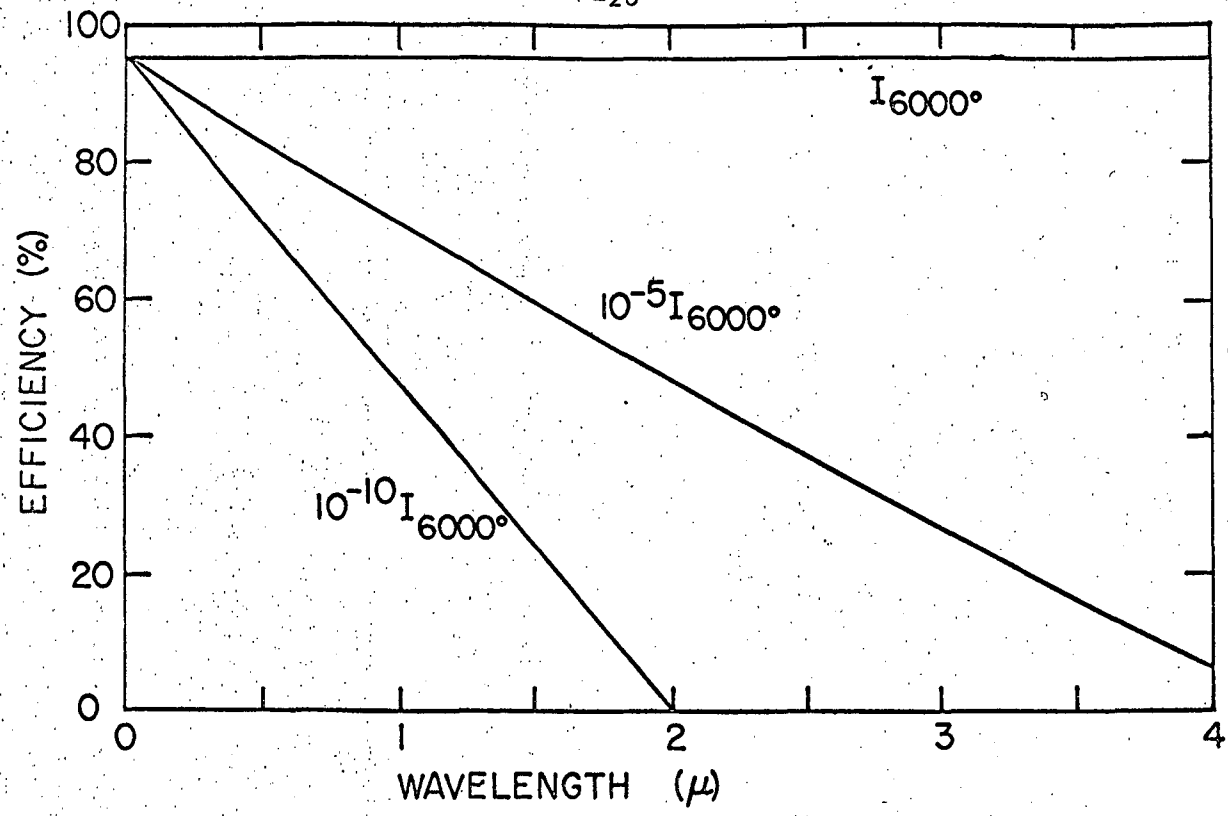

Fig. 3

MUB-8830

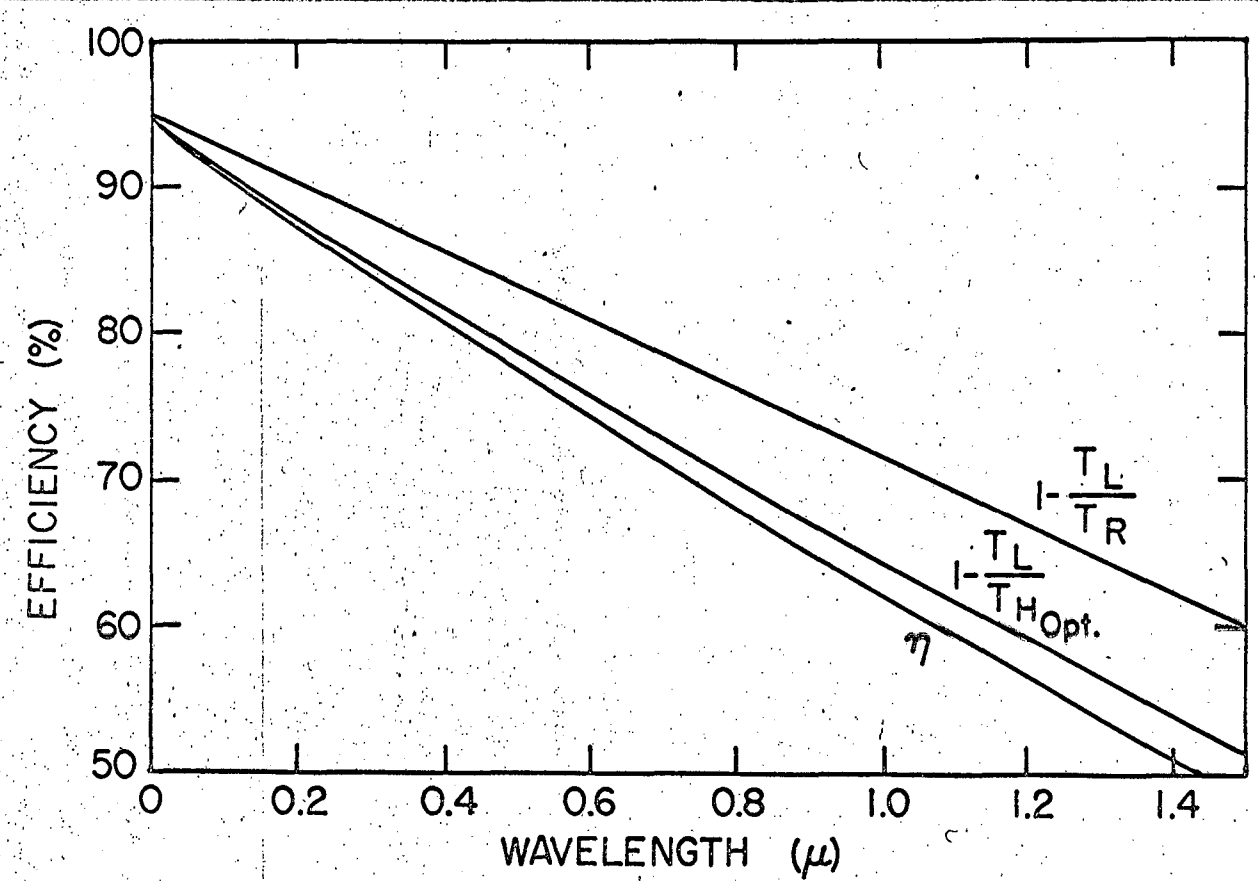

Fig. 4

MUB-8829

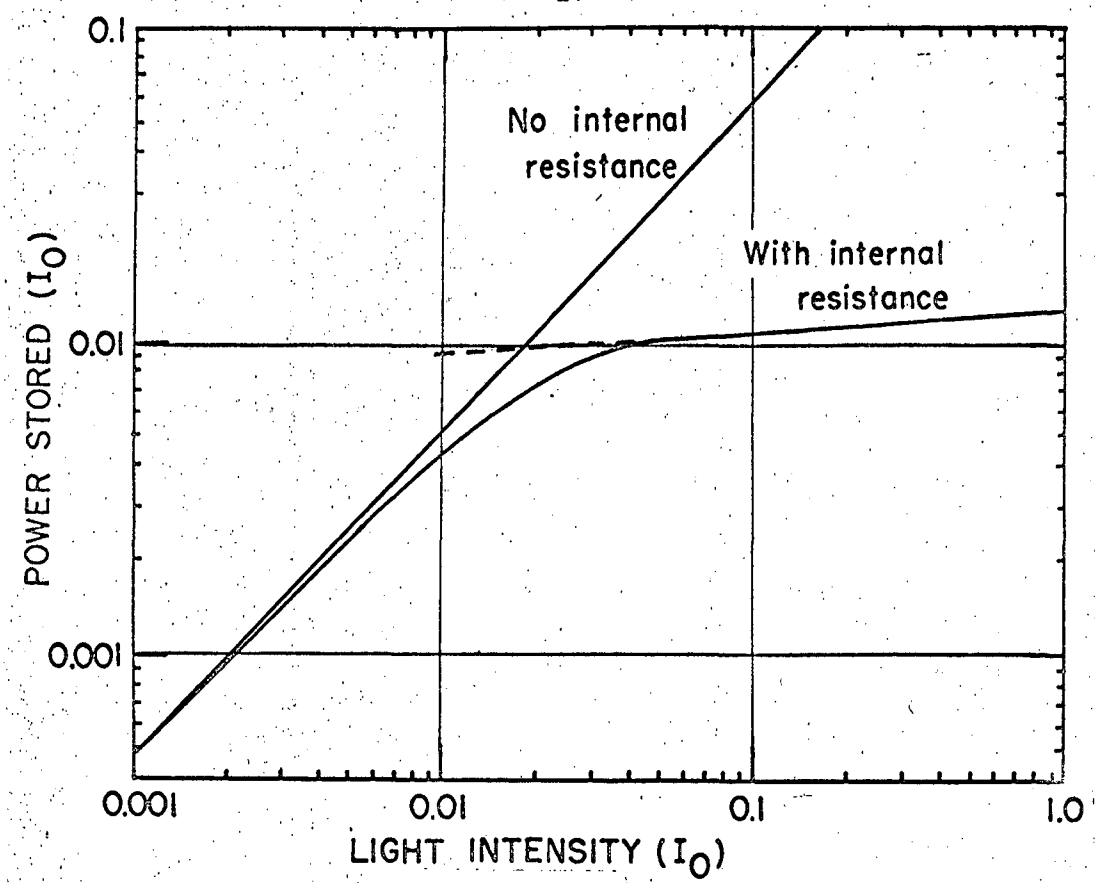

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Fig. 5

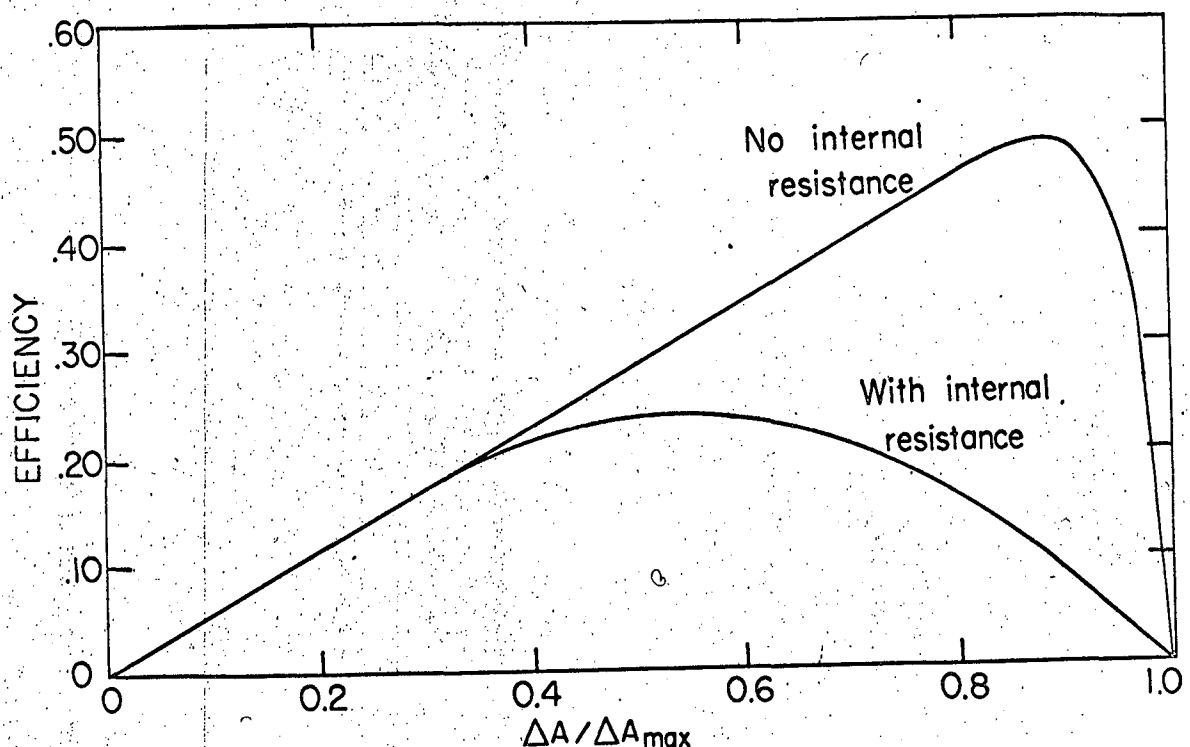

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Fig. 6