Radiation and the Irreversible Thermodynamics of Climate

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(Manuscript received 27 June 1983, in final form 9 April 1984)

ABSTRACT

Attempts to link the theory of irreversible thermodynamics to the study of climate have utilized an entity which has been identified as the entropy production rate. However, this entity does not properly account for irreversibility due to the interaction of the radiation field with matter; that is, changes in the entropy of the radiation field, which cannot in general be properly described by the thermodynamic relations, are not accounted for. Calculations show that the entity used in these attempts deviates substantially from the correct rate of entropy production, both in terms of magnitude and sensitivity.

1. Introduction

A number of authors have ventured to discuss climatology in terms of the thermodynamics of irreversible processes. Paltridge (1975) was the first to do so by speculatively connecting the steady state minimization of a climate model parameter with Prigogine's (1967) minimum entropy production theorem. Even though Paltridge (1978, 1979, 1981) later withdrew somewhat from that particular position, the irreversible thermodynamics viewpoint and its terminology remained topical; in particular, the rate of entropy production, the central parameter of irreversible thermodynamics, was subsequently discussed in connection with the work of other authors writing on the subject of climate. Inspired by the successful efforts of North (1975a,b) at explaining the simple one-dimensional Budyko–Sellers type climate models in terms of the differential equation for heat diffusion, Golitsyn and Mokov (1978) recast that climate "diffusion" into the classic forms of irreversible thermodynamics. Nicolis and Nicolis (1980) elaborated on the thermodynamic viewpoint by introducing more modern ideas from irreversible thermodynamics, including a borrowing from stability theory, the Liapunov function. Similarly to Paltridge's later papers, Grassl (1980) also discussed a climatological extremum principle for dissipation.

The second law of thermodynamics gives the entropy production rate its physical significance, requiring it to take on only positive values. However, the second law imposes no such requirement upon selected components of the overall rate, unless those selected components nearly approximate the whole of the entropy production. Thus the theory of irreversible thermodynamics can and does ignore the entropy production contribution of the radiation field, since the effects of radiation can nearly always be ignored in the thermodynamics laboratory (Wildt, 1972; Essex, 1984a,b).

Such an omission should not be expected to be valid for the case of the climate engine which is driven by radiation and which produces it as its principal by-product. Nevertheless, the results of the theory of irreversible thermodynamics are adopted, without modification, in all of the above climate papers. The incoming and outgoing radiation field, in those papers, amounts to little more than a source and sink for heat energy. The entropy lost by matter, due to heat loss resulting from the emission of radiation, is wrongly regarded as an entropy flux carried by the radiation field. While such an interpretation for that heat loss entropy change has merit in the energy exchange between elements of matter, each in local equilibrium, it is not correct for radiative heat loss to space.

To take full account of the effects of radiation on the entropy production rate, the entropy of the radiation field must be considered. But the nonequilibrium radiation entropy, which we seek, cannot be derived simply from the equilibrium radiation entropy relation alone. Moreover, the equilibrium entropy density relation itself is not a manifestation of the differential relations of thermodynamics; neither can it be derived directly from them *alone*, any more than any other equation of state (e.g., the perfect gas law) can be derived from them alone. Thermodynamics holds no remedy for the problem of nonequilibrium radiation; however, an appeal directly to nonequilibrium statistical mechanics can be made for its solution.

This paper first introduces the notion of the specific intensity of entropy radiation. Then the general expression for the entropy intensity, as deduced from the principles of nonequilibrium statistical mechanics,

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is used, together with the differential relations of thermodynamics and general balance equations, to deduce a general entropy production rate that takes into account the fact that the radiation field has entropy. This rate contains the usual bilinear terms of irreversible thermodynamics as well as unusual terms due to radiation, which disappear when radiation is not important. It is seen from this rate that the thermodynamic climate models have been using an entropy production rate that is incorrect, in principle, for the climate engine.

After a discussion of some of the reasoning behind the thermodynamic climate models, a comparison is made between two entropy production rates, one determined with and the other without the entropy of the radiation field accounted for. Specifically, the global entropy production rate without radiation entropy for a simple one-dimensional-style model, as used in the thermodynamic climate papers, is compared to the global entropy production rate for that model when radiation entropy is considered. It is demonstrated, by means of the inequalities generated in that comparison, that the entropy of the radiation field is not insignificant for the climate engine. That is, the usual entropy production rate, prescribed by irreversible thermodynamics, is not even to be regarded as an acceptable approximation to the true rate for the climate engine, since it does not agree with the correct rate in its magnitude or with its sensitivity to climate change.

2. Radiation and irreversible thermodynamics

The notion of entropy radiation was first conceived of by Wien, but Planck was the first to write general nonequilibrium expressions for it (Ore, 1955). A straightforward and simple derivation using the more modern techniques of photon statistics was done much later by Rosen (1954). The specific intensity of entropy radiation, J_ν, is a function of the specific intensity of energy radiation, I_ν:

$$J_\nu = -\frac{2k\nu^2}{c^2}\left[\frac{c^2I_\nu}{2h\nu^3}\ln\frac{c^2I_\nu}{2h\nu^3} - \left(1+\frac{c^2I_\nu}{2h\nu^3}\right)\ln\left(1+\frac{c^2I_\nu}{2h\nu^3}\right)\right], \quad (1)$$

where ν is frequency, c is the speed of light, k is Boltzmann's constant, and h is Planck's constant.

When I_ν equals the Planck function B_ν, then

$$L_\nu \equiv J_\nu(B_\nu) \quad (2)$$

represents the specific intensity of entropy radiation for heat radiation. The integral of L_ν over all frequencies can be inferred (Planck, 1913), or it can be performed directly (Essex, 1984a):

$$L = \int_0^\infty L_\nu d\nu = \frac{4}{3}\frac{\sigma}{\pi}T^3, \quad (3)$$

where T is the temperature of the radiation field, and σ is Stefan's constant.

The radiation entropy flux is derived from its associated specific intensity in the same manner by which radiation energy flux is derived, by the same weighted integral over solid angle (e.g., Planck, 1913; Rosen, 1954; Essex, 1984a,b). Thus, in general, the vector net flux of entropy radiation is written

$$\mathbf{H} = \int J_\nu(\hat{m}, \mathbf{r})\cos\theta d\Omega d\nu\hat{n}, \quad (4)$$

where $\hat{n}$ is a unit normal to the element of surface through which the radiation is passing, θ is the angle between $\hat{m}$ and $\hat{n}$, $d\Omega$ is an element of solid angle, $\hat{m}$ is a unit direction vector, and $\mathbf{r}$ is the position vector. Consequently, the flux from a black surface of temperature T is

$$H = \frac{4}{3}\sigma T^3. \quad (5)$$

It is a trivial matter to deduce the equilibrium relation between the radiation entropy density and energy density; integrating (3) over all solid angles and dividing by the speed of light clearly leads to the relation

$$s_r = \frac{4}{3}\frac{u}{T}, \quad (6)$$

where s_r is the radiation entropy density and u is the radiation energy density.

Historically, radiation has often been dealt with by means of the thermodynamic relations. Equation (6) is classically inferred in equilibrium thermodynamics texts with the use of the thermodynamical differential relations; however, that inference requires the additional equilibrium relationship between radiation pressure and density to be taken as given. It is a trivial matter to deduce (6) from the radiation pressure relation and the appropriate intensity integrals, without any reference to the differential thermodynamic relations. Equation (6) and the radiation pressure relation are not a consequence of the thermodynamic relations; they are merely consistent with them. They are two equivalent representations of the equation of state for equilibrium radiation. Furthermore, Eq. (5) cannot be deduced from Eq. (6) without using the intensity integrals, which can be used to deduce it and Eq. (6) without any involvement of the thermodynamic relations. The general relations, Eqs. (4) and (1), are not conceivable from the standpoint of the differential relations of thermodynamics; but it is these equations, and not Eqs. (5) and (3), which must figure into any precise accounting of the entropy of radiation in the atmosphere.

The thermodynamic flux of entropy between elements of matter in differing local states is quite different in nature from the elemental entropy flux described by Eq. (4). The thermodynamic flux is a consequence of the exchange of extensive thermodynamic entities, such as heat and molecular population, between those local thermodynamic systems in differing states. In such systems in local equilibrium the change of local matter entropy is determined by the Gibbs equation

$$ds = \sum_i a_i dA_i, \tag{7}$$

where s is the local entropy density of the matter, dA_i is the change in the ith extensive parameter, and a_i is the conjugate intensive parameter (e.g., chemical potential or pressure) divided by the local temperature. From equation (7) we can infer the accepted relationship between the entropy flux $\mathbf{Y}_s$ and the flux of the ith extensive parameter, $\mathbf{Y}_i$ (e.g., Callen, 1960):

$$\mathbf{Y}_s = \sum_i a_i \mathbf{Y}_i. \tag{8}$$

Clearly, for the entropy flux through some surface, Eq. (8) is incomplete since it does not include the radiation entropy flux [Eq. (4)]. In the presence of entropy radiation the entropy flux must obviously be corrected to read

$$\mathbf{Y}_s = \sum_i a_i \mathbf{Y}_i + \mathbf{H}. \tag{9}$$

In general, for entropy one may write the balance equation

$$\sigma(\mathbf{r}) = \frac{\partial \rho_s}{\partial t} + \nabla \cdot \mathbf{Y}_s, \tag{10}$$

where $\sigma(\mathbf{r})$ is the local rate of creation for entropy, or the entropy production rate, and ρ_s is the total entropy density, which is the sum of the matter and radiation field entropy densities. Equation (10) becomes, after using Eq. (9),

$$\sigma(\mathbf{r}) = \frac{\partial s_r}{\partial t} + \frac{\partial s}{\partial t} + \nabla \cdot (\sum_i a_i \mathbf{Y}_i) + \nabla \cdot \mathbf{H}. \tag{11a}$$

With the use of balance equations for the remaining extensive thermodynamic parameters A_i, the complete local entropy production becomes

$$\sigma(\mathbf{r}) = \frac{\partial s_r}{\partial t} + \sum_i a_i \epsilon_i + \sum_i \nabla a_i \cdot \mathbf{Y}_i + \nabla \cdot \mathbf{H}. \tag{11b}$$

The ϵ_i are the creation rates for the ith extensive parameter. Equations (11) represent the most general form of the instantaneous local entropy production rate. In the special situation of the thermodynamic climate models, only heat is normally considered to be created or lost in the matter, due to radiation. Therefore, if $\mathbf{F}$ is the net flux of energy radiation,

$$\sum_i a_i \epsilon_i = -\frac{1}{T}\left(\nabla \cdot \mathbf{F} + \frac{\partial u}{\partial t}\right), \tag{12}$$

hence from (11b),

$$\sigma(\mathbf{r}) = \frac{\partial s_r}{\partial t} - \frac{1}{T}\frac{\partial u}{\partial t} - \frac{1}{T}\nabla \cdot \mathbf{F} + \nabla \cdot \mathbf{H} + \sum_i \nabla a_i \cdot \mathbf{Y}_i. \tag{13}$$

The theory of irreversible thermodynamics is at present entirely concerned with the term that remains of (13) in the absence of radiation; that is,

$$\sigma(\mathbf{r}) = \sum_i \nabla a_i \cdot \mathbf{Y}_i, \tag{14}$$

where the $\mathbf{Y}_i$ are called thermodynamic fluxes, and the ∇a_i are called thermodynamic forces (or affinities). The entropy production rate (14) is said to be "bilinear" in those parameters; however, no such simple symmetry exists for Eq. (13) (Essex, 1984a). In any case, Eq. (14) is the equation used in the thermodynamic climate papers.

The historical cause of the emphasis on the simple symmetry of the entropy production rate, Eq. (14), in nonequilibrium thermodynamics was the existence of certain empirical relationships between fluxes and forces. Those relationships cause (14) to have an elementary quadratic form. The oldest (Truesdell, 1980) and perhaps most familiar example of such a relationship, or phenomenological equation as such equations are widely called, is the relationship between the energy flux and the temperature gradient,

$$\mathbb{Y}_E = -K\nabla T, \tag{15}$$

where K is, in irreversible thermodynamics, the phenomenological coefficient (e.g., De Groot and Mazur, 1962). Equation (15) normally represents, of course, Fourier heat diffusion. The domain where the fluxes can be represented by such linear functions of the forces is called the linear domain.

The careful reader will have noticed that ∇a_i for internal energy is not $-\nabla T$, but $\nabla(1/T)$. However, from (15),

$$\mathbb{Y}_E = KT^2 \nabla \frac{1}{T}, \tag{16}$$

which means that $\mathbb{Y}_E$ is a function of temperature in addition to the thermodynamic force, assuming K is a constant. This point in thermodynamics texts is either ignored or blandly dismissed by suggestions that the early heat experiments, from which (15) was inferred, considered only a small range of temperatures (e.g., Callen, 1960; De Groot and Mazur; 1962; Prigogine, 1967). Both Tykodi (1967) and Truesdell (1969) have been critical of that dismissal. Nicolis and Nicolis (1980) took care to consider a full menu of different dependencies for their phenomenological coefficient, no doubt partly because of this issue.

3. Irreversible thermodynamics in climate models

The thermodynamic viewpoint was first introduced to climate research by Paltridge (1975). Paltridge constructed an elementary one-dimensional model of the earth's oceans and atmosphere for which he suggested that the poleward flow of *all* energy could be governed by the temperature gradient as in Eq. (15). He conjectured that an extremum parameter existed which would be a minimum in the steady solution state of the model. The parameter which he found empirically to be minimized, he speculatively connected to the entropy production rate, and he speculatively connected its minimization in the steady state to Prigogine's (1967) minimum entropy production theorem.

Clearly, the real poleward energy fluxes could not be due to diffusive transport of heat; however, the empirical coefficient was conceived as something which was adjusted to account for the turbulent transport of energy. That coefficient could be adjusted to yield values of the flux which are in line with the real values of the poleward flux. Such an approach to transport processes is well known; it falls under the heading of eddy diffusion (e.g. North, 1975a; Chamberlain, 1978).

It is an assumption to introduce an empirical relation for the energy transport. It is another assumption to suggest that the thermodynamic force conjugate to the real energy transport is given by $-\nabla T$ or $\nabla(1/T)$, as is the case for diffusive heat transport. It should not be expected that the product of the real poleward flux of energy and such a force will yield the real local entropy production due to all kinds of poleward transport; that is, not without an additional empirical adjustment. The true force conjugate to the total poleward flux, if the local entropy production rate is to be forced into a single term, must also take into account the turbulent transport, in addition to all of the other processes that are blended together into the single energy flux. Without that additional adjustment, the model of the earth's atmosphere becomes identical to the heat diffusion in a metal bar, but with an unusual conductivity and a local entropy production rate which is inaccurate even in terms of Eq. (14).

The additional assumption about the thermodynamic force is not addressed in any of the climate literature concerned with thermodynamic climate models, but this assumption is universally made, tacitly or not. However, if the same can be done for the functional form of the force as was done for the flux, i.e., a further correction factor is introduced, then the entropy production may retain a simple heat diffusion form, causing the above admonition to be less serious. In any case, one would expect intuitively that the entropy production rate due to an ordered flow is less than the rate for a diffusive flow of the same magnitude. Consequently, the entropy production rate in the climate literature should at least be an upper bound to the rate indicated by (14).

As long as climate is to be considered equivalent to Fourier heat diffusion in a metal bar, the analysis of climate becomes a simple matter for the thermodynamicist. Nicolis and Nicolis (1980), one of whom is a thermodynamicist, noted the familiar form the equations had taken. They proceeded to solve for Fourier heat diffusion in a "metal bar" representative of the climate engine. They, of course, could not help finding that standard thermodynamic principles applied to climate. Golitsyn and Mokov (1978) did a similar analysis. Both papers took inspiration from the success of North (1975a,b), who showed that the quasi-empirical one-dimensional horizontal models of climate (e.g., Sellers, 1973) are special cases of the solutions of the differential equations for heat diffusion.

Paltridge (1978) had realized that the linear regime could not adequately model climate. Consequently, he withdrew from explanations using Prigogine's (1967) minimum entropy production theorem, which is only valid in the linear regime. Paltridge wrote two papers (1979, 1981) concerning a maximum dissipation principle. Supported by the work of certain fluid dynamicists, the conjectured principle suggests, that the ocean–atmosphere system selects from a number of steady state modes the largest minimum value of the entropy production rate. Grassl (1980) discussed a similar principle.

4. The radiation field and thermodynamic climate models

The thermodynamic climate models inherited Eq. (14) from irreversible thermodynamics. Radiation, it was believed, only carries away the entropy produced by and put into the climate engine, while Eq. (14) was believed to be the actual amount of entropy produced by the dissipation in the climate engine. By means of Eq. (13) we see that this cannot be correct in principle. However, the question still remains as to how well Eq. (14) approximates Eq. (13) for the case of global climate. This section demonstrates, in terms of simple models like those used in thermodynamic climate papers, that Eq. (14) cannot be regarded even as an approximation to Eq. (13) for the case of global climate; that is, the entropy of the radiation field cannot be ignored.

If (13) is integrated over a steady state ocean–atmosphere system, all terms, except the second to last, vanish after applying Gauss' law. This is best seen in Eq. (11a) where the time derivatives are zero in the steady state, and the normal components of all matter fluxes must vanish at the boundary of the atmosphere, assuming no mass loss or accretion. Thus the total entropy production rate of the planet is

$$R = \int_{\Sigma} \mathbf{H} \cdot d\mathbf{a}, \tag{17}$$

where $d\mathbf{a}$ is an element of area with an outward normal on the surface Σ which bounds the top of the atmosphere. Equation (17) indicates that the entire entropy production of a steady state climate is contained in the difference of the entropy of the outgoing terrestrial radiation from the entropy of the incoming solar radiation. It follows that any subsystem of the oceans and atmosphere could behave similarly when in the steady state. All of the entropy production could take place in the radiation field with no net evolution in the matter. Consider, for example, a bounded convection cell with air steadily expanding and rising in one part, and steadily sinking and contracting in other parts. If we can suppose ideally that there is no transport other than radiation across a fixed boundary, then the irreversibility of the convection must be expressed entirely by the radiation field.

In general, the value of R in Eq. (17) depends explicitly in a nonlocal fashion on all of the local states of a system through Eq. (4); however, its magnitude, for the case of the earth, can be simply estimated by writing it in terms of the effective temperatures of the earth and sun. Thus, after using Eq. (5), the global entropy production rate becomes

$$R = \pi r^2\left(-\frac{4}{3}\sigma T_0^3 \sin^2\theta_0 + \frac{4}{3}\sigma T_e^3 4\right), \quad (18)$$

where T_0 is the effective solar temperature, $2\theta_0$ is the angle subtended by the sun at the earth, r is the radius of the earth, and T_e is the effective temperature of the earth. The effective temperatures of the earth and sun are respectively about 250 and 5500 K. With these values the global entropy production rate is

$$R = 6 \times 10^{14}\ \mathrm{W\ K^{-1}}. \quad (19)$$

On the other hand, from Eq. (14), the global entropy production rate, as determined in thermodynamic climate models, R', would be given by

$$R' = \int_V \mathbf{Y} \cdot \nabla \frac{1}{T} dV, \quad (20)$$

where V is the volume containing the oceans and atmosphere. If the energy flux $\mathbf{Y}$ is assumed to be in the poleward direction only, then

$$R' = \int_0^\pi E(\theta) \frac{\partial}{\partial\theta}\frac{1}{T} \sin\theta d\theta, \quad (21)$$

where T is assumed to be independent of longitude, and θ represents the colatitude. Also,

$$E(\theta) \equiv \int Y_\theta r dr d\phi, \quad (22)$$

where the integration is carried out over all r and ϕ, represents the total poleward net transport of energy. An upper bound for R' is easily estimated:

$$R' < \int_0^\pi E(\theta)\frac{\partial}{\partial\theta}\frac{1}{T} d\theta < 2E_{\max}\left[\frac{1}{T_P} - \frac{1}{T_E}\right], \quad (23)$$

where the last step comes from assuming that the earth is symmetric about the equator. Here, T_P is the characteristic polar temperature and T_E is the characteristic equatorial temperature.

Using data from Sellers' (1973) model for polar and equatorial temperatures (T_E = 298 K, T_P = 253 K), and his compilation of observations and calculations of the function $E(\theta)$ ($E_{\max} = 4 \times 10^{22}$ cal y^{-1}), the upper bound of R' can be calculated as

$$R' < 6 \times 10^{12}\ \mathrm{W\ K^{-1}}. \quad (24)$$

Consequently,

$$R/R' > 10^2. \quad (25)$$

Since the left-hand side of (25) represents the ratio of the planetary entropy production rate with radiation considered, to the rate without radiation considered, it is clear that not accounting for the thermodynamic properties of the radiation field is a serious oversight in the calculation of the magnitude of the global entropy production rate.

The relative steady state magnitudes of the functions is not the only consideration in the comparison of the two functions. The relative sensitivities of the two functions to perturbations in the steady state climate also should be considered. Using the Fourier heat flux (15), in accordance with the climate literature, in (22) gives for the total poleward flux,

$$E(\theta) = \Gamma(T)\frac{\partial}{\partial\theta}\frac{1}{T}, \quad (26)$$

where

$$\Gamma(T) \equiv T^2 \int K dr d\phi. \quad (27)$$

Equation (26) used in (20) yields

$$R' = \int_0^\pi \Gamma(T)\left(\frac{\partial}{\partial\theta}\frac{1}{T}\right)^2 \sin\theta d\theta. \quad (28)$$

Then

$$\delta R' = \int_0^\pi \left\{\frac{1}{\Gamma}\frac{\partial\Gamma}{\partial T} E \frac{\partial}{\partial\theta}\frac{1}{T}\sin\theta\delta T + \frac{2}{T^2}\frac{\partial}{\partial\theta}(E\sin\theta)\delta T\right\} d\theta, \quad (29)$$

where the second term was integrated by parts, and the fact that the poleward transport vanishes at the poles was used. Note that the first term is a result of the temperature dependence of the phenomenological coefficient. The inequality

$$|\delta R'| \leq \int_0^\pi \left|\frac{2}{T}E\frac{\partial}{\partial\theta}\frac{1}{T}\right| |\delta T \sin\theta| d\theta + 2\int_0^\pi \left|\frac{\partial}{\partial\mu}[E(1-\mu^2)^{1/2}]\frac{1}{T^2}\right| |\delta T \sin\theta| d\theta, \quad (30)$$

where μ is defined as the cosine of the colatitude, arises from (29) and (27), and the fact that the magnitude of a sum is bounded by the sum of the magnitudes. The functions, other than the temperature perturbation, can be replaced by their maximum values to achieve a larger upper bound:

$$|\delta R'| < \left\{\int_0^\pi 2|\delta T \sin\theta| d\theta\right\}\left\{\left|\frac{1}{T^3} E \frac{\partial T}{\partial \theta}\right|_{\max} + \left|\frac{\partial}{\partial \mu}[E(1-\mu^2)^{1/2}]\frac{1}{T^2}\right|_{\max}\right\}. \quad (31)$$

If T_ϵ is the effective emission temperature of radiation emitted from the atmosphere at a particular colatitude, then

$$R = \frac{8}{3}\pi r^2 \sigma \int_0^\pi T_\epsilon^3 \sin\theta d\theta - \frac{4}{3}\sigma T_0^3 \sin^2\theta_0 \pi r^2. \quad (32)$$

For small perturbations between steady or quasi-steady states,

$$|\delta R| = 8\pi r^2 \sigma \gamma \int_0^\pi T_\epsilon^2 |\sin\theta \delta T| d\theta, \quad (33)$$

where for simplicity a perturbation has been selected such that $\delta T = \delta T_\epsilon$, and

$$\gamma \equiv \left|\int_0^\pi T_\epsilon^2 \sin\theta \delta T d\theta\right| \left[\int_0^\pi |T_\epsilon^2 \sin\theta \delta T| d\theta\right]^{-1}. \quad (34)$$

By excluding specialized or pathological functions from the set of arbitrary but small perturbations, δT, we may write the average,

$$T_e^2 = \int_0^\pi T_\epsilon^2 |\sin\theta \delta T| d\theta \left[\int_0^\pi |\sin\theta \delta T| d\theta\right]^{-1}. \quad (35)$$

Therefore,

$$|\delta R| = 8\pi r^2 \sigma T_e^2 \int_0^\pi |\sin\theta \delta T| d\theta. \quad (36)$$

The second factor of (31) is further maximized by replacing T by its least value T_P. Therefore, using (36) in (31) yields

$$\frac{|\delta R|}{|\delta R'|} > \left\{\frac{4\pi r^2 \sigma T_P^4}{\left(\frac{1}{T_P}|E|_{\max} \cdot \left|\frac{\partial T}{\partial \theta}\right|_{\max} + \left|\frac{\partial}{\partial \mu}[E(1-\mu^2)^{1/2}]\right|_{\max}\right)}\right\} \beta^2 \gamma, \quad (37)$$

where $\beta \equiv T_e/T_P$. Again, from Sellers' (1973) model and tabulations

$$T_P = 253 \text{ K}, \quad \left|\frac{\partial T}{\partial \theta}\right|_{\max} = 2 \text{ K deg}^{-1},$$

$$|E|_{\max} = 5.3 \times 10^{15} \text{ J s}^{-1}, \quad \left|\frac{\partial}{\partial \mu}[E(1-\mu^2)^{1/2}]\right|_{\max} = 1.3 \times 10^{16} \text{ J s}^{-1}.$$

These values, when placed into the denominator of (37), show the temperature dependence term to be nearly insignificant. This supports the lack of concern over the difference between $-\nabla T$ and $\nabla(1/T)$ discussed in the second section. The value of β^2 for the data used here is about 0.98. Thus, after substitution

$$|\delta R|/|\delta R'| > 8\gamma. \quad (38)$$

For any climate perturbation in this context where there is universal warming or cooling in the oceans and atmosphere (i.e., δT does not change sign),

$$\gamma = 1, \quad (39)$$

where γ is defined by (34). Thus the complete entropy production rate which considers radiation entropy is at least eight times more sensitive to perturbations than the more restricted rate used in climate models, given by (20), for a most fundamental mode of climatic change.

The only possibility for the two sensitivities to have the same magnitude is for the limited class of perturbation functions where $\gamma = 1/8$. In that narrow domain the negative contributions to the numerator in (34) nearly cancel the positive contributions, with the contributions from neither sign exceeding the other by more or less than ~30%.

The inequalities (38) and (25) demonstrate that the radiation terms in the entropy production rate cannot be ignored for the case of the oceans and atmosphere.

5. Conclusion

Global entropy production can be expressed in two physically distinct parts: Production in the matter, and production in the radiation field. Production in the radiation field can be described simply as the result of a conversion of 5500 K solar radiation converging in cones with vertices at the earth subtending ~0.5°, to 250 K radiation emitted in all directions. This production represents a general change in the nature of the radiation field, but does not require any change whatever in the local states of the matter which explicitly determine the change in the field. Indeed, because of the existence of the radiation entropy production, it is not necessary for changes in climate state to correspond to a net positive change in the local entropies of matter in order to preserve the second law of thermodynamics. In other words, there is no physical reason to reject changes in climate state that correspond to a net zero or negative change in the total value of the local entropies of the oceanic and atmospheric matter, as long as the overall entropy production rate remains positive. The sun exemplifies such a situation: It can be regarded as a quasi-steady system where the fusion reactions in the core lead to a slow overall negative change in the entropy of the matter which is more than compensated for by the positive overall production in the radiation field (Essex, 1984a).

The qualitative success in the modeling of climate by some of the thermodynamic climate models discussed does not contradict the position that radiation plays an important part in the global entropy production. Those model results neither prove that the extremized parameter is the global entropy production rate, nor do they prove the applicability of Prigogine's (1967) theorem or related entropy production principles to the climate engine. Neither is it true that the extremization of physical model parameters other than the entropy production must provide poor climatological results: Lin (1982) successfully modeled the climate in a one-dimensional climate model by maximizing the available potential energy, an application of the general maximum efficiency principle of Lorenz (1955). Extremum principles applying to the physics of the climate engine are far from inconceivable; but neither are spurious nonphysical extremum principles, which yield good qualitative agreement between climate models and the real atmosphere.

In retrospect, it is not so surprising that radiation should play such an important role in global entropy production. Such a position is not only theoretically justified but also is intuitively reasonable. It has been shown in Sections 2 and 3 that the extremized parameter in the thermodynamic climate models is at best an approximate upper bound to the last term in Eq. (13). In Section 4 it was further demonstrated that this parameter cannot be regarded even as an approximation to the overall entropy production rate. The extremum principle discussed in the thermodynamic climate papers could have a physical basis, but it will not be found to be equivalent simply to the extremization of the entropy production rate.

These results do not suggest that a thermodynamic approach to the understanding of climate is unsound. However, they do show, because of the importance of entropy radiation, that the climate engine is an anomalous nonequilibrium system to which the current theory of nonequilibrium thermodynamics cannot be correctly applied without modification. Thus, future studies of climate in this context have the potential to break new ground in the theory of nonequilibrium systems, let alone in climatology itself.

Thermodynamic results that take radiation into account, but are outside the scope of the current theory of irreversible thermodynamics, already exist. A minimum principle for the complete entropy production rate, including the contribution of radiation, exists. However, it is not deduced from Prigogine's (1967) theorem but from the work of Planck (1913) who conceived of such a principle long before the advent of contemporary irreversible thermodynamics. From the logical generalization of an example from Planck's work it is easily proven that the effective blackbody temperature of a planet corresponds to a state of minimum entropy production (Essex, 1984a). It can also be shown, after further development, that the state of radiative equilibrium in a gray atmosphere corresponds to a minimum entropy production rate (Essex, 1984b).

Acknowledgments. I am grateful to Dr. P. E. Merilees, Professor J. C. McConnell and Dr. N. Sargent for their remarks and advice.

REFERENCES

Callen, H. B., 1960: *Thermodynamics.* Wiley, 376 pp.
Chamberlain, J. W., 1978: *Theory of Planetary Atmospheres.* Academic Press, 330 pp.
De Groot, S. R., and P. Mazur, 1962: *Non-Equilibrium Thermodynamics.* North-Holland, 510 pp.
Essex, C., 1984a: Radiation and the violation of bilinearity in the thermodynamics of irreversible processes. *Planet. Space Sci.* (in press).
——, 1984b: Minimum entropy production in the steady state and radiative transfer. *Astrophys. J.* (in press).
Golitsyn, G. S., I. I. Mokov, 1978: Stability and extremal properties of climate models. *Izv. Acad. Sci. USSR, Atmos. Ocean. Phys.*, **14**, 271–277.
Grassl, H., 1980: The climate at a maximum entropy production by meridional atmospheric and oceanic heat fluxes. *Quart. J. Roy. Meteor. Soc.*, **107**, 153–166.
Lin, C. A., 1982: An extremal principle for a one-dimensional climate model. *Geophys. Res. Lett.*, **9**, 716–718.
Lorenz, E. N., 1955: Available potential energy and the maintenance of the general circulation. *Tellus*, **7**, 157–167.
Nicolis, G., and Nicolis, C., 1980: On the entropy of the earth-atmosphere system. *Quart. J. Roy. Meteor. Soc.*, **106**, 691–706.
North, G. R., 1975a: Analytical solution to a simple climate model with diffusive heat transfer. *J. Atmos. Sci.*, **32**, 1301–1307.
——, 1975b: Theory of energy-balance climate models. *J. Atmos. Sci.*, **32**, 2033–2043.
Ore, A., 1955: Entropy of radiation. *Phys. Rev.*, **98**, 887–888.
Paltridge, G., 1975: Global dynamics and climate—A system of minimum entropy exchange. *Quart. J. Roy. Meteor. Soc.*, **101**, 475–484.
——, 1978: The steady-state format for climate. *Quart. J. Roy. Meteor. Soc.*, **104**, 927–945.
——, 1979: Climate and thermodynamic systems of maximum dissipation. *Nature*, **279**, 630–631.
——, 1981a: Thermodynamic dissipation and the global climate system. *Quart. J. Roy. Meteor. Soc.*, **107**, 531–547.
Planck, M., 1913: *Heat Radiation.* Translation of 2nd ed. republished 1959, Dover, 224 pp.
Prigogine, I., 1967: *Thermodynamics of Irreversible Processes.* 3rd ed., Wiley, 147 pp.
Rosen, P., 1954: Entropy of radiation. *Phys. Rev.*, **96**, 555.
Sellers, W. D., 1973: A new global climate model. *J. Appl. Meteor.*, **12**, 241–254.
Truesdell, C., 1969: *Rational Thermodynamics.* McGraw-Hill, 208 pp.
——, 1980: *The Tragicomical History of Thermodynamics 1822–1854.* Springer-Verlag, 372 pp.
Tykodi, R., 1967: *Thermodynamics of Steady States.* Macmillan, 217 pp.
Wildt, R., 1972: Thermodynamics of the gray atmosphere IV. *Astrophys. J.*, **174**, 69–77.