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Thermodynamics of the conversion of diluted radiation

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Abstract. The photon density in diluted black-body radiation is $\epsilon (0<\epsilon<1)$ times that for the black-body radiation at temperature T from which it originated. If σ is Stefan's constant and B is a geometrical factor, it is shown that the energy and entropy flux due to such radiation is

$$\Phi = B\epsilon\sigma T^4/\pi \qquad \Psi = \tfrac{4}{3}B\epsilon X(\epsilon)\sigma T^3/\pi \qquad (X(1)=1)$$

where $X(\epsilon)$ is a function calculated here for the first time. A special type of steady-state non-equilibrium situation is defined, and called *effective equilibrium*, for which the *effective temperatures* $T/X(\epsilon)\equiv T^*$ of the various components of a system are equal. In this state the system cannot yield work. The maximum efficiency η_0 of such systems is investigated.

The application to solar radiation (diffuse and direct) proves possible and involves the function

$$\lambda(x) = 1-\tfrac{4}{3}x+\tfrac{1}{3}x^4.$$

In order to allow for diffuse and direct radiation the calculation is somewhat more complicated than previous ones. It shows that, for a black absorber, $\eta_0 \sim 0{\cdot}7$ (diffuse) rises to $0{\cdot}93$ as the radiation becomes more direct. However, for a grey absorber the efficiency might range typically from 60% to 83% for absorptivity $\alpha = 0{\cdot}9$. For one pump p and a black absorber at ambient temperature T,

$$\eta_0 = \lambda(T/T_p^*).$$

1. Introduction

The thermodynamically permitted efficiencies of solar energy conversion, although too high to be attained in realistic applications, are nevertheless of interest. They are estimated in this paper for conversion into work of direct and of diffuse radiation, and of a combination of the two. The latter possibility means (more abstractly) that the process is driven by two 'pumps'. It is not much more difficult to set up balance equations for n pumps, and to allow in addition the transfer of heat from the system of interest to a sink. It has proved convenient to introduce the new concept of an *effective temperature* (equation (2.13)). Its equality for the sink and for all the pumps is taken to define in part what is here called *effective equilibrium*, a condition which implies that no work can be extracted from the system.

The present paper develops further the results of the authors cited in the references (other than Bateman).

2. Entropy and energy of diluted black-body radiation

Diluted unpolarised black-body radiation is defined by the photon number $n(\epsilon, \nu, T)$ per unit volume per unit frequency range

$$n(\epsilon, \nu, T) = 8\pi\nu^2\epsilon c^{-3}(\exp(h\nu/KT)-1)^{-1} \qquad (0<\epsilon\leqslant 1) \tag{2.1}$$

where ϵ is a 'dilution factor' (independent of frequency) of the radiation, and T is the 'undiluted' temperature. The appropriate spectral radiance, i.e. the spectral radiant power emitted from a surface per unit area of that surface per unit solid angle, is

$$K(\epsilon, \nu, T) = ch\nu n(\epsilon, \nu, T)/4\pi. \tag{2.2}$$

The spectral entropy density, which corresponds to the spectral energy density $h\nu n(\epsilon, \nu, T)$, is

$$s(\epsilon, \nu, T) = 8\pi\nu^2 k[(1+x)\ln(1+x) - x\ln x]/c^3. \tag{2.3}$$

Here

$$x \equiv x(\epsilon, \nu, T) \equiv c^2 K(\epsilon, \nu, T)/2h\nu^3 = \epsilon(\exp(h\nu/kT)-1)^{-1} \tag{2.4}$$

and is the number of photons per unit volume of space and per unit volume of wavevector space per unit frequency range. The spectral entropy power emitted from a surface per unit area per unit solid angle corresponds to (2.2) and is

$$L(\epsilon, \nu, T) = cs(\epsilon, \nu, T)/4\pi. \tag{2.5}$$

These results can be obtained from pages 294–7 of Landsberg (1961).

These formulae will be applied to an isotropic emitter which also absorbs radiation from a distant source. In both cases they have to be integrated over frequencies and over solid angles ω. The latter integration extends over a hemisphere for emission, and over the solid angle subtended by the source at the absorber for absorption. Thus the radiant power emitted from, or absorbed by, a surface per unit area is

$$\Phi(\epsilon, T) = \iint K(\epsilon, \nu, T)\cos\theta \,\mathrm{d}\nu\,\mathrm{d}\omega \equiv B\int K(\epsilon, \nu, T)\,\mathrm{d}\nu \tag{2.6}$$

where is the angle made by rays with the normal to the surface and

$$B = \int \cos\theta\,\mathrm{d}\omega.$$

Substituting from (2.2),

$$\Phi(\epsilon, T) = B\sigma\epsilon T^4/\pi \tag{2.7}$$

where σ is Stefan's constant. The normal black-body emission formula is obtained for emission over a hemisphere ($B=\pi$) and for $\epsilon = 1$. The analogous entropy power emitted or absorbed by a surface per unit area is

$$\Psi(\epsilon, T) = \iint L(\epsilon, \nu, T)\cos\theta\,\mathrm{d}\nu\,\mathrm{d}\omega = B\int L(\epsilon, \nu, T)\,\mathrm{d}\nu. \tag{2.8$'$}$$

Using (2.5), a more radical modification of the black-body result is found:

$$\Psi(\epsilon, T) = \tfrac{4}{3}B\sigma\epsilon X(\epsilon)T^3/\pi, \tag{2.8}$$

where, with $x = \epsilon(e^y - 1)^{-1}$

$$X(\epsilon) \equiv \tfrac{45}{4}\pi^{-4}\epsilon^{-1} \int_0^\infty y^2[(1+x)\ln(1+x) - x\ln x]\,\mathrm{d}y. \tag{2.9}$$

If $\epsilon = 1$, (2.9) represents an integration sometimes performed for black-body radiation to yield unity:

$$X(1) = 1. \tag{2.10}$$

The evaluation of the integral in (2.9) is given in appendix 2.

The energy $U(\epsilon, T, V)$ of diluted black-body radiation in a reflecting enclosure of volume V is from (2.1).

$$U(\epsilon, T, V) = V\int_0^\infty h\nu n(\epsilon, \nu, T)\,d\nu = 4\epsilon V\sigma T^4/c. \tag{2.11}$$

Similarly, by integrating (2.3) the entropy of diluted black-body radiation in this enclosure is

$$S(\epsilon, T, V) = \tfrac{16}{3}\epsilon X(\epsilon) V\sigma T^3/c. \tag{2.12}$$

An effective temperature T^* will now be introduced for diluted black-body radiation, and is defined by

$$\frac{1}{T^*} \equiv \left(\frac{\partial S(\epsilon, T, V)}{\partial U(\epsilon, T, V)}\right)_{\epsilon, V} = \frac{X(\epsilon)}{T}. \tag{2.13}$$

It is found (figure 1) that dilution lowers the effective temperature from $T^* = T$ at $\epsilon = 1$. The 'temperature' defined here does not refer to an equilibrium situation since the different spectral components of diluted black-body radiation have different (absolute) temperatures, except when $\epsilon = 1$, which corresponds to black-body (equilibrium)

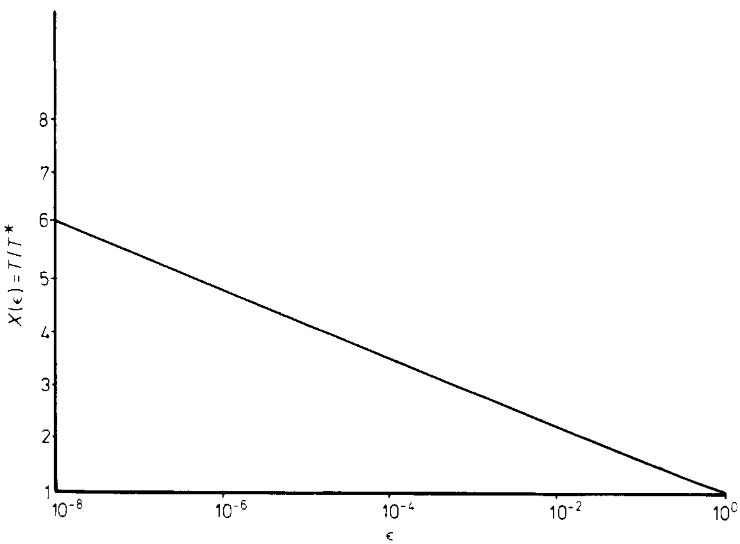

Figure 1. Increasing dilution (smaller ϵ) leads to a fall in the effective temperature T^*. Theoretical curve based on (2.13) and appendix 2.

radiation. From (2.7), (2.8) and (2.13)

$$\frac{1}{T^*}=\left(\frac{\partial\Psi(\epsilon, T)}{\partial\Phi(\epsilon, T)}\right)_\epsilon=\frac{X(\epsilon)}{T} \tag{2.14}$$

associates an effective temperature with the flux of diluted black-body radiation across a surface.

3. Balance equations for an absorber–emitter of diluted black-body radiation

The rates of change in the energy and entropy of the absorber (–emitter) are, with all quantities referred to unit area of its surface,

$$\dot{E}=\Phi_{pa}-\dot{Q}-\Phi_s-\dot{W} \tag{3.1}$$

$$\dot{S}=\Psi_{pa}-(\dot{Q}/T)-\Psi_s+\dot{S}_g. \tag{3.2}$$

Here Φ_{pa} and ψ_{pa} are rates of energy and entropy absorbed from the pumps, i.e. from the energy sources; $\dot{Q}$ is the rate of transfer of heat across the boundary (of the absorber) to the ambient, both of which are assumed to be at temperature T; Φ_s and ψ_s are the rates of energy and entropy emission by the absorber to a sink; $\dot{W}$ is the rate of mechanical, chemical or other work performed. Since the absorber has no moving parts, it is conceptually clearest to suppose that $\dot{W}$ is the rate at which energy is passed by the absorber to a separate 100% efficient mechanism which then converts this energy into the type of work considered. $\dot{S}_g$ is the rate of entropy generation in the absorber. The conduction of heat Q may be regarded as due to an infinitesimal temperature excess of the absorber surface above the ambient. Elimination of $\dot{Q}$ leads to

$$\dot{W}=\Phi_{pa}-T\Psi_{pa}-(\Phi_s-T\Psi_s)-T\dot{S}_g \tag{3.3}$$

when the absorber is in a steady state.

While this framework is rather general, we shall in this paper interpret Φ_s and Ψ_s as referring to diluted black-body radiation emitted to the ambient, which therefore acts as the sink. If there are n pumps p1, ..., pn, then

$$\Phi_{pa}=\Phi_{p1a}+\Phi_{p2a}+\ldots+\Phi_{pna}. \tag{3.4}$$

If the quantities distinguished by suffixes

$$j=p1, \ldots, pn; p1a, \ldots, pna; s \tag{3.5}$$

all refer to diluted black-body radiation, then effective temperatures (2.14)

$$\frac{1}{T_j^*}\equiv\left(\frac{\partial\Psi_j}{\partial\Phi_j}\right)_{\epsilon_j}, \tag{3.6}$$

can be introduced for them. The suffices p1, p2, etc (which will be required for the efficiency (6.9)) apply to the diluted black-body radiation of the pumps, while p1a, etc, refer to the characteristics of radiation p1, etc, in the absorber, if all other radiation is absent. In the steady state with the T_j^* independent of time the rate of energy emitted or absorbed per unit area is, by (2.7) and (2.13),

$$\Phi_j=B_j\sigma\epsilon_j(X(\epsilon_j))^4T_j^{*4}/\pi. \tag{3.7}$$

These results will now be generalised.

4. Balance equations in a more general context

We now consider a more general situation. Suppose that for each j in (3.5) there exists

(i) an effective temperature T_j^*;
(ii) a temperature-independent quantity β_j such that

$$\Phi_j = \beta_j T_j^{*4}; \tag{4.1}$$

(iii) a temperature-independent coefficient γ_j such that

$$\Phi_j = \gamma_j U_j \qquad \Psi_j = \gamma_j S_j. \tag{4.2}$$

These conditions hold for diluted black-body radiation by virtue of (2.13), (3.7), (2.7), (2.8), (2.11) and (2.12) with

$$\beta_j = B_j \sigma \epsilon_j (X(\epsilon_j))^4/\pi \tag{4.3}$$

and $\gamma_j = B_j c/4\pi V_j$.

A result analogous to (4.1) can be inferred for Ψ_j using (3.6), whence

$$\psi_j = \int \mathrm{d}\Phi_j/T_j^* = \tfrac{4}{3}\beta_j T_j^{*3} + f_j(\epsilon_j). \tag{4.4}$$

Here f_j is the 'constant' of integration. It will be assumed that $\Psi_j = 0$ when $T_j^* = 0$, whence $f_j = 0$.

Using (3.4), (4.1) and (4.4) in (3.3)

$$\dot{W} = \sum_{i=1}^{n} \beta_{\mathrm{p}i\mathrm{a}} T_{\mathrm{p}i\mathrm{a}}^{*4}[1 - (\tfrac{4}{3}T/T_{\mathrm{p}i\mathrm{a}}^*)] - \beta_{\mathrm{s}} T_s^{*4}[1 - (\tfrac{4}{3}T/T_s^*)] - T\dot{S}_{\mathrm{g}}, \tag{4.5}$$

an equation needed for efficiency calculations (see equation (6.9)).

5. Significance of the equality of effective temperatures

Although non-black-body radiations cannot be in equilibrium (e.g. § 2), one can get close to such a situation by considering the absorber to be in a steady state ($\dot{E} = \dot{S} = 0$) with

$$\dot{Q} = \dot{W} = \dot{S}_{\mathrm{g}} = 0. \tag{5.1}$$

One then has, by (3.1), (3.2) and (4.4),

$$\sum_{i=1}^{n} \beta_{\mathrm{p}i\mathrm{a}} \mathrm{T}_{\mathrm{p}i\mathrm{a}}^{*4} = \beta_{\mathrm{s}} T_{\mathrm{s}}^{*4} \tag{5.2}$$

$$\sum_{i=1}^{n} \beta_{\mathrm{p}i\mathrm{a}} T_{\mathrm{p}i\mathrm{a}}^{*3} = \beta_{\mathrm{s}} T_{\mathrm{s}}^{*3}. \tag{5.3}$$

For one pump ($n = 1$) this approximation to equilibrium therefore has the property

$$T_{\mathrm{p1a}}^* = T_{\mathrm{s}}^*. \tag{5.4}$$

We shall call the situation specified by

$$\dot{E} = \dot{S} = 0 \qquad T_{\mathrm{p1a}}^* = \ldots = T_{\mathrm{p}n\mathrm{a}}^* = \mathrm{T}_{\mathrm{s}}^* \qquad \dot{Q} = 0 \qquad \dot{S}_{\mathrm{g}} = 0 \tag{5.5}$$

effective equilibrium. For this case (5.3) yields

$$\sum_{i=1}^{n} \beta_{\mathrm{p}i\mathrm{a}} = \beta_{\mathrm{s}}, \tag{5.6}$$

whence (5.2) implies via (3.1) that $\dot{W} = 0$: in effective equilibrium the system cannot perform work. As the β's are temperature-independent, the result (5.6) also holds away from effective equilibrium.

For different degrees of dilution $\epsilon_j (j = \mathrm{p}i\mathrm{a}, \ldots, \mathrm{p}n\mathrm{a}; \mathrm{s})$ of the various types of radiation the pump and sink transfer rates in (3.1) and (3.2) will not in general balance:

$$\sum_{i=1}^{n} \Phi_{\mathrm{p}i\mathrm{a}} \neq \Phi_{\mathrm{s}} \qquad \sum_{i=1}^{n} \Psi_{\mathrm{p}i\mathrm{a}} \neq \Psi_{\mathrm{s}}. \tag{5.7}$$

Such a balance can, however, be established by allowing the absolute temperatures to reach different values appropriate to the ϵ_j, higher temperatures being required for the greater dilution (smaller ϵ's). One such scheme is to allow the *effective* temperatures to be the same. It is then easily seen using (5.6) that equalities hold in (5.7). Effective equilibrium is always possible in principle by ensuring that the remaining relations (5.5) are satisfied in addition.

6. Application to solar radiation

The results of the previous sections will now be applied to the direct conversion of solar radiation into work. A model using three pumps will be used. Eliminating β_{p3a} by (5.6), the rate of working per unit area of the absorber surface is, by (4.5),

$$\begin{aligned}\dot{W} = \beta_{\mathrm{p1a}}\left\{T_{\mathrm{p1a}}^{*4}\left(1-\frac{4}{3}\frac{T}{T_{\mathrm{p1a}}^{*}}\right)-T_{\mathrm{p3a}}^{*4}\left(1-\frac{1}{3}\frac{T}{T_{\mathrm{p3a}}^{*}}\right)\right\}\\ +\beta_{\mathrm{p2a}}\left[T_{\mathrm{p2a}}^{*4}\left(1-\frac{4}{3}\frac{T}{T_{\mathrm{p2a}}^{*}}\right)-T_{\mathrm{p3a}}^{*4}\left(1-\frac{4}{3}\frac{T}{T_{\mathrm{p3a}}^{*}}\right)\right]\\ -\beta_{\mathrm{s}}\left[T_{\mathrm{s}}^{*4}\left(1-\frac{4}{3}\frac{T}{T_{\mathrm{s}}^{*}}\right)-T_{\mathrm{p3a}}^{*4}\left(1-\frac{4}{3}\frac{T}{T_{\mathrm{p3a}}^{*}}\right)\right]-T\dot{S}_{\mathrm{g}}.\end{aligned} \tag{6.1}$$

Each of the quantities in (6.1) will now be discussed for the solar radiation model. The sun will be assumed to emit black-body radiation of temperature $T_{\odot}$, to be directly over the absorber and to subtend a solid angle $\omega_0 = \pi \sin^2 \delta$ where δ is the half-angle of the cone with the sun as base and vertex at the earth's surface.

6.1. *The sink radiation*

The absorber is assumed to be a grey body with absorptivity α (independent of frequency) and with surface temperature T, emitting diluted black-body radiation into a solid angle 2π. The dilution factor is given by $\epsilon_{\mathrm{s}} = \alpha$ and hence (2.14) and (4.3) give

$$T_{\mathrm{s}}^{*} = T/X(\alpha) \qquad \Phi_{\mathrm{s}}/T_{\mathrm{s}}^{*4} \equiv \beta_{\mathrm{s}} = \sigma\alpha(X(\alpha))^{4}. \tag{6.2,3}$$

6.2. *The first pump*

This is the direct part of solar radiation, photon density n_{d}, say, incident on the absorber at the earth's surface. The photon density due to diffuse radiation when added to n_d yields the total photon density N_d at the absorber. The photon density of solar radiation just outside the atmosphere is still larger and will be denoted by $N_\odot$. This leads to a dilution factor t due to transmission through the atmosphere, and a dilution factor d which measures the fraction of direct photons at the absorber:

$$t \equiv N_d/N_\odot \qquad d = n_d/N_d \qquad (0 \leq d < 1).$$

As the radiation enters the absorber it suffers additional dilution by a factor α whence $\epsilon_{p1a} = \alpha t d$ and (2.14) and (4.3) give

$$T^*_{p1a} = T_\odot/X(\alpha t d) \qquad \beta_{p1a} = (\sin^2 \delta)\sigma\alpha t d(X(\alpha t d))^4. \tag{6.4,5}$$

6.3. *The second pump*

The second pump applies to the diffuse component of the solar radiation incident on the absorber with $\epsilon_{p2a} = \alpha t(1-d)(\omega_0/4\pi)$. The factor $\omega_0/4\pi$ accounts for dilution due to scattering from the small solid angle ω_0 into the full angle 4π during the conversion from direct to diffuse radiation. The factor $(1-d)$ is a measure of the proportion of the incident radiation which is diffuse (i.e. which is not direct). The relevant solid angle of absorption is 2π, and (2.14) and (4.3) give

$$T^*_{p2a} = \frac{T_\odot}{X[\alpha t(1-d)\omega_0/4\pi]} \tag{6.6}$$

$$\beta_{p2a} = \sigma\alpha t(1-d)\omega_0(X[\alpha t(1-d)\omega_0/4\pi])^4/4\pi. \tag{6.7}$$

6.4. *The third pump*

The third pump applies to radiation, not necessarily diluted black body, from the ambient which is assumed to be such that the constraints of § 4 are met and that there is effective equilibrium between the sink radiation and the ambient radiation after absorption:

$$T^*_{p3a} = T^*_s = T/X(\alpha). \tag{6.8}$$

In other words, it is assumed that no work can be obtained by absorption of the ambient radiation alone.

By inserting (6.3), (6.5) and (6.7) into (5.6) one finds

$$\beta_{p3a} = \sigma\alpha(X(\alpha))^4 - (\sin^2 \delta)\sigma\alpha t d(X(\alpha t d))^4 - \sigma\alpha t(1-d)\omega_0(X[\alpha t(1-d)\omega_0/4\pi])^4/4\pi.$$

It depends on absorptivity α because β_{p3a} refers to ambient radiation *after absorption*; the dependence on t and d occurs since the ambient radiation falling on the absorber should clearly depend on the amounts of direct and diffuse sunlight present. That the ambient radiation after absorption is not of diluted black-body form is clear by noting that β_{p3a} is not of the form (6.3).

We now define an efficiency η for the conversion of solar power incident on the absorber into rate of working:

$$\eta = \frac{\dot{W}}{\Phi_{p1} + \Phi_{p2}} = \alpha\left(\frac{\dot{W}}{\Phi_{p1a} + \Phi_{p2a}}\right). \tag{6.9}$$

Using (6.8) in (6.1) this becomes, noting $\dot{S}_g \geq 0$,

$$\eta/\alpha \leq 1 - \tfrac{4}{3}T\left(\frac{\beta_{p1a}T^{*3}_{p1a} + \beta_{p2a}T^{*3}_{p2a}}{\beta_{p1a}T^{*4}_{p1a} + \beta_{p2a}T^{*4}_{p2a}}\right) - \frac{(\beta_{p1a}+\beta_{p2a})T_s^{*2}}{\beta_{p1a}T^{*4}_{p1a} + \beta_{p2a}T^{*4}_{p2a}}[1-(\tfrac{4}{3}T/T_s^*)] \equiv \eta_0/\alpha \tag{6.10}$$

which is plotted using (6.2)–(6.7) in figures 2 and 3 with $T_\odot = 5760$ K, $T = 300$ K and $\delta = 4{\cdot}65 \times 10^{-3}$ rad.

7. Discussion

Figure 2 shows the expected increase in efficiency η_0 as the radiation in the absorber becomes less diluted (as αt approaches unity). For fixed α and t, η_0 is expected to increase with d (the proportion of sunlight which is direct), and this is shown in figure 3. In practice, α and t will take values which are quite near unity. For example, some black laquers are now available with absorptivities in the region 0·96–0·98, and absorptivities of materials around 0·90 are common. Although atmospheric absorption is frequency dependent, a frequency-independent factor t is a fair approximation and is in any case required in so far as attention is confined to diluted black-body radiation. For a clear day t is typically 0·65, and it is of order 0·2 for a cloudy day. These numbers are obtained from figure 2 of Landsberg and Mallison (1976). Using these values for t, and $\alpha = 0{\cdot}9$, η_0 as given by figure 2 gives 60.2% for diffuse sunlight and 82·8% for direct sunlight.

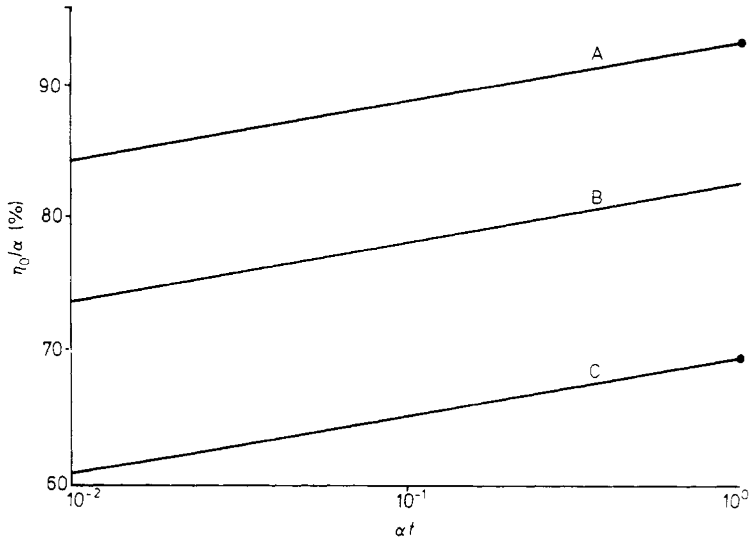

Figure 2. The maximum conversion efficiency η_0, given by (6.10), is plotted as η_0/α as a function of αt, assuming $T_\odot = 5760$ K, $T = 300$ K, $\delta = 4{\cdot}65 \times 10^{-3}$ rad. α is the absorptivity of the absorber and t is the atmospheric transmission coefficient. d is the fraction of the incident photon density residing in direct radiation. A, $d = 1$ (direct sunlight); B, $d = 0{\cdot}3$; C, $d = 0$ (diffuse sunlight).

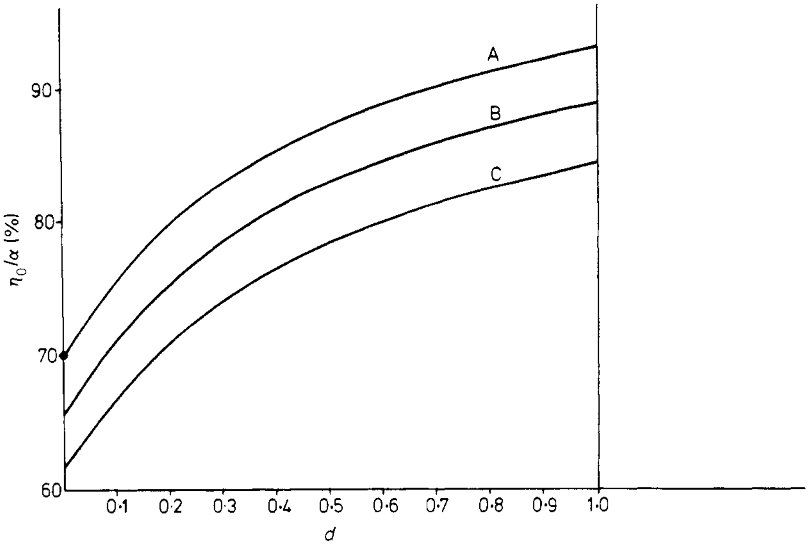

Figure 3. Similar to figure 2, but η_0/α is shown as a function of d. A, $\alpha t = 1$; B, $\alpha t = 10^{-1}$; C, $\alpha t = 10^{-2}$.

The curves for $d = 0$ and $d = 1$ in figure 2 result from (6.10) when one of the pumps, either pump 1 (direct sunlight) or pump 2 (diffuse sunlight), is absent:

$$\eta_{0k}/\alpha = \lambda(T/T^*_{\text{pka}}) - (T^*_{\text{s}}/T^*_{\text{pka}})^4 \lambda(T/T^*_{\text{s}}) \approx \lambda(T/T^*_{\text{pka}}) \tag{7.1}$$

where $k = 1$ or 2 and $\lambda(x) \equiv 1 - \frac{4}{3}x + \frac{1}{3}x^4$. The approximate result is valid for $\alpha t > 10^{-4}$, and hence for all practical situations. If the absorber is black ($\alpha = 1$) and also $t = 1$ then by (6.4) and (6.6), (7.1) gives for direct and diffuse radiation respectively

$$\eta_{01} = \lambda(T/T_\odot) \tag{7.2}$$

$$\eta_{02} = \lambda(X(\omega_0/4\pi)T/T_\odot). \tag{7.3}$$

(7.2) was first given by Landsberg and Mallison (1976); the proof was given by Landsberg (1977). Press (1976) obtained η_{01} and an approximation to η_{02} (he did not explicitly give the third term in the efficiency (7.3)). An approach to (7.2) from 'availability' considerations is given in appendix 1.

A further application of the results is to the conversion of radiation into plant free energy in photosynthesis, which is an equivalent form of energy to that described here as 'work'. One matter made quantitative by figure 2 is that decreasing light intensity (corresponding to decreasing t) reduces the free-energy conversion efficiency, a point made by Duysens (1958) and confirmed by Spanner (1963).

A distinction between maximal efficiencies in terms of the λ function, involving an effective temperature $T^*_\odot = T_\odot/X(\epsilon)$, and a Carnot-type efficiency $\eta_{\text{C}} = 1 - T/\tau$, involving another type of temperature, will become clearer if one notices that for a black absorber the latter is obtainable from (3.3) as

$$\eta = W/\Phi_{\text{p}} = 1 - (T\Psi_{\text{p}}/\Phi_{\text{p}}) \tag{7.4}$$

provided

$$\Phi_{\text{s}} = \Psi_{\text{s}} = 0 \text{ (no sink)} \qquad \tau = \Phi_p/\Psi_p. \tag{7.5}$$

Just as T^* can be the absolute temperature (if $\epsilon = 1$), so τ can be the absolute temperature (in the normal Carnot cycle). In particular, consider the example of a pump consisting of a near-monochromatic beam of frequency ν. Its (absolute) temperature T_ν may be defined by the Planck formula (say (2.1), with $\epsilon = 1$), and (7.4) and (7.5) yield $\eta = 1 - T/\tau$ with

$$\tau^{-1} = \tau_1^{-1} \equiv T_\nu^{-1} - k(e^{h\nu/kT_\nu} - 1)\ln(1 - e^{-h\eta\nu/kT_\nu})/h\nu, \tag{7.6}$$

which for the case of low brightness ($kT_\nu \ll h\nu$) simplifies to

$$\tau_1 \approx T_\nu. \tag{7.7}$$

Thus, in the limiting condition, τ can be the monochromatic (absolute) temperature T_ν of a beam.

An alternative route to T_ν occurs if a temperature

$$\tau_2 \equiv \dot{\Phi}_p/\dot{\Psi}_p = dU/dS \tag{7.8}$$

(in terms of time derivatives) is required. For a monochromatic beam this yields $\tau_2 = T_\nu$. A proof is possible via (2.1) to (2.6) and (2.8′), with $\epsilon = 1$, $T = T_\nu$, and the integrals restricted to a very narrow frequency width, provided $\dot{x} \neq 0$. This argument therefore requires, via (2.4), T_ν to be a function of time.

In previous work (7.6) has been used in a Carnot efficiency by Bell (1964; his T_e) and Leontovich (1975). On the other hand, T_ν has been used by Knox (1977; his T_R) in a Carnot efficiency, when τ_1 would have been strictly correct. None the less, this use of T_ν is justifiable in the sense of (7.7) since for red light (~680 nm) and $T_\nu \sim 1350$ K, $h\nu/kT_\nu \sim 16$. Its justification in the sense of (7.8) would not be satisfactory since his T_R is a steady-state temperature. In the approximation $1 - \frac{4}{3}(T_{cold}/T_{hot})$ to the λ function one should strictly use T^* (equation (2.13)), which refers to a spectrum of radiation, rather than T_ν (cf Spanner 1963). A fuller discussion of previous work will be given shortly.

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Appendix 1. Conversion efficiency from the 'availability'

When considering a black absorber the quantity η_0 as obtained in (7.2) is no longer a property of the absorber but of the radiation and ambient temperature alone. The absorber here performs a *reversible* conversion process. In general, the maximum possible useful work obtainable from a reversible process on a system at temperature T_1 in the presence of an infinite environment of temperature T_0 is called the 'availability' or 'exergy' of the system in that environment. This quantity is (Haywood 1974) $A_1 - A_0$, where

$$A \equiv U - T_0 S + p_0 V.$$

Here U_1, S and V are the internal energy, entropy and volume respectively of the system, p_0 is the environmental pressure and the suffices '1' and '0' refer to the system in its initial state and in its dead state (i.e. equilibrium with the environment) respectively. We can obtain (7.2) by applying this notion to black-body radiation occupying a volume V at temperature T_1. The availability of the radiation is

$$A_1 - A_0 = V\{aT_1^4 - \tfrac{4}{3}aT_1^3T_0 + \tfrac{1}{3}aT_0^4\}$$

where $a \equiv 4\sigma/c$ is a radiation constant. The ratio of the availability of the radiation to its initial internal energy is then $1 - \frac{4}{3}(T_0/T_1) + \frac{1}{3}(T_0/T_1)^4 \equiv \lambda(T_0/T_1)$. The expression also holds for a steady-flow (cyclic) conversion process (§ 3) in which case we have $\eta = \lambda(T_0/T_1)$ as the conversion efficiency of the rate of input of internal energy into the rate of useful work output (cf (7.2)). Press (1976) used this argument implicitly to find the maximum conversion efficiency of solar radiation into work, and Petela (1964) obtained (7.2) by an exergy argument in the context of heat transfer. Petela also outlines a method to calculate the exergy of arbitrary radiation, which is similar to that which is followed in §§ 2 and 3, although his results for diluted radiation are in error due to failure to include the factor $X(\epsilon)$ in the entropy flux equation (his equation (7)).

Appendix 2. An integral

The integral

$$I \equiv \int_0^\infty y^2[(1+x)\ln(1+x) - x\ln x]\,dy$$

with $x \equiv \epsilon/(e^y - 1)$ has the solution

$$I = (2+6\epsilon)\xi(4) - 2\left((1-\epsilon)\Phi(1-\epsilon, 4, 1) - \epsilon\sum_{n=1}^{\infty}\frac{(1-\epsilon)^n}{n^3}\Phi(1-\epsilon, 1, n)\right) \tag{A.1}$$

where (Bateman 1953)

$$\Phi(z, s, \nu) \equiv \sum_{n=0}^{\infty} z^n/(\nu+n)^s \tag{A.2}$$

and

$$\xi(k) = \sum_{n=1}^{\infty} n^{-k} \tag{A.3}$$

is the zeta function of Riemann. For small ϵ $(0<\epsilon<0{\cdot}1)$ (A.1) simplifies to

$$I \approx \epsilon\left(6\xi(4) + 2\xi(3) - \sum_{n=1}^{\infty} n^{-1}\xi(3, n+1)\right) + 2\xi(3)\epsilon\ln(\epsilon^{-1}) + \epsilon^2(\xi(2) - \xi(3)) \tag{A.4}$$

where

$$\xi(k, \nu) = \sum_{n=0}^{\infty}(n+\nu)^{-k} \tag{A.5}$$

is the generalised zeta function. Using tabulated values of the zeta function, (A.4) leads via (2.9) to

$$X(\epsilon) \approx 0{\cdot}9652 + 0{\cdot}2777\ln(\epsilon^{-1}) + 0{\cdot}0511\epsilon \tag{A.6}$$

for $0<\epsilon<0{\cdot}1$. Press (1976) obtained the first two terms in (A.6) by solving I numerically, but did not have the general result (A.1).

For $\epsilon = 1$, (A.1) simplifies to

$$I = 8\xi(4) = \tfrac{4}{45}\pi^4, \tag{A.7}$$

the result for black-body radiation.

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