Journal of Solar Energy Engineering

Discussion

The Second Law Efficiency of Solar Energy Conversion¹

S. M. Jeter.² The ongoing controversy concerning the maximum useful work inherent in a quantity of solar radiation now includes the reassertion of a result due to Spanner [1]. This result is the first formulation in Table 1. Spanner had presented his result as an approximation, but Gribik and Osterle [2] propose the formulation as being exact.

One could only conclude from this formulation that no work could be extracted from radiant energy unless the temperature of the source were more than four-thirds the temperature of the sink. This is false, as can be demonstrated by the simple thermomechanical converter illustrated in Fig. 1. This device includes a putative ideal concentrator which receives the unsullied beam radiation (idealized as dilute thermal radiation) from the source and focuses it to the strength of ideal blackbody emission at the mouth of the cavity. The large cavity with reflecting walls is maintained at near-equilibrium at some intermediate collection temperature. As previously presented [5], the overall collection and conversion efficiency of this combination of ideal concentrator, blackbody cavity, and reversible heat engine with sink at T_o is:

$$\eta = \left(1 - \frac{T_c^4}{T_s^4}\right) \left(1 - \frac{T_o}{T_c}\right) \tag{1}$$

where T_c = collector (cavity) temperature. For a source at 5800 K and sink at $3T_s/4 = 4350$ K, an overall conversion efficiency of about 0.0592 is obtained for T_c around 5092 K. This result, while small, is non-zero and refutes the results of [1] and [2].

Spanner's result is an approximate formulation of the availability of a system of cavity radiation. The approximation is explicitly stated in [1], and as evidenced by the numerical evaluations in Table 1 it is quite accurate for T_s $>> T_{o}$ but is generally in error. A brief reiteration of the analysis of Gribik and Osterle will reveal the source of the error. As shown in Fig. 2, the resource is a volume filled with cavity radiation at T_s , the "system," while the "medium" is a sink at T_o . A reversible engine is interposed between the system and the medium. The reversible work which would be produced when the cavity is cooled to absolute zero is the integral,

$$W_{sv} = \int_{s}^{v} \delta Q \left(1 - \frac{T_o}{T} \right)$$
 (2)

where T = temperature of the system, s refers to the initial state, $T = T_s$, and v refers to the final state, T = 0, which has the value,

$$W_{sv} = Va(T_s^4 - 4T_s^3 T_o/3)$$
(3)

Technology, Atlanta, Ga. 30332.

where V = volume of the system, $a = U/(VT^4)$, and U =energy of a system of radiation of volume, V, and temperature, T. Since the initial energy in the system U_s is V_a T_s^4 , the following conversion efficiency could be proposed:

$$\eta_1 = \frac{W_{sv}}{U_s} = 1 - \frac{4T_o}{3T_s} \quad \text{(incorrect).} \tag{4}$$

The preceding result is faulty because W_{sv} is not the maximum work obtainable from an interaction between the system and its medium. The maximum work, W_{so} , is obtained when the system is brought into equilibrium with the sink (i.e., to the temperature T_{o}). It is unnecessary to expend work to drive

Table 1 Alternative formulations for the maximum conversion of solar energy to work

Formulation Evaluation¹ Reference
1.
$$1 - \frac{4}{3} \frac{T_o}{T_s}$$
 0.931034 [1] and [2]
2. $1 - \frac{4}{3} \frac{T_o}{T_s} + \frac{1}{3} \left(\frac{T_o}{T_s}\right)^4$ 0.931037 [3] and [4]

2.
$$1 - \frac{1}{3} - \frac{1}{T_s} + \frac{1}{3} \left(\frac{1}{T_s} \right)$$
 0.931037 [3] and [4]
3. $1 - \frac{T_o}{T_s}$ 0.948276 [5]

 $\overline{T_s} = 5800 \text{ K}, T_o = 300 \text{ K}$

IDEAL CONCENTRATOR

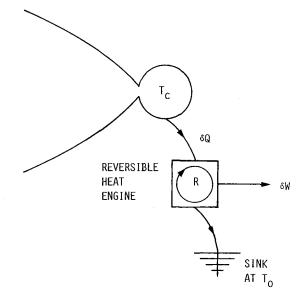


Fig. 1 A conceptualization of a thermomechancial converter with high, but not limiting, conversion efficiency

¹By J. A. Gribik and J. F. Osterle, and published in the February 1984 Issue of ASME JOURNAL OF SOLAR ENERGY ENGINEERING, Vol. 106, pp. 16-21. ²Assistant Professor, School of Mechanical Engineering, Georgia Institute of

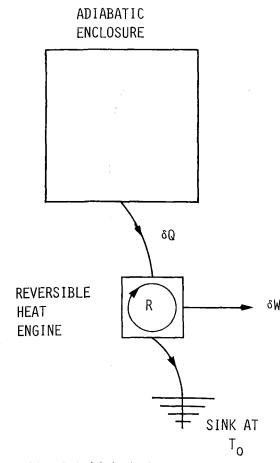


Fig. 2 A hypothetical device for the conversion of cavity radiation to work

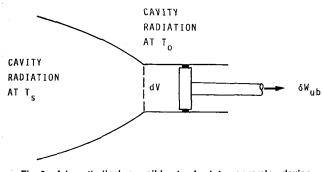


Fig. 3 A hypothetical reversible steady-state conversion device

the system to absolute zero temperature, and this unnecessary work done to "destroy" the radiation should not be subtracted from the maximum potential work. Changing to the proper final state in equation (2) yields the result

$$W_{so} = Va\left(T_s^{4} - 4\frac{T_s^{3}T_o}{3} + \frac{1}{3}T_o^{4}\right)$$
(5)

where s refers to the initial state, $T = T_s$, o refers to the final state, $T = T_o$, and the corresponding conversion efficiency is

$$\eta_2 = \frac{W_{so}}{U_s} = 1 - \frac{4 T_o}{3 T_s} + \frac{1}{3} \frac{T_o^4}{T_s^4}$$
(6)

which is in accord with [3] and [4]. Spanner's approximation was essentially to ignore the energy, U_o , remaining in the control volume in the final state. This simplification assumes the vacuum state as the final state, T = 0, rather than a final $T = T_o$. When corrected for this approximation, Spanner's procedure yields precisely the same formulation as item 2 in Table 1. A more nearly direct procedure for deriving equation (5) is to define the system as a volume of cavity radiation at T_s and evaluate the availability from the formula [6],

$$A_s = (U_s - U_o) + P_o (V_s - V_o) - T_o (S_s - S_o).$$
(7)
Since V_o can equal $V_s = V$,

$$A_{s} = (U_{s} - U_{a}) - T_{a} 4(U_{s}/T_{s} - U_{a}/T_{a})/3$$
(8)

which reduces to equation (5) and gives the same result as equation (6).

Alternatively, the same result can be obtained by recognizing that the empty cavity in the vacuum state v is itself a resource. Taking the medium to be not just a sink at T_o but a more realistic combination of sink and cavity radiation at T_o , the system has a residual availability in the vacuum state of

$$A_{\mu} = P_{\rho} V \tag{9}$$

where P_o = radiation pressure at T_o . Substituting the well-known result, $P_o = U_o/3V$, and adding to equation (3) gives the same result as equation (5).

Equation (5) is recognized as the correct formulation for the availability of a system of cavity radiation at T_s relative to a medium of cavity radiation at T_o , and equation (6) is a corresponding "conversion efficiency"; however, equation (6) is not the result applicable to the collection and conversion of solar energy. Solar energy does not occur in discrete packages or deposits but is continuously emitted from the sun; consequently, the continuous steady-flow process must be investigated.

The model for the steady-flow collection and conversion of solar energy is shown in Fig. 3. Cavity radiation at T_s is to the left of the cylinder which is otherwise surrounded by the medium, cavity radiation at T_o . During a differential process, the small quantity of radiation that enters the cylinder is

$$\delta E_{in} = dU + \delta W_b = -\frac{4}{3} dU \tag{10}$$

where dU = internal energy within the cylinder and δW_b = boundary work on the piston. One should note that "flow work" is not operable in this system since cavity radiation comprises particles, photons, which do not interact; consequently, there is no boundary work at the inlet to the cylinder. The boundary work at the piston, δW_b , comprises work expended on the medium and the useful work, δW_{ub} , which could be delivered to a reservoir external to the system and medium,

$$\delta W_{ub} = (P - P_o) dV = (dU - dU_o)/3$$
(11)

where $dU_o =$ energy in the cylinder at T_o . The radiation now in the cylinder could be isolated and its availability, dA, recovered yielding net useful work:

$$\delta W_{\mu} = dA + \delta W_{\mu b} \tag{12}$$

where dA = availability of radiation in the cylinder. From equation (5)

$$dA = dU \left(1 - \frac{4 T_o}{3 T_s} + \frac{1}{3} \frac{T_o^4}{T_s^4} \right).$$
(13)

Consequently,

$$\delta W_u = \frac{4}{3} dU \left(1 - \frac{T_o}{T_s} \right), \tag{14}$$

and the steady-state conversion efficiency, the ratio of equation (14) to equation (10), is just the Carnot efficiency:

$$\eta = \frac{\delta W_u}{\delta E_{in}} = 1 - \frac{T_o}{T_s}.$$
 (15)

Much of the essence in this controversy concerns the definition of maximum conversion efficiency. One school of thought, represented by the results in Table 1, asserts that the

Journal of Solar Energy Engineering

maximum conversion efficiency is a property of the resource and the medium alone. This allows a purely thermodynamic analysis to yield a fundamental result, embodied in equation (15), which serves as a limiting benchmark for both practical and conceptual systems. The result reaffirmed herein is presented in this spirit and supports the very widely-held apprehension that thermal radiation is heat.

An alternative approach is to hypothesize a suitably idealized conceptual system (e.g., an array of dilute narrow-band absorbers), and analyze the performance of such a system in detail. This approach requires the consideration of both collection and conversion efficiencies as in the analysis leading to equation (1). An example of this analysis is Haught's investigation [7] of the conversion efficiencies of arrays of thermal converters and quantum converters radiatively coupled to their environment.

References

1 Spanner, D. C., Introduction to Thermodynamics, Academic Press, New York, 1964, p. 225-226

2 Gribik, J. A., and Osterle, J. F., "The Second Law Efficiency of Solar Energy Conversion," ASME JOURNAL OF SOLAR ENERGY ENGINEERING, Vol. 106, Feb. 1984, pp. 16-21.

3 Petela, R., "Exergy of Radiation," ASME Journal of Heat Transfer, Vol. 86, May 1964, p. 187-192.

4 Results confirming [3] include: Press, W. H., "Theoretical Maximum for Energy from Direct and Diffuse Sunlight," *Nature*, Vol. 264, 1976, p. 735; Landsberg, P. T., "A Note on the Thermodynamics of Energy Conversion in Plants," Photochemistry and Photobiology, Vol. 26, 1977, pp. 313-314; and Parrott, J. E., letter, Solar Energy, Vol. 22, 1979, pp. 572-573.

5 Jeter, S. M., "Maximum Conversion Efficiency for the Utilization of Direct Solar Radiation," Solar Energy, Vol. 26, 1981, pp. 231-236. 6 Keenan, J. H., Thermodynamics, Wiley, New York, 1941.

7 Haught, A. F., "Physics Considerations of Solar Energy Conversion," ASME JOURNAL OF SOLAR ENERGY ENGINEERING, Vol. 106, No. 3, Feb. 1984, pp. 3-15.

A. De Vos¹ and H. Pauwels.² Recently, Gribik and Osterle [1] reviewed the literature, related to the theoretical maximum efficiency of devices converting blackbody radiation into useful work. Such a theory is very useful for evaluating solar devices, as undiluted sunlight can very satisfactorily be approximated by black body radiation with a temperature $T_s =$ 6000 K.

Gribik and Osterle compare three different expressions for the efficiency η of a converter working between two heat reservoirs, one at the sun temperature T_s (i.e., 6000 K) and one at the ambient temperature T_o (e.g., 300 K):

$$\eta_1(t) = 1 - t, \tag{1}$$

$$\eta_2(t) = 1 - \frac{4}{3}t + \frac{1}{3}t^4, \qquad (2)$$

$$\eta_3(t) = 1 - \frac{4}{3} t, \tag{3}$$

where $t = T_o/T_s$ denotes the dimensionless temperature ratio $(0 \leq t \leq 1).$

Formula (1) is the well known Carnot efficiency, which is recognized by Jeter [2-3], as the true upper limit for the efficiency of solar energy conversion. Equation (2) has been derived by Petela [4], by Landsberg and Mallinson [5-7], and by Press [8]. Finally, expression (3) is the maximum attainable efficiency according to Spanner [9]. Figure 1 depicts the various relationships η versus t.

We see that for t obeying 0 < t < 1, $\eta_1(t) > \eta_2(t) > \eta_3(t)$. Whereas both η_1 and η_2 obey $0 < \eta < 1$ for 0 < t < 1, $\eta_3(t)$ is

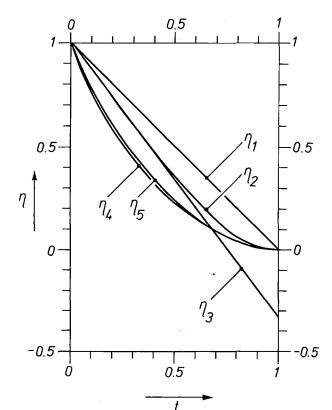


Fig. 1 The maximum efficiency η of a solar energy converter, as a function of $t = T_o/T_s$, the ratio of the surrounding's temperature T_o to the sun's temperature T_s , according to the various expressions (1), (2), (3), (21)-(22), and (23)-(24)

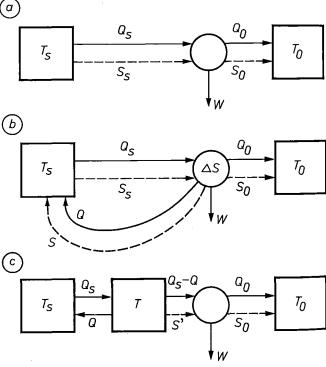


Fig. 2 Three models for describing the conversion of solar energy Q_sinto work W

negative for t > 0.75. The latter property already makes expression (3) suspicious, but Gribik and Osterle nevertheless conclude from their study that equation (3) is the correct value of the maximum efficiency η .

In the following discussion, we point out the error in Span-

¹Bontinckstraat 83, B-9280 Berlare, Belgium.

²Laboratorium voor Elektronica en Meettechniek, Rijksuniversiteit te Gent, Sint-Pietersnieuwstraat 41, B-9000 Gent, Belgium.

ner's theory, construct, step by step, the exact expression for the efficiency η , and review important literature on the subject, not mentioned by Gribik and Osterle.

Figure 2(a) shows the classical diagram of a reversible engine converting a heat Q_s from the hot reservoir into work W, while depositing a heat Q_o to the cold reservoir. The heats Q_s and Q_o are accompanied by the entropies S_s and S_o , respectively, whereas the work W is not accompanied by any entropy, as the engine is supposed to be reversible.

We now write down the first and second law of thermodynamics:

$$W_{t} + Q_{o} - Q_{s} = 0 \tag{4}$$

and

$$S_o - S_s = 0. \tag{5}$$

These laws are then supplemented by

$$S_o = Q_o / T_o \tag{6}$$

and

$$S_s = Q_s / T_s. \tag{7}$$

Eliminating S_o and S_s from the set (5)-(7) gives rise to

$$Q_o = \frac{T_o}{T_s} Q_s.$$

Substituting this result into (4) finally yields

$$W = \left(1 - \frac{T_o}{T_s}\right) Q_s,$$

giving rise to the Carnot value for the efficiency $\eta = W/Q_s$.

Spanner's model is elaborated in a completely similar way as the Carnot model. Equations (4)-(6) are supposed to be still valid, but equation (7) is replaced by

$$S_s = \frac{4}{3} \cdot \frac{Q_s}{T_s}.$$
 (8)

By eliminating S_s , S_o , and Q_o from the set (4), (5), (6), (8), we obtain

$$W = \left(1 - \frac{4}{3} - \frac{T_o}{T_s}\right) Q_s,$$

giving rise to the Spanner efficiency (3).

The error giving rise to Spanner's result is the supposition that equations (4) and (5) still hold. However, the conversion of radiation into work cannot be performed with deposition of a waste heat Q_o to the reservoir T_o only, neither can it be performed without entropy creation. Indeed, in order to convert radiation energy, we first of all have to absorb the radiation. According to Kirchhoff's law, any absorber is at the same time an emittor, so that an energy Q is re-emitted, accompanied necessarily with an entropy S. In Fig. 2(b), Q and S are added to the model, as if radiated completely to the sun. This choice has been made for convenience only, as in practice part of this radiation can reach the surroundings. But at least a part of Q (and S) is necessarily emitted towards the sun.

The second omission in Spanner's calculation is the fact that emission of radiation without absorption of identically the same radiation (and vice versa absorption of radiation without emission of identical radiation) is an irreversible process, as pointed out by Planck [10]. Therefore, an entropy ΔS is created on the surface of the solar absorber. Therefore, a ΔS is symbolically located in the converting device of Fig. 2(b).

So, we have now the following set of four equations:

$$W + Q_o - Q_s = -Q \tag{9}$$

$$S_o - S_s = -S + \Delta S \tag{10}$$

$$S_o = Q_o / T_o \tag{11}$$

$$S_s = (4/3) \cdot (Q_s/T_s).$$
 (12)

This new set yields:

$$\eta = 1 - \frac{4}{3} - \frac{T_o}{T_s} - \frac{Q}{Q_s} + \frac{T_o S}{Q_s} - \frac{T_o \Delta S}{Q_s}$$
(13)

correcting Spanner's equation

$$\eta = 1 - \frac{4}{3} \frac{T_o}{T_s} \, .$$

In order to evaluate the new formula (13), we need explicit expressions for Q, S and ΔS . For this purpose, we have to make a precise choice for the absorbing unit. We will make some different choices in the following paragraphs, leading to various useful results.

The simplest absorbing device is a black body. We suppose this body is at temperature T (not excluding a priori the possibility that T equals the surrounding temperature T_o). In this case, we have:

In this case, we have:

and

$$Q = \frac{T^4}{T_s^4} Q_s \tag{14}$$

$$S = \frac{4}{3} \cdot \frac{Q}{T} = \frac{4}{3} \cdot \frac{T^{3}}{T_{s}^{4}} Q_{s}.$$
 (15)

In these equations we have implicitly made the assumption that the sun "surrounds" the absorber completely, i.e., illuminates the latter from a 4π solid angle (fully concentrated sunlight).

Substitution into (13) yields

$$\eta = 1 - \frac{4}{3} \frac{T_o}{T_s} - \frac{T^4}{T_s^4} + \frac{4}{3} \frac{T_o T^3}{T_s^4} - \frac{T_o \Delta S}{Q_s}.$$
 (16)

We can now proceed in two ways. In a first approach we do not care about the exact value of ΔS , and only take into account that it is a positive (or zero) quantity. We conclude that

$$\eta \le 1 - \frac{4}{3} - \frac{T_o}{T_s} - \frac{T^4}{T_s^4} + \frac{4}{3} - \frac{T_o T^3}{T_s^4}.$$
 (17)

This expression still contains the unknown parameter T. After some examination, one can easily verify that the expression is maximal for $T = T_0$:

$$1 - \frac{4}{3} - \frac{T_o}{T_s} - \frac{T^4}{T_s^4} + \frac{4}{3} - \frac{T_o T^3}{T_s^4} \le 1$$
$$- \frac{4}{3} - \frac{T_0}{T_s} + \frac{1}{3} - \frac{T_o^4}{T_s^4}, \qquad (18)$$

leading to

$$\eta < 1 - \frac{4}{3} t + \frac{1}{3} t^4, \tag{19}$$

the Petela-Landsberg-Press result. It is, however, important to stress that the equality signs in (17) and (18) are not valid under the same conditions. Therefore, no equality sign is allowed in (19).

A second approach takes into account the explicit expression for ΔS [10-11]:

$$\Delta S = \frac{Q_s - Q}{T} + S - S_s = Q_s \left(\frac{1}{3} - \frac{T^3}{T_s^4} - \frac{4}{3} - \frac{1}{T_s} + \frac{1}{T}\right).$$
(20)

Substitution into (16) yields

$$\eta = \left(1 - \frac{T_o}{T}\right) \left(1 - \frac{T^4}{T_s^4}\right). \tag{21}$$

As we can still freely choose the value of the parameter T, we maximize η with respect to T. This gives rise to the fifth degree equation

$$4T^{5} - 3T_{o}T^{4} - T_{o}T^{4} = 0.$$
 (22)

Formula (21), together with equation (22), defines a fourth efficiency formula $\eta_4(t)$, depicted on Fig. 1. This efficiency ex-

Journal of Solar Energy Engineering

pression has been mentioned by different authors: Müser [12], Castans [13–14], Jeter [2–3], and De Vos and Pauwels [11, 15, 16]. It has been derived in the present paper by introducing corrections to Spanner's model. It can, however, also be deduced in a shorter way, not needing, e.g., equations (15) and (20). Figure 2(c) shows how to proceed: the converter is divided into two parts: the absorbing part (containing the reemission of radiation as well as the entropy creation) and a reversible (or Carnot) part. The set (4)–(7) is now replaced by the set

$$W + Q_o - (Q_s - Q) = 0$$

$$S_o - S' = 0$$

$$S_o = Q_o / T_o$$

$$S' = (Q_s - Q) / T$$

Solving for W yields

$$W = \left(1 - \frac{T_o}{T}\right)(Q_s - Q).$$

Taking (14) into account, this result indeed becomes

$$W = \left(1 - \frac{T_o}{T}\right) \left(1 - \frac{T^4}{T_s^4}\right) Q_s.$$

The model of Fig. 2(c) has recently been reviewed by De Vos [17].

We think it is useful to mention one important aspect of this model. If the efficiency of the converter would be defined as the useful work W divided by the *net* energy $Q_s - Q$ transferred from the sun to the converter, the efficiency would be

$$\eta = \frac{W}{Q_s - Q} = 1 - \frac{T_o}{T}.$$

If one would then put the temperature T of the converter equal to the suns temperature T_s , one would obtain the Carnot efficiency

$$\eta_1(t) = 1 - t$$
 $(t = T_o/T_s).$

This is to be expected since the absorber emits the same radiation as it receives and is thus no longer a creator of entropy. But, unfortunately, the conversion of this net energy transfer occurs infinitely slowly since $Q_s - Q$ tends to 0 (which is typical for reversible processes). The energy $Q_s - Q$ is also the energy lost by the sun, and if we were responsible for keeping the sun hot, and would have to pay its fuel, the above definition of efficiency would be meaningful. Since this is, however, not the case, the universally accepted definition of the efficiency of solar energy conversion is

$$\eta = \frac{W}{Q_s}$$

and the Carnot efficiency has no relevance for this definition. Since so many people (e.g., [2, 3]) believe that only the Carnot efficiency is the "ultimate efficiency," we felt obliged to make the above statement.

One can easily consider more than one absorbing body, which can adopt different temperatures T. If the bodies are selectively black, they can absorb different parts of the solar spectrum and so realize higher conversion efficiencies than the single-body converter.

Only numerical calculations can be used to evaluate such "multicolor" systems. De Vos and Vyncke [18] published results for devices with *n* absorbing units, *n* equaling 2, 3, and 4. Table 1 gives results for $T_s = 6000$ K and $T_o = 300$ K and thus t = 1/20.

If *n* tends to $+\infty$, we end up with a system where every small frequency interval of the solar spectrum is absorbed in an appropriate absorber at an appropriate temperature *T*. Such an infinite system was introduced by Haught [19-21]. Independently of Haught, a photovoltaic equivalent was in-

n	η (in percent)
1 2 3 4 	84.8 = $\eta_4(0.05)$ 86.1 86.3 86.4
+∞	$86.8 = \eta_5(0.05)$

Table 2

$$\frac{1}{t \approx 0} \frac{t \approx 1}{t \approx 1} \frac{1}{\text{Ref.}}$$

$$\frac{1}{\eta_1(t) = 1 - t} \frac{1 - t}{(1 - t)} \frac{1 - t}{(1 - t)}$$

$$\eta_2(t) \approx 1 - \frac{4}{3} t \frac{2(1 - t)^2}{(1 - t)^2}$$

$$\eta_3(t) = 1 - \frac{4}{3} t \frac{-\frac{1}{3} + \frac{4}{3}(1 - t)}{(1 - t)^2} \frac{1}{(1 - t)^2} \frac{1}{(1 - t)^2}$$

$$\eta_4(t) \approx 1 - \frac{5}{4^{4/5}} t^{4/5} \frac{(1 - t)^2}{(1 - t)^2} \frac{1}{(1 - t)^2} \frac{1}{(1 - t)^2}$$

$$\eta_5(t) \approx 1 + \frac{30\xi(3)}{\pi^4} t \log(t) \frac{(1 - t)^2}{(1 - t)^2} \frac{1}{(2 - t)^2}$$

troduced by De Vos [22], and thermodynamically analyzed by De Vos and Pauwels [15]. Pauwels, De Vos, and Vyncke [18, 23], proved that such an "omnicolor" system is the thermodynamically optimal device for converting solar energy into work. We will denote the resulting conversion efficiency by η_5 . We have:

$$\eta_5(t) = \frac{15}{\pi^4} t^4 \int_0^{+\infty} \frac{u^2 x^2 \exp(u-x)}{[\exp(u-x)-1]^2} du,$$
 (23)

where x is the solution of the transcendental equation

$$\frac{(1+x)\exp(u-x)-1}{[\exp(u-x)-1]^2} = \frac{1}{\exp(tu)-1}.$$
 (24)

Formula (23)-(24) was published by De Vos, Grosjean, and Pauwels [15, 16, 24] and was reviewed by Landsberg [7]. Figure 1 shows the function $\eta_5(t)$. We see that this efficiency is only slightly larger than $\eta_4(t)$. This property is also illustrated in Table 1.

We can summarize the above as follows:

(a) Both the Carnot efficiency $\eta_1(t)$ and the Landsberg efficiency $\eta_2(t)$ are useful upper bounds for solar energy conversion. They can, however, not be reached or even approached by any physical system (except at t = 0 and t = 1).

(b) The Spanner efficiency $\eta_3(t)$ has no physical meaning at all and has to be considered as a useless tool.

(c) The Müser-Castans efficiency $\eta_4(t)$ is a very useful formula and gives the upper limit for conversion of solar energy by a specific and simple device: a single black body absorber, combined with a Carnot heat engine.

(d) Finally, the efficiency $\eta_5(t)$ is the true expression for the upper limit of solar energy conversion efficiency.

Figure 1 illustrates the different behavior of the five $\eta(t)$ functions. In addition, Table 2 gives the series expansions of $\eta(t)$ in the neighbourhood of t = 0 (expansion for small t) and in the neighbourhood of t = 1 (expansion for small 1-t).

All above enumerated formulae, as well as Fig. 1 and Tables 1 and 2, are concerned with the conversion of non-diluted black body radiation, i.e., with fully concentrated sunlight. All results can easily be generalized for diluted black body radiation, i.e., natural sunlight or moderately concentrated sunlight. The reader is referred to the literature cited for further details.

1 Gribik, J., and Osterle, J., "The Second Law Efficiency of Solar Energy Conversion," ASME JOURNAL OF SOLAR ENERGY ENGINEERING, Vol. 106, 1984, pp. 16-21.

2 Jeter, S., "Maximum Conversion Efficiency for the Utilization of Direct Solar Radiation," Solar Energy, Vol. 26, 1981, pp. 231-236.

3 Jeter, S., "Response to Dr. Castans' Comments," Solar Energy, Vol. 30, 1983, p. 293.

4 Petela, R., "Exergy of Radiation," ASME Journal of Heat Transfer, Vol. 86, 1964, pp. 187-192.

5 Landsberg, P., and Mallinson, J., "Thermodynamic Constraints, Effec-tive Temperatures and Solar Cells," *Proceedings of the C.N.E.S.-C.N.R.S.* Conference on Solar Electricity, Toulouse, 1976, pp. 27-46.

6 Landsberg, P., "A Note on the Thermodynamics of Energy Conversion in Plants," Photochemistry and Photobiology, Vol. 26, 1977, pp. 313-314.

7 Landsberg, P., "Non-Equilibrium Concepts in Solar Energy Conversion," in Energy Transfer Processes in Condensed Matter, B. Di Bartolo, ed., Plenum Press, New York, 1984, pp. 537-592.

8 Press, W., "Theoretical Maximum for Energy from Direct and Diffuse Sunlight," Nature, Vol. 264, 1976, pp. 734-735.
9 Spanner, D., "Introduction to Thermodynamics," Academic Press, Lon-

don, 1964, p. 226.

10 Planck, M., "Vorlesungen über die Theorie der Wärmestrahlung," Barth Verlag, Leipzig, 1923; in translation: "The Theory of Heat Radiation," Mac Millian, London, 1923, and Dover, New York, 1959.

11 De Vos, A., and Pauwels, H., "Comment on a Thermodynamical Paradox Presented by P. Würfel," Journal of Physics C: Solid State Physics,

Vol. 16, 1983, pp. 6897-6909.12 Müser, H., "Thermodynamische Behandlung von Elektronenprozessen in Halbleiter-Randschichten," Zeitschrift für Physik, Vol. 148, 1957, pp. 380-390.

13 Castans, M., "Bases Fisicas del Aprovechamiento de la Energia Solar," Revista de Geofisica, Vol. 35, 1976, pp. 227-239.

14 Castans, M., "Comments on Maximum Conversion Efficiency for the

Utilization of Direct Solar Radiation," Solar Energy, Vol. 30, 1983, p. 293. 15 De Vos, A., and Pauwels, H., "On the Thermodynamic Limit of Photovoltaic Energy Conversion," Applied Physics, Vol. 25, 1981, pp. 119-125.

16 Pauwels, H., and De Vos, A., "Determination and Thermodynamics of Maximum Efficiency Photovoltaic Device," Proceedings of the 15th I.E.E.E. Photovoltaic Specialists Conference, Orlando, Fla., 1981, pp. 377-382.

17 De Vos, A., "Efficiency of Some Heat Engines Operating at Maximum Power Conditions," *American Journal of Physics*, Vol. 53, 1985, pp. 570-573.

18 De Vos, A., and Vyncke, D., "Solar Energy Conversion: Photovoltaic versus Photothermal Conversion," *Proceedings of the 5th E.C. Photovoltaic*

Solar Energy Conference, Athinai, 1983, pp. 186-190. 19 Haught, A., "Physics Considerations of Solar Energy Conversion," United Technologies Research Report 80-9, East Hartford, Conn., 1980. 20 Haught, A., "Physics Considerations of Solar Energy Conversion," Pro-

ceedings of the 3rd International Conference on Photochemical Conversion and Storage of Solar Energy, Boulder, Colo., 1980, pp. 443-445.

21 Haught, A., "Physics Considerations of Solar Energy Conversion," ASME JOURNAL OF SOLAR ENERGY ENGINEERING, Vol. 106, 1984, pp. 3-15.

22 De Vos, A., "Detailed Balance Limit of the Efficiency of Tandem Solar

Cells," Journal of Physics D: Applied Physics, Vol. 13, 1980, pp. 839-846. 23 Pauwels, H., and De Vos, A., "Determination of the Maximum Efficiency Solar Cell Structure," Solid-State Electronics, Vol. 24, 1981, pp. 835-843

24 De Vos, A., Grosjean, C., and Pauwels, H., "On the Formula for the Upper Limit of Photovoltaic Solar Energy Conversion Efficiency," Journal of Physics D: Applied Physics, Vol. 15, 1982, pp. 2003-2015.

Authors' Closure

Professor Jeter rejects our conclusions regarding the maximum useful work obtainable from solar energy, and re-states his case for a "Carnot" limit to this quantity. The discrepancy between our result and his involves two issues. The first is the temperature to which solar radiation should be reduced in order to determine the maximum work available from it. We say absolute zero and Jeter says T_o , the temperature of the ambient radiation. The second issue is whether or not radiation is heat. We say no and Jeter says yes. We will now take up these issues in turn.

As to the first, we showed in our paper that the energy (hence the temperature) of radiation must be reduced to zero when determining how much useful work is obtainable from it in order to properly take account of the fact that thermal radiation is annihilated upon absorption, not just cooled down. On this issue Jeter says only that "it is unnecessary to expend work to drive the system to zero temperature." He does not say why.

In regard to the second issue – whether or not radiation is heat - Jeter says at one point "the result reaffirmed here (the Carnot limit) suggests the very widely-held apprehension that thermal radiation is heat," and at another point "(the Carnot limit) is in accord with elementary thermodynamics and confirms the widely-held identification of energy in radiant transfer with heat." Now, thermal radiation viewed as a photon gas does have energy and does have entropy. In addition, heat may accompany radiation emission and radiation absorption. But thermal radiation is not heat. The relationship between radiation and heat is readily explained (as we did in our paper and will repeat here) by the well-known "black particle in a cylinder with piston" experiment (see our Fig. 7). Let the particle receive an amount of heat Q_1 from a reservoir at T_1 and convert it into radiation isothermally. During this conversion the volume of the cylinder increases from zero to V_1 . It can be shown that the radiant energy contained in V_1 is now 0.75 Q_1 and the work done by the expanding radiation is 0.25 Q_1 . (The work done against the ambient radiation need not be considered since it will cancel out when the cylinder volume is later returned to zero). Now let us expand this radiation reversibly and adiabatically to $T_2 = 0.75 T_1$. It can be shown that the work done in this expansion just equals the work which would be required to compress the radiation isothermally back to zero volume converting the radiation into heat at T_2 . This heat is 0.75 Q_1 and the *net* work is just 0.25 Q_1 . Thus, in the overall process, heat is converted partially into work at the Carnot efficiency as it must. However, radiant energy at T_1 is converted into heat at 0.75 T_1 without the performance of work. Therefore, in this experiment, no work can be extracted from radiant energy unless the temperature of the source is more than four-thirds the temperature of the sink. Yet this is precisely the statement that Jeter says is false. If one were to confuse radiant energy with heat one would be led to this conclusion. For, if the words "radiant energy" in the statement above were replaced by the word "heat," the statement would clearly be wrong as the experiment demonstrates. A detailed analysis of this experiment (in the reverse or heat pump direction) is given in our paper.

A direct indication of this confusion (between radiation and heat) is shown in Jeter's equation (10). This equation governs the first step in the experiment described above; namely, the isothermal conversion of heat into radiant energy and work. The left-hand-side of this equation is clearly heat, but is called "quantity of radiation." In the development associated with this equation the amount of work which could be obtained from this "radiation" (really *heat*) is properly determined to be governed by the Carnot efficiency formula. But the work which could be obtained from the radiation which this heat produces is governed by Spanner's formula which we continue to maintain is the correct one.

Our next comment addresses Jeter's claim that Spanner only meant his result to be approximate. What Spanner actually does at the point in his writing to which Jeter refers, is calculate the difference between the work obtainable from radiation at T_s absorbed by a device at T_o and the work obtainable from the radiation at T_{o} emitted by this device. Subtracting the availability of the emitted radiation accounts for the third term in Jeter's equation (6). Spanner then points out that the third term is negligible (hence the approximation) when solar radiation is considered. Thus the two term equation (Spanner's formula) is exact if absorbed radiation only is considered, but is approximately true even if both absorbed and emitted radiation are considered. The development proceeds as follows, with B the available work, E_s the solar radiation absorbed, and E_0 the thermal radiation emitted.

$$B = E_{s} \left(1 - \frac{4}{3} - \frac{T_{o}}{T_{s}} \right) - E_{0} \left(1 - \frac{4}{3} - \frac{T_{o}}{T_{o}} \right)$$
$$= E_{s} \left(1 - \frac{4}{3} - \frac{T_{o}}{T_{s}} + \frac{1}{3} - \frac{E_{0}}{E_{s}} \right)$$

where the Spanner formula is used. But if the radiation at T_s and the device at T_o exchange radiation only with each other

$$\frac{E_0}{E_s} = \left(\frac{T_o}{T_s}\right)^4$$

Therefore $B = E_s \left(1 - \frac{4}{3} \frac{T_o}{T_s} + \frac{1}{3} \left(\frac{T_o}{T_s}\right)^4\right)$

As Spanner observes, the last term is negligible for solar radiation.

The last paragraph serves also as a response to the criticism of Spanner's work offered by De Vos and Pauwels in their discussion. They contend that Spanner considers only radiation absorbed by the device and not the radiation which the device emits. This is not true as we show above and, as we show further, if Spanner had not made the approximation indicated he would have arrived at the Petela result. However, it must be remembered that the Petela result yields the net exergy exchange only (as De Vos and Pauwels observe) if the sun "surrounds the absorber completely"; or, which amounts to the same thing, the radiator and absorber exchange radiation only with each other. Thus Spanner's work does not lead to the result they say it does and, therefore, their criticism that his approach leads to the prediction of negative efficiencies at low values of T_s is unfounded. De Vos and Pauwels go on to criticize the Petela equation on the basis that it represents an unapproachable upper bound rather than an approachable one. This is true if one allows (as they do) the device temperature to "float." Since in the problem we address this temperature is stipulated to be T_o , this criticism too is unfounded.

Their fourth efficiency is irrelevant to this discussion since it refers to a different problem; namely, the conversion efficiency possible with a system which consists of a collector at Twhich absorbs the radiation from a source at T_s , emits radiation at T, and supplies heat to a Carnot engine operating between T and T_o . For this situation (which is not our situation) their efficiency is correct.

Finally, we would like to observe that neither of these discussions are really discussions of our work. In both of them the authors reject Spanner's work (which they manage to misinterpret) and then go on to present their own theory without any reference to our analyis of the problem. The problem we address can be stated simply. Given a batch of radiation delivered by the sun to the earth, how much work can it do? In answering this question we accept the following principles. (1) Radiation can be viewed as a photon gas. (2) A photon gas has momentum (hence can exert pressure), energy, and entropy. (3) The fact that radiation has these properties permits the use of well established availability (or exergy) analyses to determine the maximum possible work it can do. (4) In applying exergy analysis it must be acknowledged that photons do not interact (hence there is no flow work) and are annihilated upon absorption. If these principles are accepted our results follow automatically and happen to agree with those obtained by Spanner, but not those obtained by the other authors cited who attempted to solve the same problem. We welcome criticism of our work which challenges one or more of these principles, which if wrong should be corrected.