NASA TM - 83228

NASA Technical Memorandum 83228

THERMODYNAMIC LIMITS TO THE EFFICIENCY OF SOLAR ENERGY CONVERSION BY QUANTUM DEVICES

NASA-TM-83228 19820010823

A. M. Buoncristiani, C. E. Byvik, and B. T. Smith

November 1981

NASA
National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665

Table of Contents

N82-18697 #

NOMENCLATURE

$A(T)$	temperature-dependent coefficient, $2\pi(kT)^3/(hc)^2$
E_0	energy threshold of a quantum device
E_1	cutoff energy of a quantum device
$\dot{E}$	incident radiation energy flux
$\dot{E}'$	re-radiated energy flux
$\dot{F}_{RAD}$	free energy flux of the radiation field
h	Planck's constant
$H(n)$	entropy dependence on the photon distribution, $(1+n)\ \ell n(1+n) - n\ \ell n(n)$
k	Boltzmann's constant
$n(z)$	photon distribution function, $(e^z - 1)^{-1}$
$\dot{Q}$	heat flux
R_{Sun}	radius of the Sun
$R_{Earth\ orbit}$	mean radius of Earth orbit
$\dot{S}$	incident radiation entropy flux
$\dot{S}'$	re-radiated entropy flux
$\dot{S}^{int}$	entropy flux arising from internal irreversibilities
T	absolute temperature
T_R	quantum device operating temperature
T_S	source temperature
$\dot{W}$	flux of useful work
z	normalized energy parameters, $h\nu/kT$
z_0	normalized energy parameter, $h\nu_0/kT$
z_1	normalized energy parameter, $h\nu_1/kT$
γ	dilution constant $(R_{Sun}/R_{Earth\ orbit})^2$
Δ	difference operator

$\eta(z)$	efficiency evaluated at z
$\eta(z_0,z_1)$	efficiency of a quantum device with a threshold z_0 and a cutoff z_1
η_{max}	maximum conversion efficiency by a non-quantum device
ν	radiation frequency
ν_0	radiation frequency at threshold energy

THERMODYNAMIC LIMITS TO THE EFFICIENCY OF SOLAR ENERGY CONVERSION BY QUANTUM DEVICES

A. M. Buoncristiani
Christopher Newport College
Newport News, Virginia 23606, U.S.A.

C. E. Byvik
NASA Langley Research Center
Hampton, Virginia 23665, U.S.A.

B. T. Smith
Christopher Newport College
Newport News, Virginia 23606, U.S.A.

SUMMARY

The second law of thermodynamics imposes a strict limitation to the energy converted from direct solar radiation to useful work by a quantum device. This limitation requires that the amount of energy converted to useful work (energy in any form other than heat) can be no greater than the change in free energy of the radiation fields. Furthermore, in any real energy conversion device, not all of this available free energy in the radiation field can be converted to work because of basic limitations inherent in the device itself. We present a thermodynamic analysis of solar energy conversion by a completely general prototypical quantum device. This device is completely described by two parameters, its operating temperature T_R and the energy threshold of its absorption spectrum. We derive an expression for the maximum thermodynamic efficiency of a quantum solar converter in terms of these two parameters and the incident radiation spectrum. We present efficiency curves for assumed solar spectral irradiance corresponding to air mass zero (AM Ø) and air mass 1.5 (AM 1.5).

INTRODUCTION

Devices which convert the energy of solar radiation into energy in some other form can be divided into two broad categories. One category, thermal conversion devices, includes blackbody absorbers which convert solar energy into thermal energy that is used as process heat. The other category consists of quantum conversion devices which selectively absorb incident photons and convert some of their energy into electrical or chemical energy. The efficiency of any quantum conversion device is defined as the ratio of the energy converted to useful work, that is the energy converted to any form other than heat, to the total incident energy. In this paper we develop an upper bound for the efficiency of a general quantum conversion device. In another report (ref. 1), we consider the efficiency resulting from a hybrid quantum-thermal device which uses the thermal energy discarded by a quantum device.

We consider that the radiant energy from a solar source at a characteristic blackbody temperature T_S is incident upon a receiving device maintained at a fixed temperature T_R. There are two different types of limitations that restrict the efficiency of quantum conversion devices. The first limitation is imposed by the second law of thermodynamics and, as we shall show in the following paragraphs, requires that the amount of energy converted to useful work cannot exceed the change in free energy of the radiation field. Landsberg and Malinson (ref. 2) have shown that if all the available free energy of the radiation field were to be converted to useful work the solar efficiency could not exceed a maximum value given by

$$\eta_{max} = 1 - \frac{4}{3} (T_R/T_S) + \frac{1}{3} (T_R/T_S)^4 . \qquad (1)$$

The second limitation on solar energy conversion efficiency arises from the specific spectral response of the device itself. Since the spectral response characteristic limits the distribution of energy absorbed by the device, not all the free energy in the radiation field is available for conversion to useful work. Consequently the expression in equation (1) gives an overestimate of the maximum efficiency. In this paper we shall derive an upper bound for the maximum efficiency of a quantum conversion device taking into account the absorption characteristics of the device. We shall consider two types of general spectral response: threshold devices which absorb photons with energy greater than some value E_0 and bandwidth devices which have a cutoff energy E_1 above threshold energy.

THE THERMODYNAMIC LIMITATION

In this section we sketch an argument leading to the basic thermodynamic limitation on quantum energy conversion devices. To our knowledge the argument was first presented in a clear and complete form by Landsberg and his coworkers (ref. 2). Essentially it involves a balance of the energy and entropy flux at the receiving device. Radiation from a source at temperature T_S is incident upon a quantum device maintained at a fixed temperature T_R. The radiation incident upon the receiver is characterized by an energy flux $\dot{E}$ (power per receiver area) and an entropy flux $\dot{S}$ (power per receiver area-degree Kelvin). Similarly the radiation from the receiver (re-radiation) is characterized by its own energy and entropy flux $\dot{E}'$ and $\dot{S}'$. This incident and re-radiated flux is depicted in figure 1. The energy converted to useful work and the heat transferred to the surroundings of the receiver are also represented as an energy flux $\dot{W}$ and $\dot{Q}$ (power per receiver area). If the processes occurring within the receiver are thermodynamically irreversible there will be an internal generation of entropy and this is represented as an entropy flux $\dot{S}^{int}$. The second law of thermodynamics requires that this internal entropy flux satisfy the inequality

$$[\dot{S}^{int} \geq 0] \quad . \tag{2}$$

The arrows in figure 1 represent transfer of energy or entropy to or from the quantum receiving device; it remains now to keep these quantities properly balanced. On one hand, energy conservation requires that the incident energy flux equal the emergent energy flux so we have that

$$\dot{E} = \dot{E}' + \dot{W} + \dot{Q} \tag{3}$$

On the other hand, steady state operation requires that the sum of external and internal entropy flux changes be zero, from which follows the relation

$$\dot{S} - \dot{S}' - \dot{Q}/T_R + \dot{S}^{int} = 0 \quad . \tag{4}$$

Eliminating $\dot{Q}$ from the above two equations leads to the following expression for $\dot{W}$,

$$\dot{W} = (\dot{E} - T_R\dot{S}) - (\dot{E}' - T_R\dot{S}') - T_R\dot{S}^{int} \tag{5}$$

In classical thermodynamics, the work done on a body in an isothermal reversible process is equal to its change in free energy (F ≡ E-TS). Thus, we identify the first two terms in the expression for $\dot{W}$ as the change in the free energy of the radiation fields $-\Delta\dot{F}_{RAD}$. Since the term representing the energy irreversibly lost ($T_R\dot{S}^{int}$) is non-negative, an upper bound on the useful work obtains, namely the flux of useful work cannot exceed the change in the free energy flux of the radiation field

$$\dot{W} \leq (\dot{E} - T_R\dot{S}) - (\dot{E}' - T_R\dot{S}') \tag{6}$$

$$< = -\Delta\dot{F}_{RAD} .$$

THE SPECTRAL RESPONSE OF A QUANTUM DEVICE

A general thermodynamic argument leads to the conclusion that the useful work obtained from a quantum device is limited to the change in free energy of the radiation field. In any realistic device, not all of the free energy available in the radiation field can be converted to useful work because of limitations in the spectral response of the device itself (ref. 3). The spectral response is a unique characteristic of each device so, in order to insure that our discussion is independent of such specific device characteristics, we adopt a simple but general model for a generalized spectral response. First we shall consider a device with an energy threshold E_0. Subsequently we shall show how results obtained from a threshold model can be extended to include other response characteristics such as a bandwidth device with an energy cutoff. We consider a threshold device to be one for which: (a) no absorbed photon with energy below the threshold value can contribute to the useful work; and (b) those absorbed photons with energy above the threshold contribute only the threshold energy to the useful work. The energy in excess of threshold is thermalized to heat energy. The maximum efficiency of such a quantum device depends upon the receiver temperature T_R and upon a dimensionless parameter $z_0 = E_0/kT_S$ which normalizes the device threshold energy $E_0 = h\nu_0$ to a measure of the source energy. This efficiency can be expressed as an integral over the spectral distribution of the change in free energy of the radiation fields:

$$\eta\ (z_0) = \frac{\int_{\nu_0}^{\infty} (h\nu_0/h\nu)\ (-\Delta\ \dot{F}_{RAD})\ d\nu}{\text{Total Incident Energy}} \tag{7}$$

In the next section we show how to evaluate this integral from data giving the solar spectral irradiances; we carry out this evaluation for data on the AM Ø (ref. 9) and the AM 1.5 (ref. 5) spectrum. The maximum efficiency of a bandwidth device, having energy threshold E_0 and energy cutoff E_1, depends upon the two dimensionless parameters z_0 and $z_1 = E_1/kT_S$ and it can be expressed simply in terms of the integral obtained in equation (7) by

$$\eta\ (z_0,\ z_1) = \eta\ (z_0) - \frac{z_0}{z_1}\ \eta\ (z_1)\ . \tag{8}$$

FREE ENERGY OF THE RADIATION FIELD

The equilibrium energy and entropy flux distributions of a blackbody radiator at temperature T are well known (ref. 6). It is convenient for our purposes to express them in the following form:

$$\dot{E}(T) = A(T)\ z^3\ n(z) \tag{9}$$

$$\dot{S}(T) = \frac{A(T)}{T}\ z^2\ H(n)$$

In these equations z is the dimensionless parameter $(h\nu/kT)$ while

$$A(T) = 2\pi\ (kT)^3/(hc)^2\ . \tag{10}$$

The quantity $n(z)$ is the photon distribution function which, in the case of a blackbody radiator, is just the Bose-Einstein distribution (ref. 3)

$$n(z) = (e^z - 1)^{-1}\ . \tag{11}$$

The selective absorption or scattering of photons at various frequencies by the atmosphere will alter this distribution and we shall have to determine $n(z)$ in that case from spectral data. The function $H(n)$ is given by

$$H(n) = (1 + n)\ \ell n(1 + n) - n\ \ell n(n)\ . \tag{12}$$

The energy and entropy flux emitted from the Sun is given by equation (9) with $T = T_S$. The flux arriving at the Earth is diminished by the geometrical factor

$$\gamma = (R_{Sun}/R_{Earth\ orbit})^2 \tag{13}$$

We take for in energy and entropy flux distribution incident upon the receiving energy conversion device the expressions

$$\dot{E} = \gamma \cdot A\ (T_S)\ z^3 \cdot n \tag{14}$$

$$\dot{S} = \frac{\gamma\ A(T_S)}{T_S}\ z^2\ \ H(n)$$

The spectral irradiance data (refs. 4 and 5) give us $\dot{E}$ for selected wavelengths. Using these values and the first of equation (10) we then find the value of n at each of these wavelengths. This allows the determination of $\dot{S}$. Thus from given spectral data, the free energy of the incident radiation field $(\dot{E} - T_R\dot{S})$ can be found. In this determination it is necessary to fix a value for the temperature of the Sun. In these calculations we chose this value to be $T_S = 5792$ K obtained when the total energy for the AM Ø distribution (the solar constant) is set equal to $\gamma \cdot \sigma T^4$ (ref. 2). The free energy of the re-radiated fields is given by equation (9) with $T = T_R$. Some of the re-radiated energy however, may come from the receiver surroundings. In calculating the change in free energy of the radiation fields we scale the emergent radiation by the factor γ so as to include only that part of the re-radiated energy which comes from the incident radiations.

The results of calculations of the maximum solar efficiency for known spectral data at AM Ø for T=0 K and AM 1.5 for T_R=0 K and 580 K are shown in figure 2. The AM Ø spectral data indicates that the maximum solar conversion efficiency by a receiver maintained at 0 K above the atmosphere is 44 percent and that it occurs for a device with energy threshold $E_O = 0.9$ eV. The curves for other values of T_R are not shown in this figure but, for example, at 300 K, the maximum efficiency drops to about 40 percent. Since the AM Ø spectrum does not differ significantly from the $T_S = 6000$ K blackbody spectrum results previously obtained (ref. 3) are adequate for this case.

The AM 1.5 spectral data produces a broader efficiency curve which maximizes for $T_R = 0$ K at an efficiency of 48 percent. The efficiency curve for AM 1.5 is generally higher than the one for AM Ø despite the fact that the total irradiance reaching the atmosphere is much larger than that reaching the surface of the Earth. This occurs because the selective absorption of the Earth's atmosphere yields a higher proportion of high energy photons in the AM 1.5 spectrum than is found in the AM Ø spectrum. More photons are absorbed in the near IR ($E_O \rightarrow 1.2$ eV) than at higher energies resulting in an overall increase in efficiency by a threshold device and a shift in the location of the maximum efficiency to higher threshold energies. The effect of increased receiver temperature can be seen in the curve for $T_R = 580$ K.

If the receiver temperature were equal to the source temperature the calculated efficiency should be zero. As a check on our numerical calculations we carried them out for this case and found that the efficiency at any energy did not exceed 0.033, and was less than 0.001 for most values of the energy. Given the uncertainty present in the spectral irradiance data (refs. 4 and 5) themselves, this margin of error in the numerical calculation is acceptable.

The results of these calculations can be used to evaluate the maximum efficiency of any quantum solar energy conversion device. The curves shown in figure 2 can be used with equation (8) to determine the efficiency of any bandpass device. Such an evaluation of efficiency should be valuable in assessing and comparing the efficiency of various solar energy conversion systems.

Langley Research Center
National Aeronautics and Space Administration
Hampton, VA 23665
November 1981

REFERENCES

1. Byvik, C. E.; Buoncristiani, A. M.; and Smith, B. T.: Thermodynamic Limits for Solar Energy Conversion by a Quantum-Thermal Hybrid System. NASA TM-83229, November 1981.

2. Landsberg, P. T.; and Malinson, J. R.: Thermodynamic Constraints, Effective Temperatures, and Solar Cells. International Colloquium on Solar Electricity (CNES, Toulouse), 1976, pp. 27-46. A connected introductory account is given in Chapter 13 of Landsberg, P. T.: Thermodynamics and Statistical Mechanics. Oxford University Press, New York, 1979. See also the recent review article by Landsberg, P. T.; and Tonge, G.: Thermodynamic Energy Conversion Efficiencies. J. of Applied Phys., vol. 51, 1980, pp. R1-R20.

3. Buoncristiani, A. M.; Byvik, C. E.; and Smith, B. T.: The Ultimate Efficiency of Photosensitive Systems. NASA TM-83230, December 1981.

4. Thekaekara, M. P.: Solar Energy in Space. Proceedings of the Symposium on Solar Radiation, Smithsonian Institute, N76-15997, 1973.

5. Brandhorst, H. W., Jr.: Revised Terrestrial-Photovoltaic Measurement Procedures. NASA TM-73702, 1978.

6. Landau, L. D.; and Lifshitz, E. M.: Statistical Physics. Pergammon Press, London, 1958.

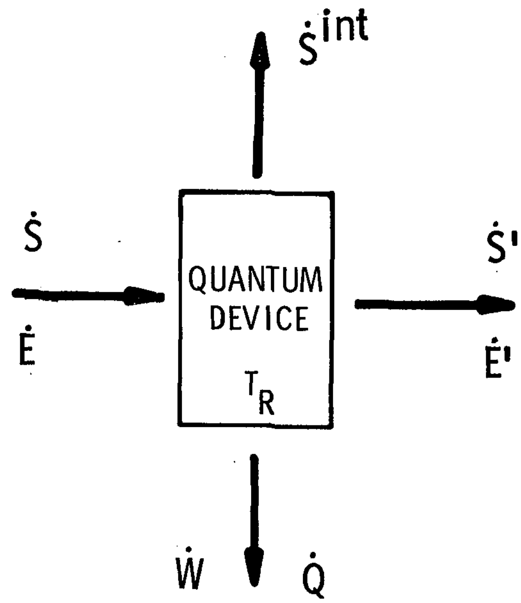

Figure 1. Schematic diagram of the energy, entropy, work, and heat flux at a quantum device operating at a temperature T_R.

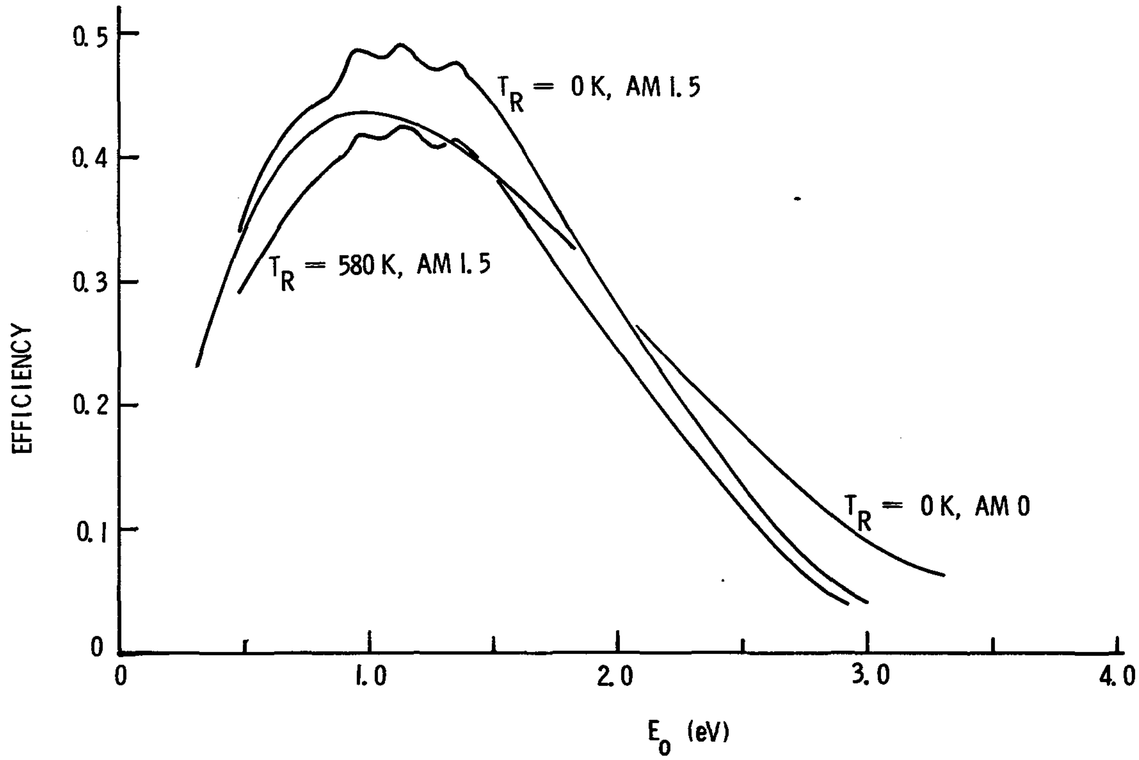

Figure 2. The efficiency of a quantum device as a function of threshold energy at T_R=0 K for AM Ø and T_R=0 and 580 K for AM 1.5 solar spectra.

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-83228		

4. Title and Subtitle
THERMODYNAMIC LIMITS TO THE EFFICIENCY OF SOLAR ENERGY CONVERSION BY QUANTUM DEVICES

5. Report Date
November 1981

6. Performing Organization Code
506-55-13-03

7. Author(s)
* A. M. Buoncristiani, C. E. Byvik, and *B. T. Smith

8. Performing Organization Report No.

9. Performing Organization Name and Address
NASA Langley Research Center
Hampton, VA 23665

10. Work Unit No.

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, DC 20546

13. Type of Report and Period Covered
Technical Memorandum

14. Sponsoring Agency Code

15. Supplementary Notes
*Christopher Newport College, Newport News, Virginia 23606

16. Abstract
The second law of thermodynamics imposes a strict limitation to the energy converted from direct solar radiation to useful work by a quantum device. This limitation requires that the amount of energy converted to useful work (energy in any form other than heat) can be no greater than the change in free energy of the radiation fields. Furthermore, in any real energy conversion device, not all of this available free energy in the radiation field can be converted to work because of basic limitations inherent in the device itself. We present a thermodynamic analysis of solar energy conversion by a completely general prototypical quantum device. This device is completely described by two parameters, its operating temperature T_R and the energy threshold of its absorption spectrum. We derive an expression for the maximum thermodynamic efficiency of a quantum solar converter in terms of these two parameters and the incident radiation spectrum. We present efficiency curves for assumed solar spectral irradiance corresponding to air mass zero (AM ∅) and air mass 1.5 (AM 1.5).

17. Key Words (Suggested by Author(s))
Solar Energy
Conversion Efficiency
Quantum Devices
Thermodynamic Efficiency

18. Distribution Statement
Unclassified -- Unlimited

Subject Category -- 44

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	13	A02