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The Exergy of Thermal Radiation and its Relevance in Solar Energy Conversion

by

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B.Eng. (honours) McGill, 1996
M. A. Sc., Victoria, 1998

A Thesis Submitted in Partial Fulfillment of the
Requirements for the Degree Of

DOCTOR OF PHILOSOPHY

in the Department of
Mechanical Engineering

We accept this thesis as conforming
to the required standard

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ABSTRACT

Driven by the importance of optimizing energy systems and technologies, the field of exergy analysis was developed to better illuminate process inefficiencies and evaluate performance. Exergy analysis provides important information and understanding that cannot be obtained from energy analysis. The field of exergy analysis is well formulated and understood except for thermal radiation (TR) heat transfer. The exergy flux, or maximum work obtainable, from TR has not been unambiguously determined. Moreover, many thermodynamic textbooks are misleading by incorrectly implying that the entropy and exergy transport with TR is calculated by using the same expressions that apply to heat conduction.

Research on the exergy of TR was carried out by Petela. However, many researchers have considered Petela's analysis of the exergy of TR to be irrelevant to the conversion of TR fluxes. Petela's thermodynamic approach is considered irrelevant because, others argue, that it neglects fundamental issues that are specific to the conversion of fluxes, issues that are unusual in the context of exergy analysis. The purpose of the research in this thesis is to determine, using fundamental thermodynamic principles, the exergy flux of TR with an arbitrary spectrum and its relevance to solar radiation (SR) conversion.

In this thesis it is shown that Petela's result can be used for the exergy flux of blackbody radiation (BR) and represents the upper limit to the conversion of SR approximated as BR. The thesis shows this by resolving a number of fundamental issues:

1) Inherent Irreversibility
2) Definition of the Environment
3) Inherent Emission
4) Threshold Behaviour
5) Effect of Concentrating TR

This thesis also provides a new expression, based on inherent irreversibility, for the exergy flux of TR with an arbitrary spectrum. Previous analysis by Karlsson assumes that reversible conversion of non-blackbody radiation (NBR) is theoretically possible, whereas this thesis presents evidence that NBR conversion is inherently irreversible.

In addition the following conclusions and contributions are made in the thesis:

- Re-stated the general entropy and exergy balance equations for thermodynamic systems so that they correctly apply to TR heat transfer.
- Provided second-law efficiencies for common solar energy conversion processes such as single-cell Photovoltaics.
- Showed that Omnicolor (infinite cell) conversion, the widely held ideal conversion process for SR, is not ideal by explaining its non-ideal behaviour in terms of exergy destruction and exergy losses.
- Presented an ideal (reversible) infinite stage thermal conversion process for BR fluxes and presented two-stage thermal conversion as a practical alternative.
- Showed that Prigogine's minimum entropy production principle cannot be used as a governing principle in atmospheric modeling, and that in general, it may have little significance.
- Presented a graybody model of the planet that may prove useful in understanding the thermodynamics of the Earth system.
- Showed that the expression derived from the Clausius equality for reversible processes is applicable, whereas the statement for irreversible processes is not applicable, when there is significant heat transfer by TR.
- Showed that the 4/3 coefficient in the BR entropy expression can be obtained by simply using the concept of equilibrium and the experimentally observable relationship for BR energy (energy $\propto T^4$).

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Nomenclature

Table N-1: Thermal Radiation (TR) Energy, Entropy and Exergy

	Energy		Entropy		Exergy*	
	Symbol	Units	Symbol	Units	Symbol	Units
Internal	U	J	S	J/K	Ξ	J
Specific **	u	J/m^3	s	J/m^3K	ξ	J/m^3
Flow Rate	$\dot{E}$	W	$\dot{S}$	W/K	$\dot{\Xi}$	W
Irradiance or Flux	H	W/m^2	J	W/Km^2	M	W/m^2
Spectral Irradiance	H_ν	J/m^2	J_ν	J/Km^2	M_ν	J/m^2
Radiance	K	W/m^2sr	L	W/Km^2sr	N	W/m^2sr
Spectral Radiance	K_ν	J/m^2sr	L_ν	J/Km^2sr	N_ν	J/m^2sr
Dimensionless Spectral Radiance	y_ν	none	z_ν	none	not defined	——

* Ξ and ξ are the Greek letters corresponding to the English X and x, respectively. The symbols M and N were chosen following the pattern H,K and J,L for energy and entropy quantities.

** The specific energy and entropy for TR are per unit volume rather than per unit mass as they are for material related quantities, for example see Equ. (2.3).

a	Alternative symbol for the specific exergy of a material system (J/kg); the symbol ξ is used in this thesis
a	BR constant $=4\sigma/c=(7.61)10^{-16} J/m^3K^4$
a	Planetary albedo (no units)
A	Alternative symbol for the exergy of a material system (J); the symbol Ξ is used in this thesis
A	Surface area of collector (m^2)
B	Alternative symbol for exergy flux; the symbol $\dot{\Xi}$ is used in this thesis
c	Speed of light = $(2.9979)10^8$ m/s
C	Concentrating factor
$\dot{E}$	Energy flow rate (W)
h	Planck's constant = $(6.626)10^{-34}$ J s
H	Energy irradiance or flux (W/m^2)
H_ν	Spectral energy irradiance (J/m^2)
$I(\varepsilon)$	Function for GR entropy in Eq. (3.7)
$\dot{I}$	Rate of irreversibility (W)
J	Entropy irradiance or flux (W/Km^2)
J_ν	Spectral entropy irradiance (J/Km^2)
J_i	Generalized thermodynamic flux (i.e. J_M, J_{Th})
k	Boltzmann's constant = $(1.38)10^{-23}$ J/K
K	Energy radiance (W/m^2sr)
K_ν	Spectral energy radiance ($J/m^2 sr$)
L	Entropy radiance (W/Km^2sr)
L_ν	Spectral entropy radiance (J/Km^2sr)
L_{ij}	Phenomenological coefficients (i.e. L_{11}, L_{12}, L_{21}, L_{22})

m	Function for GR entropy in Eq. (3.9)
M	TR exergy irradiance (W/m^2)
M_ν	Spectral exergy irradiance (J/m^2)
$n(\varepsilon)$	Coefficient for GR entropy, Eq. (3.14)
N	TR exergy radiance (W/m^2sr)
N_ν	Spectral exergy radiance ($J/m^2\,sr$)
N_i	Mol number of species i in the environment
NPD	Percent difference in exergy radiance N, see Equ. (7.17)
p	State of polarization, p=1 for plane polarized, p=2 for unpolarized
P	Pressure (N/m^2)
q	Heat flux (W/m^2)
$q_{\nu\Omega}$	Integrand of Eq. (7.7)
dQ	Infinitesimal heat transfer (J)
$\dot{Q}$	Heat transfer rate (W)
r	Mean radius of planetary orbit (m)
R	Radius of the planet (m)
s	Specific entropy-per unit volume (J/m^3K)
S	Entropy of the system (J/K)
$\dot{S}$	Entropy flow rate (W/K)
$\dot{S}_{\nu\Omega}$	Integrand of Eq. (7.8)
T	Material emission temperature (K)
T_ν	Spectral temperature (K)
u	Specific internal energy-per unit volume (J/m^3)
U	Internal energy of the system (J)
V	Volume (m^3)

$\dot{W}$	Work transfer rate (W)
x	Temperature ratio T_o/T
x	Non-dimensional group, $h\nu/kT$
X_i	Generalized thermodynamic force (i.e. X_M, X_{Th})
$X(\varepsilon)$	Function for GR entropy in Eq. (3.7)
dY	Differential unit of area (Karlsson's notation, normally dA)
α	Unit step function in Eq. (4.35)
ε	Emissivity for gray radiation (GR)
φ, ϕ	Spherical Coordinates
η	Efficiency
μ	Quantum excitation energy
ν	Frequency (s^{-1})
$\nu, d\nu$	Frequency interval $d\nu$ about frequency ν
ν_o	Cutoff (threshold) frequency
π	Physical constant, 3.14159...
$\dot{\pi}$	Entropy production rate per unit volume (W/Km^3)
Π	Entropy production (J/K)
$\dot{\Pi}$	Entropy production rate (W/K)
θ	Temperature ratio T/T_o ($\theta = 1/x$)
σ	Stefan-Boltzmann constant = $(5.67)10^{-8}\ W/m^2K^4$
$\dot{\sigma}$	Entropy production rate per unit surface area
Ω	Solid angle (sr)
Ξ	Internal exergy of the system (J)
$\dot{\Xi}$	Exergy Flux (W), note that Karlsson [21] uses the symbol B

Note that two symbols, a and x, are conventionally used for different quantities so it is assumed that their symbolism will be determined from context.

SUBSCRIPTS/SUPERSCRIPTS

A	Stage A
Abs	Absorbed
B	Stage B
BR at T_o	Blackbody Radiation with emission temperature T_o
c	Conduction
C	Converter
Dest	Destruction
Emi	Emission
f	Final
fm	Fundamental minimum
i	Initial
Inc	Incident
m	Material system
N	Net

o	Environment
out	Outgoing
p	Petela
P	Planet
Q	Quantum system
Q+Th	Quantum/Thermal hybrid
r	Radiation
Ref	Reflected
RM	Radiation-matter
s	Source
S	Sun
Sf	Surface of the Sun
T	at temperature T
ν	Frequency

ABBREVIATIONS

BB	Blackbody
BR	Blackbody Radiation
CV	Control Volume
DBR	Diluted Blackbody Radiation
ERBE	National Aeronautics and Space Administration (NASA) Earth Radiation Budget Experiment
GR	Graybody Radiation
GS	Guoy-Stodola Theorem
HE	Heat Engine
NBR	Non-Blackbody Radiation
SCQ	Single-Cell Quantum Conversion
SR	Solar Radiation
SST	Single-Stage Thermal Conversion
TER	Thermal Energy Resevoir
TOA	Top of the Atmosphere
TR	Thermal Radiation
TST	Two-Stage Thermal Conversion

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Chapter 1 Introduction

1.1 Motivation

Engineering texts are often misleading because they state that heat transfer has three forms, conduction, convection, and radiative transfer, and proceed to evaluate the entropy and exergy flux in a way that does not apply to TR heat transfer. For example, see Moran and Shapiro's [1] text on the fundamentals of engineering thermodynamics. The entropy and exergy flux of heat conduction are given by the energy flux divided by the local temperature (q/T) and $q(1-T_o/T)$, respectively, where T_o is the environmental temperature. The entropy flux of BR is not given by the q/T relation and recently it was shown that the entropy flux of non-blackbody radiation (NBR) is even farther removed from q/T [2], see section 3.2. However, a general exergy flux expression for TR with an arbitrary spectrum has not been clearly determined. Also, a discordance exists between researchers who have used an exergy analysis approach and researchers who have investigated the upper limit to the conversion efficiency or maximum work output from solar radiation (SR) conversion.

Our motivation for considering the exergy flux of TR stems from the fact that exergy analysis is an effective and illuminating form of second law analysis that:

a) identifies entropy production or exergy destruction as the true indicator of non-ideal behaviour,
b) pinpoints components or sub-processes contributing most to the overall non-ideal behaviour of a system,
c) correctly evaluates the significance of emissions to the surroundings such as exhaust gases from a coal-fired power plant, and
d) provides second-law efficiencies that give a true evaluation of performance by comparing performance to ideal operation, in contrast to first-law energy efficiencies which are usually misleading.

Exergy analysis gives a much better indication than energy analysis of whether it is beneficial and cost effective to modify or re-design equipment. By determining and comparing the exergy destruction rate of individual components or sub-processes we are better able to focus our resources and efforts on improving performance.

Turning to the exergy of TR, all matter emits TR continuously as a result of its temperature so TR is an inherent part of our environment and it is an important energy transfer mechanism in the thermodynamic analysis of many systems in addition to solar conversion such as (1) industrial boilers and furnaces, (2) spacecraft cooling and solar power systems, (3) heating and lighting systems that act by means of radiation, (4) biochemical (photosynthesis) processes that occur in plants, (5) cryogenic devices, and (6) circulation of the atmosphere.

Petela carried out research to determine the exergy of blackbody radiation (BR). However, omnicolor conversion is considered by many researchers to be the ideal theoretical process for the conversion of solar radiation (SR) approximated as BR. For example, Haught [3] states regarding omnicolor conversion that the "results obtained are independent of the specific form of the thermal and quantum radiation conversion device and serve as an upper bound on the efficiency with which radiant energy can be converted to useful work in any actual device." In agreement with Haught, De Vos and Pauwels [4] also state that an infinite series of optimized omnicolor collectors is "the thermodynamically optimal device for converting solar energy into work."

Petela's [5] blackbody radiation (BR) exergy result is thought to neglect fundamental theoretical issues that are specific to the conversion of TR fluxes. For example, Haught [3] states that "Thermodynamic treatments of the radiation field which derive the conversion efficiency from the available work content of the radiant flux neglect the limitations (re-radiation, threshold absorption, etc.) inherent in the conversion process." Giving cause for this viewpoint, some thermodynamicists have stated that the issue of inherent irreversibilities and inherent emission (re-radiation) can be ignored in order to determine the maximum work obtainable from TR conversion.

The viewpoint that Petela's result is not relevant to solar energy conversion centers on three main questions that arise. First, exergy is a quantity that depends on the system and its environment, so how can an environment be defined for TR? Bejan [6] states that "there is no such thing as an "environment" of isotropic blackbody radiation (and pressure), as is assumed most visibly in the availability type derivation."

Second, how is it appropriate to assume that the conversion of BR fluxes can be reversible even though it appears that the conversion of TR fluxes is inherently irreversible? De Vos and Pauwels [4] state that "the conversion of radiation into work cannot be performed...without entropy creation." It is true that entropy is created by any conversion device in practice but this does not mean that the conversion process is irreversible even in the theoretical case as is implied.

Third, how does the inherent emission of TR affect the maximum work obtainable? Any device that absorbs TR for conversion must also emit TR. De Vos and Pauwels [7] state that the "power flow from the solar cell is rightly considered lost." Also Landsberg [8] comments on the effect of inherent emission when he notes that Petela's efficiency is "pulled down below the Carnot efficiency because of the black-body emission from the converter which does not contribute to the useful work output."

As mentioned above exergy analysis is an effective form of second-law analysis. Thus, it is important that these issues regarding TR exergy are resolved. This will allow second-law efficiencies to be determined for common solar energy conversion processes and provide insight that may lead to practical device improvements.

Note that the motivation for the research presented in chapter 9 (On the Entropy of Thermal Radiation in Engineering Thermodynamics) and chapter 10 (Planetary Entropy Production and its Relevance in Atmospheric Modeling) is discussed in sections 9.1 and 10.1, respectively.

1.2 Objectives and Scope

The difficulties that arise in determining the exergy of TR and its relevance in solar energy conversion may be summarized and addressed as follows:

1) Exergy is a quantity that depends on the system and its environment, so how is the environment defined for TR?
2) The conversion of TR appears to be inherently irreversible. Is this the case and if so how does it affect the maximum work obtainable from TR conversion?
3) Any device that absorbs TR must also emit TR. What is the effect of this inherent emission on TR exergy?
4) What is the relevance of TR exergy to solar energy conversion?

It is the objective of the present work to resolve these four main issues and to improve the effectiveness of exergy analysis of engineering systems when TR transfer is significant. This research can help us to better model, analyze, design, and optimize systems where TR transfer is important.

Furthermore, we have two more sets of objectives relating to atmospheric modeling and to the applicability of fundamental thermodynamic equations when TR is involved. Regarding the thermodynamics of the Earth system our purpose is to:

1) Determine the relevance of Prigogine's minimum entropy production principle as a governing principle in atmospheric modeling.
2) Present a graybody model of the planet to improve our thermodynamic understanding of the Earth system.
3) Examine the significance of Stephens and Obrien's conclusion that the Earth is near a state of maximum entropy production.

Regarding the entropy of thermal radiation in engineering thermodynamics our objectives are to:

1) Determine the applicability of the Clausius statements for reversible and irreversible processes when TR transfer is involved.
2) Present an alternative straightforward derivation of BR entropy in an attempt to find a physical reason for the 4/3 coefficient (see section 3.1).

Chapter 2 Principles of Exergy Analysis

2.1 Exergy and the Method of Exergy Analysis

Exergy[1] analysis is an effective and illuminating form of second law analysis. Exergy is defined as the maximum amount of work that can be produced by a stream of material or a system as it comes into equilibrium with its environment. Exergy may be loosely interpreted as a universal measure of the work potential or quality of different forms of energy in relation to a given environment. The first law states that energy is never 'used up' it is simply degraded or converted from one form to another. For example, a hot beverage will cool to the temperature of its environment, a balloon will burst if it's punctured, and a fuel will burn if it's ignited. Although energy is not destroyed, the exergy or potential for a system to do work is lost.

To illustrate the benefits of second law analysis consider the operation of a typical thermal power-plant. For example, a power plant may have roughly 1/5 of the energy of the incoming fuel leaving by the smoke stack, 2/5 rejected by waste heat, and 2/5 leaving as the desired work output usually in the form of electricity. The first-law perspective is that 3/5 of the incoming energy source is emitted or lost to the surroundings. However, second law analysis shows that even under ideal operation work cannot be obtained without sending a certain minimum amount of energy and products to the environment. The corresponding maximum ideal level of work output that can be obtained is the exergy of the fuel in a particular environment. In the example power-plant considered above 3/5 of the fuel energy may be directed to the environment but it is of relatively low quality and thus may only represent a small fraction of the exergy of the fuel, in the order of 1/10.

---

[1] Exergy is also known by the terms availability and essergy.

In addition to correctly evaluating and understanding the reasons for emissions to the surroundings, exergy analysis provides efficiencies that are true indicators of performance. Exergetic (second-law) efficiencies compare the *exergetic value* of the desired output to the ideal limit, the *exergy* of the energy source. First-law energy efficiencies are misleading for thermal or chemical processes because they compare the desired *energy* output to the *energy* input. For example, first-law efficiencies for heat engines compare the work output to a theoretically unachievable upper limit, the energy of the heat source.

Also, exergy analysis gives a true indication of whether it is beneficial and cost effective to modify or re-design the equipment. Exergy analysis identifies exergy destruction (entropy production) as the true indicator of non-ideal performance. Analysis of a multi-component system pinpoints the components contributing most to the overall irreversibility of the system. Also, the decision to utilize any exergy 'losses' with emissions from the system (such as 'waste' heat) or by-products of the process is based on their exergetic value.

2.2 The Environment and Surroundings

Moran [9, p. 45] describes the terms environment and surroundings as: "The surroundings compromise everything not included in the system. One part of the surroundings is some portion of the Earth and its atmosphere, the intensive properties of which do not change significantly as a result of any of the processes under consideration. It is to this that the term environment applies."

We must develop a model for the environment because the physical world is complicated and cannot be described in every detail. The characteristics of the environment model are:

- The environment is assumed to be large with respect to the system and to have homogeneous and time-invariant intensive properties. The changes in the extensive properties are so small relative to the size of the environment that the intensive properties remain unchanged.

- The environment experiences only internally reversible processes in which the sole work mode is associated with volume change (PdV).
- The environment experiences heat transfer at a uniform temperature T_o.

2.3 The Gouy-Stodola Principle

The Gouy-Stodola principle [10, p. 24] states that for any fixed environment the exergy destruction rate, termed the rate of irreversibility ($\dot{I}$), is directly proportional to the entropy production rate ($\dot{\Pi}$). The entropy production rate is an absolute quantity whereas the exergy destruction rate is a relative quantity that depends on the choice of reference heat reservoir, normally taken as the temperature of the environment T_o:

$$\dot{I} = T_o \, \dot{\Pi} \tag{2.1}$$

2.4 Closed System Exergy and the Exergy Transfer with Mass Flow

Exergy is a measure of the departure of a closed system from that of its environment. The exergy[2] (Ξ) of a system closed to mass flow is the theoretical maximum amount of work that can be produced as the system reaches the dead state (equilibrium with its environment)

$$\Xi = (U - U_o) + P_o(V - V_o) - T_o(S - S_o) \tag{2.2}$$

where U is internal energy, V is volume, S is entropy, P_o and T_o are the environment pressure and temperature, and U_o, V_o and S_o are the dead state properties of the system (see for example Bejan [11]). The system is in the dead state when mutual equilibrium is reached between the environment and the system, when the system has pressure P_o and temperature T_o. Note that in all

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[2] The Greek symbols Ξ and ξ correspond to the upper and lower case English letter *x* for *e*xergy. The symbols *A*, *B* and *a* are sometimes used in place of Ξ, $\dot{\Xi}$ and ξ and originate from the alternative name for exergy, *a*vailability.

the equations introduced in this section kinetic energy, gravitational potential energy, and chemical exergy have not been included. On a per mass basis equation (2.2) becomes

$$\xi = (u - u_o) + P_o(v - v_o) - T_o(s - s_o) \tag{2.3}$$

The rate of exergy transfer when mass flows across a system boundary is given by

$$\dot{\Xi} = \dot{m}\{(h - h_o) - T_o(s - s_o)\} \tag{2.4}$$

where h is the enthalpy ($h = u + Pv$).

2.5 The Exergy Flux of Heat Conduction and Convection

Consider heat transfer Q (heat conduction and convection) between a control mass and some other system where initially the control mass is at the dead state (equilibrium with its environment), and the process experienced by the control mass is internally reversible and constant volume. It can be shown that the exergy of the control mass in its final state is

$$\Xi = \int_o^f \left(1 - \frac{T_o}{T_s}\right) dQ \tag{2.5}$$

where T_o is the environmental temperature, o denotes the dead state, f denotes the final state, and dQ denotes an infinitesimal heat transfer at the boundary of the control mass where the temperature is T_s. Note that for this particular process the exergy of the system is strictly thermal exergy (no mechanical or chemical exergy). The integrand of equation (2.5) times dQ gives the exergy transfer with the heat transfer dQ. The exergy of heat transfer is the maximum work that can be obtained using the environment as a reservoir of zero-grade thermal energy. The Carnot heat engine (HE) provides a theoretical means of producing this maximum ideal work output (reversibly).

2.6 General Balance Equations for a Control Volume (CV)

The exergy balance equation for a system takes into account the exergy transfer rates across the system boundary by heat and work transfer, and the exergy destruction rate that occurs within the system due to irreversibilities:

$$\frac{d\Xi_{CV}}{dt} = \int_{CV\ boundary} q\left(1-\frac{T_o}{T_b}\right)dA - \left(\dot{W}_{CV} - P_o\frac{dV_{CV}}{dt}\right) + \sum_i \dot{\Xi}_i - \dot{I}_{CV} \tag{2.6}$$

where the subscript *CV* denotes control volume, the subscript *b* denotes the boundary of the CV, *q* is the heat flux across the system boundary where the temperature is T_b, and *dA* is a unit of area on the system boundary. The second last term accounts for exergy transfer with mass flow and is a summation term because multiple mass flows may cross the boundary of a system. Note that the subscript *i* is used to indicate mass flows into the system so any outgoing mass flows would have a negative sign.

The thermal-mechanical exergy balance equation is a simple combination

$$\frac{d\Xi_{CV}}{dt} = \frac{dE_{CV}}{dt} - T_o\frac{dS_{CV}}{dt} \tag{2.7}$$

of the energy

$$\frac{dE_{CV}}{dt} = \int_{CV\ boundary} q\ dA - \left(\dot{W}_{CV} - P_o\frac{dV_{CV}}{dt}\right) + \sum_i \dot{m}_i h_i \tag{2.8}$$

and the entropy balance equations

$$\frac{dS_{CV}}{dt} = \int_{CV\ boundary} \frac{q}{T_b}\ dA + \sum_i \dot{m}_i s_i + \dot{\Pi}_{CV} \tag{2.9}$$

2.7 Thermal Radiation (TR) and the Exergy Concept

TR is generated by the acceleration of electric charges in atoms or molecules of a material as a result of its temperature (thermal vibrations). TR can travel through a vacuum whereas heat conduction and convection are forms of energy transfer by direct material interaction and movement. TR does not interact with itself so one would expect that there is no flow work as with mass flows.

In trying to define the exergy radiance of TR one expects that the exergy depends on: (1) the energy and entropy carried by the radiation, (2) the polarization of the TR, and (3) the environmental character. However, the entropy of TR is completely determined by the energy spectrum so entropy may not be an independent parameter. Secondly, polarization is a geometric parameter so it does not play a role in determining a fundamental form of the expression for the exergy flux of TR (the polarization p is simply a coefficient in the entropy expression (3.2)). For simplicity, in this thesis it is assumed that the TR is unpolarized (p=2). Once the fundamental form of the exergy flux expression for TR is determined it may be altered to take into account polarization.

Chapter 3 Background on the Entropy of Thermal Radiation (TR)

3.1 Expressions for the Entropy of Thermal Radiation

The correct evaluation of the entropy flux of TR can be important when determining the second-law performance of energy conversion devices. Many thermodynamic texts incorrectly imply that the entropy flux of TR heat transfer has the same form as that of conductive heat transfer, that is the heat flux divided by the local temperature (q/T). Wright [2] has shown that misuse of the q/T relation for TR transfer from an energy conversion device can cause very significant errors and always causes the irreversibility of the device to be underestimated whether it is hot or cold relative to its surroundings.

The energy and entropy of unpolarized[1] TR is correctly calculated using the spectral energy and entropy expressions derived by Max Planck [12] using equilibrium statistical mechanics:

$$K_\upsilon = \frac{ph}{c^2}\frac{\upsilon^3}{e^{\frac{h\upsilon}{kT}}-1} \tag{3.1}$$

and

$$L_\upsilon = \frac{pk\upsilon^2}{c^2}\left\{\left(1+\frac{c^2K_\upsilon}{2h\upsilon^3}\right)\ln\left[1+\frac{c^2K_\upsilon}{2h\upsilon^3}\right]-\left(\frac{c^2K_\upsilon}{2h\upsilon^3}\right)\ln\left[\frac{c^2K_\upsilon}{2h\upsilon^3}\right]\right\} \tag{3.2}$$

where p=2 for unpolarized TR considered in this thesis. Equation (3.1) expresses the spectral energy radiance of BR, i.e., the energy flow rate per unit frequency, area, and solid angle. A plot of K_v versus frequency v for various values of temperature T gives a family of BR energy spectra. After substituting (3.1) into (3.2) we can obtain a family of BR entropy spectra.

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[1] Unpolarized is specified for simplicity, see section 2.5 for more information.

For an arbitrary TR, the entropy spectrum is found by substituting K_v data, rather than (3.1) for BR, into (3.2). The entropy radiance L of any TR spectrum can be calculated by integrating L_v over frequency. That is, the entropy radiance L is the area under the L_v spectrum.

Landsberg and Tonge [13] used a non-equilibrium statistical mechanics approach to obtain the same result as Planck. They concluded[2] "This result, usually obtained from equilibrium statistical mechanics, is therefore of wider significance and represents a non-equilibrium entropy."

The energy spectrum of TR emitted from a solid depends on the nature of the emitting material and its temperature. Some materials can be adequately approximated as blackbody (BB) or graybody while others may have a unique spectra that cannot be adequately modeled as either BB or gray body.

For BR, equations (3.1) and (3.2) can be integrated over frequency and solid angle to obtain the energy and entropy irradiances (fluxes):

$$H_{BR} = \pi K_{BR} = \sigma T^4 \qquad J_{BR} = \pi L_{BR} = \tfrac{4}{3}\sigma T^3 \tag{3.3}$$

Irradiances (H and J) are the integration of the radiances (K and L) over solid angle and have units of energy or entropy flow rate per unit area. To compare the entropy flux of BR emission to that of heat conduction we can express the entropy irradiance as

$$J_{BR} = \frac{4}{3}\frac{H_{BR}}{T} \tag{3.4}$$

Note that TR transfer is generally a net transfer between incident, reflected, and emitted TR but in (3.4) we are considering TR emission alone.

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[2] Two assumptions were specified for this result to be exact: (1) the probability of finding N_j bosons in quantum state j is independent of the occupation numbers of the other quantum states, and (2) the probability of an additional particle occupying a state j is independent of the number already in that state.

By definition the spectral energy irradiance for isotropic gray radiation (GR) emission is

$$H_{GR} = \pi K_{GR} = \varepsilon \sigma T^4 \tag{3.5}$$

However, the entropy is not as easily calculated because the spectral entropy is not a linear function of the spectral energy. For GR the entropy irradiance is

$$J_{GR} = \pi L_{GR} = \frac{2\pi k^4}{c^2 h^3} T^3 \int_0^\infty x^2 \left\{ \left(1 + \frac{\varepsilon}{e^x - 1}\right) \ln\left(1 + \frac{\varepsilon}{e^x - 1}\right) - \left(\frac{\varepsilon}{e^x - 1}\right) \ln\left(\frac{\varepsilon}{e^x - 1}\right) \right\} dx \tag{3.6}$$

where $x = h\nu/kT$. The entropy of GR (3.6) is a simple cubic function of the material emission temperature. This is also true of any TR emission that has an energy spectrum with a fixed shape independent of emission temperature [2]. The definite integral in (3.6) is a function of ε only and is called $I(\varepsilon)$ here, but was first recognized by Landsberg and Tonge [14] as $\varepsilon X(\varepsilon) 4\pi^4/45$. Thus, we have:

$$J_{GR} = \tfrac{45}{4\pi^4} I(\varepsilon)\ J_{BR} = \varepsilon X(\varepsilon) J_{BR} \tag{3.7}$$

The integral $I(\varepsilon)$ has not been solved in closed form. Stephens and Obrien [15] presented an infinite series solution and Landsberg and Tonge [14] presented the approximate limiting solution for $\varepsilon < 0.10$:

$$X(\varepsilon) \approx 0.9652 - 0.2777 \ln \varepsilon + 0.0511\ \varepsilon \tag{3.8}$$

Note that Landsberg and Tonge [14] refer to gray radiation (GR) as diluted blackbody radiation (DBR).

Wright [2] presented an approximation for the entropy of GR that is accurate over a large range of emissivities:

$$I(\varepsilon) \approx \varepsilon \left\{ \tfrac{4\pi^4}{45} - m \ln \varepsilon \right\} \tag{3.9}$$

where m is optimized for a specific emissivity range. The approximation (3.9) is such that the blackbody result is obtained for $\varepsilon = 1$ and the whitebody result for $\varepsilon = 0$. Using (3.9) the entropy of GR becomes:

$$J_{GR} \approx \varepsilon\left\{1 - m\tfrac{45}{4\pi^4}\ln\varepsilon\right\}\tfrac{4}{3}\sigma T^3 = \varepsilon\left\{1 - m\tfrac{45}{4\pi^4}\ln\varepsilon\right\}J_{BR} \qquad (3.10)$$

If m is approximated as a constant the resulting expressions are within 0.8% of the numerical integration data over the emissivity range $0.005 \leq \varepsilon \leq 1$. The accuracy of the approximation can be increased by replacing the constant for m with a linear function of emissivity. Table 3-1 shows the maximum percent error in the entropy calculation for various emissivity ranges, for two cases $m=C_1$ and $m=C_2-C_3\varepsilon$. Note that the accuracy of the approximation is strongly dependent on the lower limit of the emissivity range.

Table 3-1: Accuracy of the Approximation for the Entropy of GR for two cases: $m = C_1$ and $m=C_2 - C_3\varepsilon$

Emissivity Range	Case 1		Case 2		
	C_1	Max. Error (%)	C_2	C_3	Max. Error (%)
0.005 to 0.200	2.319	0.72	2.336	0.260	0.33
0.005 to 1.0	2.317	0.77	2.336	0.260	0.33
0.010 to 1.0	2.310	0.71	2.328	0.200	0.33
0.050 to 1.0	2.285	0.49	2.311	0.175	0.16
0.200 to 1.0	2.319	0.23	2.292	0.150	0.03

Alternatively, the entropy radiance of any NBR can be approximated as that of BR with the same energy radiance

$$J_{NBR} \approx \tfrac{4}{3}\sigma^{\frac{1}{4}}H_{NBR}^{\frac{3}{4}} \qquad (3.11)$$

and for GR

$$J_{GR} \approx \tfrac{4}{3}\sigma\varepsilon^{\frac{3}{4}}T^3 \qquad (3.12)$$

The error is relatively low in using the approximation (3.12) for GR over a wide range of emissivities (e.g., less than 1% for $\varepsilon>0.5$). Likewise, this entropy approximation is relatively accurate for any NBR as long as the spectral emissivities are not too low. Note that Equations (3.11) and (3.12) always overestimate the entropy of NBR because BR represents the state of maximum entropy for a given energy. Figure 3-1 shows the percentage that the entropy of GR is overestimated by using (3.12).

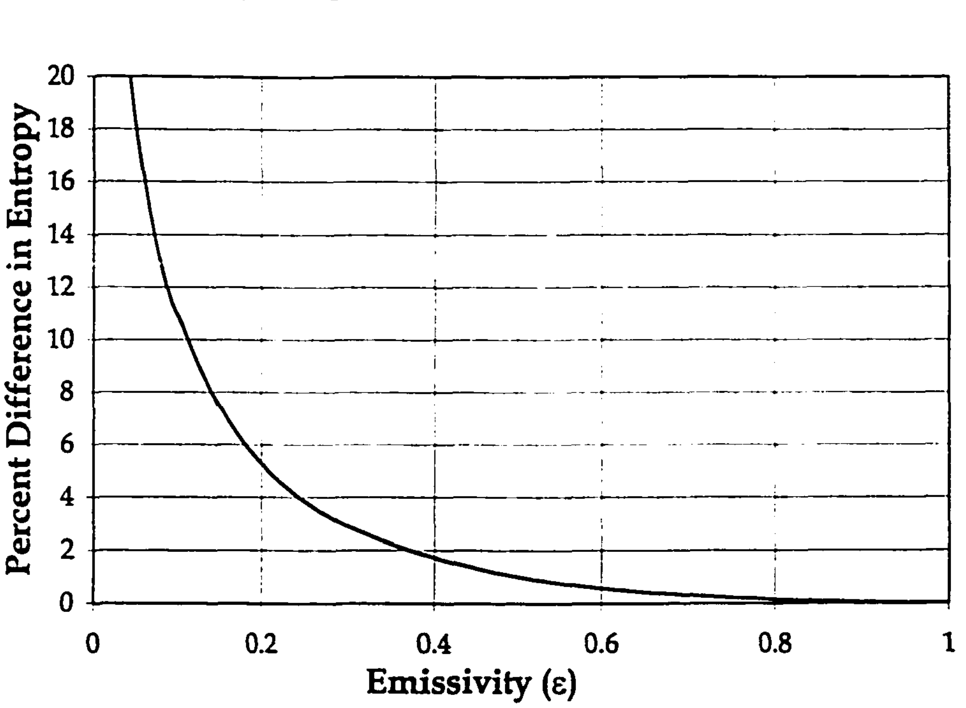

Figure 3-1: Percent difference in entropy between GR and BR with the same energy, as a function of emissivity.

For emissivity values greater than 0.50 the percent difference in entropy is very small, less than 1%. At $\varepsilon = 0.20$ the percent difference is about 5% and at $\varepsilon = 0.10$ it is 10.5%.

3.2 Comparison of the Entropy Flux of TR Emission to that of Heat Conduction

For heat conduction the entropy flux is the ratio of the heat flux and the local temperature (*q/T*). For TR this relationship does not hold. The entropy flux of isotropic[3] TR emission can be compared to that of heat conduction by expressing the entropy flux as

$$J_{Emi} = n\left(\frac{H_{Emi}}{T}\right) \tag{3.13}$$

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[3] Isotropy is specified so that we can consider fluxes (irradiances), rather than radiances, in a simple manner.

where n is dependent on the character[4] of the TR and the subscript *Emi* denotes emission. For BR $n = 4/3$ as shown in equation (3.4). For GR the coefficient n is given by [2]

$$n = \tfrac{4}{3}\left(1 - m\tfrac{45}{4\pi^4}\ln\varepsilon\right) \tag{3.14}$$

Figure 3-2 illustrates the function n for GR using the approximation $m = 2.311 - 0.175\varepsilon$ listed in Table 3-1.

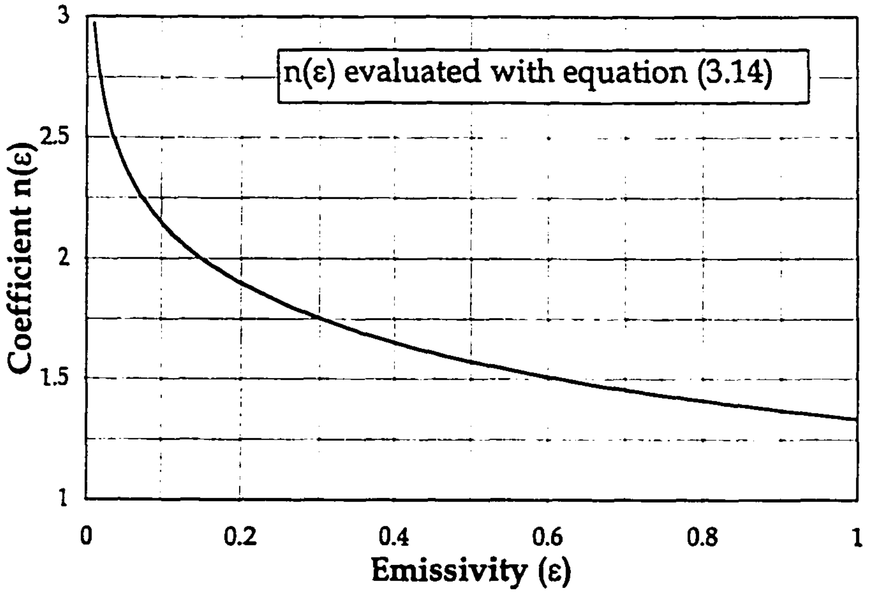

Figure 3-2: The coefficient *n* for GR.

For GR the coefficient n increases as emissivity decreases. For example, n reaches 2.5 for $\varepsilon = 0.05$. So the entropy flux of NBR emission can be much greater than that given by using the relation for heat conduction (q/T). It is surprising that n for NBR is greater than 4/3. BR is known as equilibrium TR and as maximum entropy. However, BR has a minimum ratio of entropy to energy for all TR with the same emission temperature. This observation means that the entropy flux of NBR emission is farther removed from q/T than that of BR emission [2].

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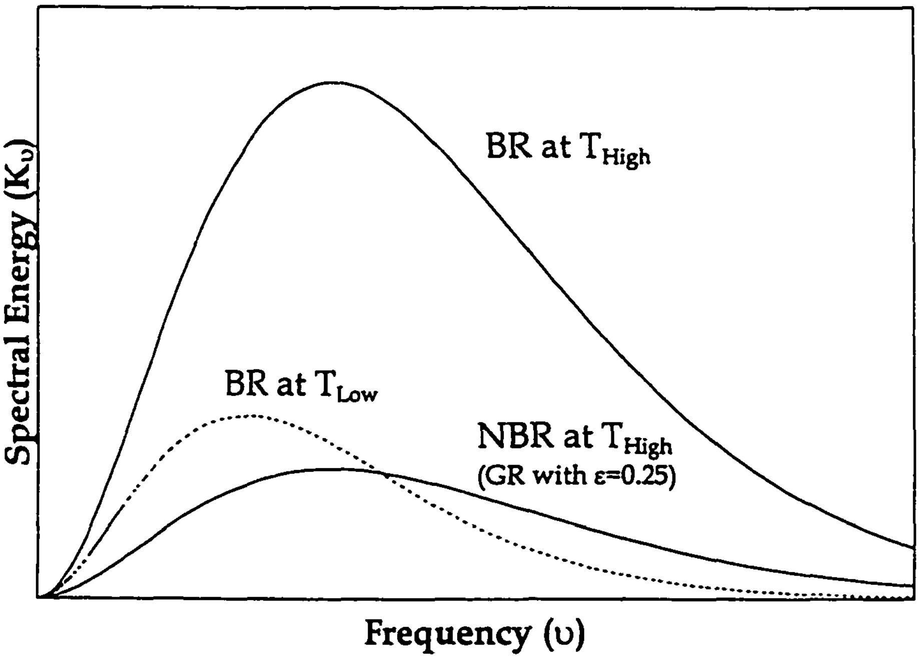
[4] The coefficient n is only a constant independent of emission temperature if the shape of the NBR energy spectrum is invariant within the temperature range of interest. This condition is by definition satisfied for BR and GR.

Figure 3-3 illustrates the BR and NBR spectrums at the same emission temperature, T_{High}, and the BR spectrum at temperature T_{Low} that has the same energy as the NBR spectrum at T_{High}. Note that the area under the K_ν spectrum gives the energy radiance K. The ratios of entropy to energy irradiances (fluxes) for the three spectrums in Figure 3-3 may be expressed as a continued inequality:

$$\left(\frac{J}{H}\right)_{\substack{BR\ @ \\ T_{Low}}} > \left(\frac{J}{H}\right)_{\substack{NBR\ @ \\ T_{High}}} > \left(\frac{J}{H}\right)_{\substack{BR\ @ \\ T_{High}}} \tag{3.15}$$



Chapter 4 Background Research Related to the Exergy of TR

Research on the ideal conversion of thermal radiation (TR) usually follows one of three general approaches. First, some researchers consider the work output from an enclosed blackbody radiation (BR) system as discussed in section 4.1. A second approach (section 4.2) is based on the Gouy-Stodola theorem and the entropy production rate when a TR source flux is absorbed by a surface at the environment temperature T_o. Thirdly, as discussed in section 4.3, researchers in solar engineering have calculated the maximum conversion efficiencies of various solar conversion processes.

4.1 Conversion of Enclosed Blackbody Radiation (BR)

A number of researchers have considered the ideal conversion of an enclosed BR system and Bejan [6] provides an excellent review and unifying interpretation of the different approaches used.

In 1964 Petela [5] used a piston-cylinder approach to determine the maximum work output obtainable from an enclosed equilibrium BR system. Figure 4-1 shows the evacuated enclosure with perfectly reflecting walls and a moveable piston. The enclosed radiation system is thermally isolated from its surroundings. BR at temperature T_o occupies the volume of space on the backside of the piston.

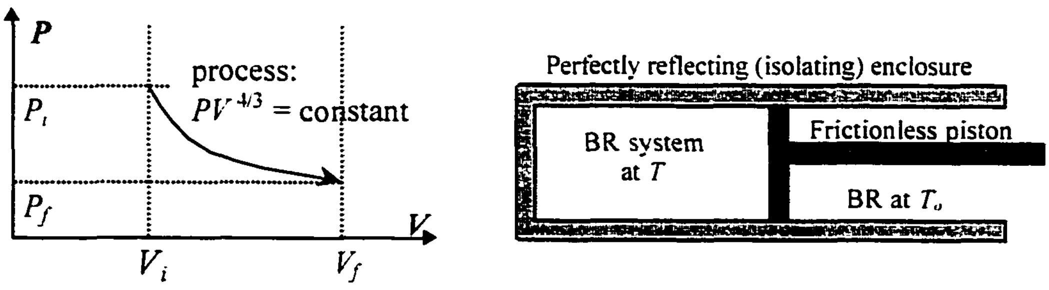


Figure 4-1: Piston-cylinder device and the associated PV diagram for $PV^{4/3}$ = const.

The entropy and internal energy of the BR system are

$$U = aT^4V \tag{4.1}$$

and

$$S = \tfrac{4}{3}aT^3V \tag{4.2}$$

So the fundamental equation of state for the BR system is

$$U = (aV)^{-\frac{1}{3}}\left(\tfrac{3}{4}S\right)^{\frac{4}{3}} \tag{4.3}$$

The system delivers maximum work as it settles into the dead state by an isentropic (reversible and adiabatic) expansion process. Using the relation for BR pressure, $P = U/3V$, it can be straightforwardly shown from (4.3) that $S = constant$ for an isentropic process means that $PV^{4/3} = constant$ as illustrated in Figure 4-1. The work produced during this process is given by

$$W_{out} = \int_{V_i}^{V_o} (P - P_o)\ dV \tag{4.4}$$

where $P = constant\ V^{-4/3}$. After carrying out the integration the work output can be expressed as

$$W_{out} = aV\left\{T^4 - \tfrac{4}{3}T_oT^3 + \tfrac{1}{3}T_o^4\right\} \tag{4.5}$$

Petela proceeds to define the maximum conversion efficiency as the ratio of the maximum work output to the initial energy of the system:

$$\eta_p \equiv \frac{W_{out}}{U_i} = 1 - \frac{4}{3}\frac{T_o}{T} + \frac{1}{3}\left(\frac{T_o}{T}\right)^4 \tag{4.6}$$

Figure 4-2 shows the qualitative plot of η_p versus temperature T and also the analogous plot for heat conduction in materials, $1\text{-}T_o/T$.

Petela's efficiency can also be expressed as

$$\eta_p = 1 - \frac{4}{3}x + \frac{1}{3}x^4 \tag{4.7}$$

where x is the ratio of the environment temperature to the temperature of the BR source, T_o/T. This same result was obtained by other researchers using different approaches. For example Edgerton [16] uses the straightforward application of the concept of non-flow exergy:

$$A \equiv (U-U_0)+P_0(V-V_0)-T_0(S-S_0) \tag{4.8}$$

to arrive at Petela's efficiency.

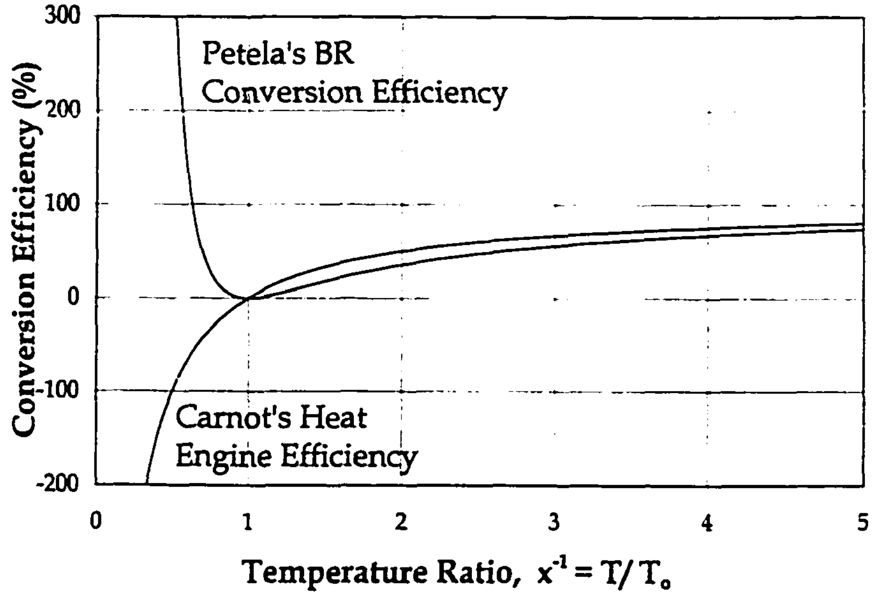


Figure 4-2: Qualitative plot of Petela's efficiency η_p versus temperature T and the analogous plot for heat conduction.

Consider the thermal counterpart of Petela's mechanical piston-cylinder approach for the conversion of an enclosed BR system as depicted in Figure 4-3. The BR system at temperature T is in thermal contact with the environment through a reversible Carnot heat engine. The thermally conductive section of the enclosure is very small so that changes in its internal energy and entropy may be neglected. The thermally conductive section is also thin and has a high thermal conductivity such that entropy production due to heat conduction may be neglected. The remaining wall of the enclosure is perfectly insulating so that its internal energy and entropy may be neglected as well. The work output during the constant volume cooling process is:

$$W_{out} = \int_{T_i}^{T_0} (1 - T_0/T)dQ \tag{4.9}$$

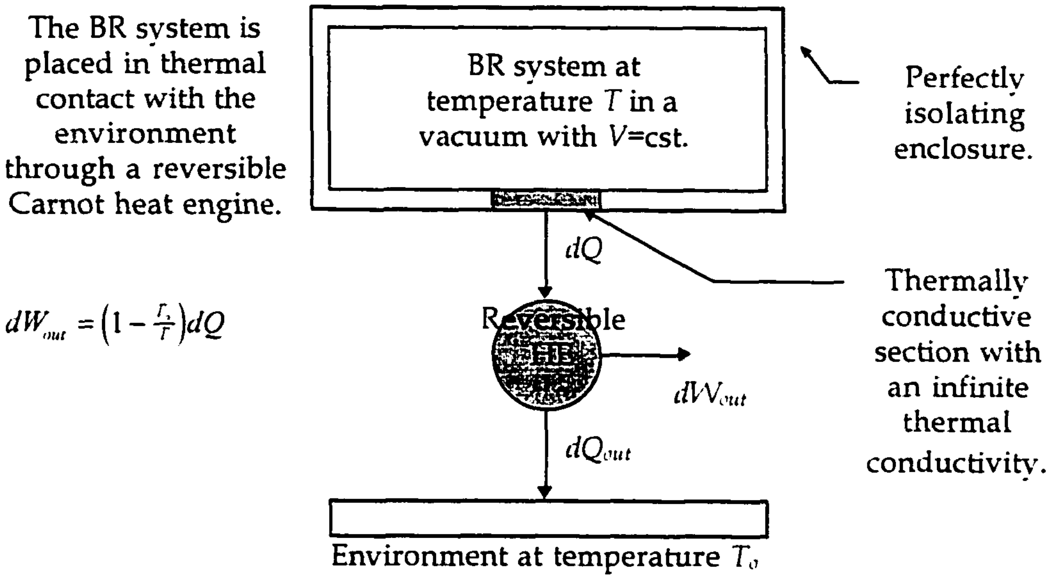
The first law applied to the BR system shows that $dQ = -dU$, and since $U=aT^4V$ we have $dQ = -4aVT^3dT$, so by substituting this (4.9) becomes

$$W_{out} = -4aV\int_{T_i}^{T_o}(1-T_o/T)T^3dT \tag{4.10}$$

After carrying out the integration we arrive at Petela's result:

$$W_{out} = aVT_i^4\left\{1-\tfrac{4}{3}x+\tfrac{1}{3}x^4\right\} \tag{4.11}$$

If the initial temperature T_i is less than T_o then the HE depicted in Figure 4-3 will operate with the environment at T_o, and the BR system, as the high and low temperature reservoirs, respectively, and (4.11) will give the correct work output.


The BR system is placed in thermal contact with the environment through a reversible Carnot heat engine.

$$dW_{out} = \left(1-\tfrac{T_o}{T}\right)dQ$$

Perfectly isolating enclosure.

Thermally conductive section with an infinite thermal conductivity.

Figure 4-3: BR system connected to a reversible Carnot heat engine.

However, at least two other maximum conversion efficiencies have been presented in literature. The most common are Spanner's efficiency [17]:

$$\eta_{Spanner} = 1-\tfrac{4}{3}x \tag{4.12}$$

supported by Gribik and Osterle [18,19], and Jeter's efficiency [20]:

$$\eta_{Jeter} = 1-x \tag{4.13}$$

Bejan [6] shows that the differences between these efficiencies is simply based on their definitions. Bejan considers three steps:

(1) reversible filling of the evacuated enclosure with BR at temperature *T*,
(2) reversible cooling of the BR system from *T* to T_o, and
(3) reversible emptying of the BR system at T_o from the enclosure.

All three efficiencies are the ratio of work output to the initial internal energy of the BR system at temperature *T*, but the work output is defined differently for each efficiency. In Petela's efficiency the work output is extracted in step 2 only. In Spanner's efficiency the net work output is from steps 2 and 3 combined and in Jeter's efficiency it is from steps 1, 2, and 3.

4.2 Approaches used to Determine the Exergy Flux of TR

4.2.1 Petela's approach for BR exergy: TR exchange between parallel blackbody plates

In Petela's approach two parallel regions of material are separated by a vacuum, as shown in the Figure 4-4. Surface *A* is maintained at temperature *T* by a thermal energy reservoir (TER) whereas surface *E* is in thermal contact with the Environment at temperature T_o. When $T \neq T_o$ there is a net transfer of radiant energy and entropy between the surfaces. Both surfaces are of blackbodies so TR emitted by one surface is completely absorbed by the other surface.

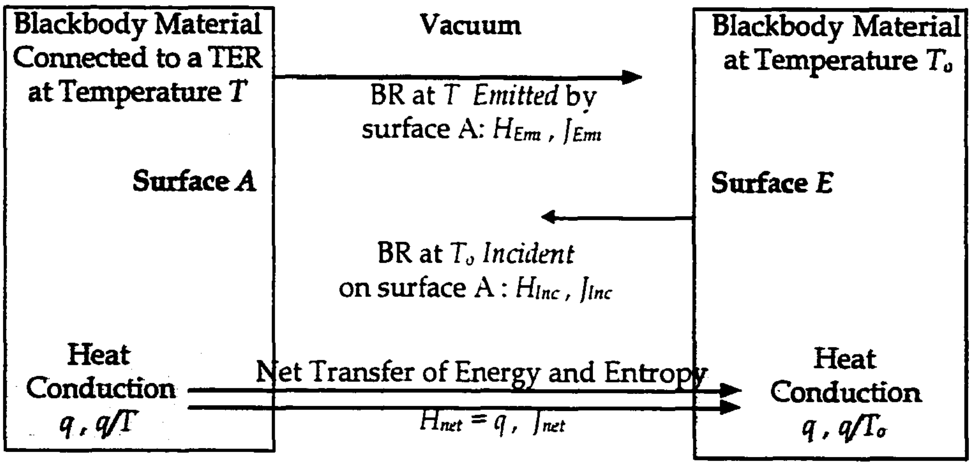


Figure 4-4: TR exchange between two parallel blackbody surfaces.

In this approach the Guoy-Stodola principle is used as a basis for determining the exergy of the TR fluxes. This principle implies that the exergy destruction rate, termed the rate of irreversibility, is equal to the product of the total entropy production rate and the environmental temperature, that is $\dot{I} = T_0\dot{\Pi}$. The exergy of the radiation is then calculated with an exergy balance at either of the material surfaces.

The following limitations are imposed in Petela's analysis for simplicity:

1) A vacuum exists between the two surfaces.
2) The exchange of radiation is steady state.
3) All TR is isotropic and the geometry is such that the problem is 1D. Note that all fluxes and entropy production rates in this analysis are per m^2 of surface area.

Consider the case when the net energy flux is towards the environment, that is surface A is hot ($T>T_0$) relative to surface E, as shown in Figure 4-5. Heat conduction entering the control volume has an energy flux q, an entropy flux q/T, and an exergy flux of $q(1-T_0/T)$.

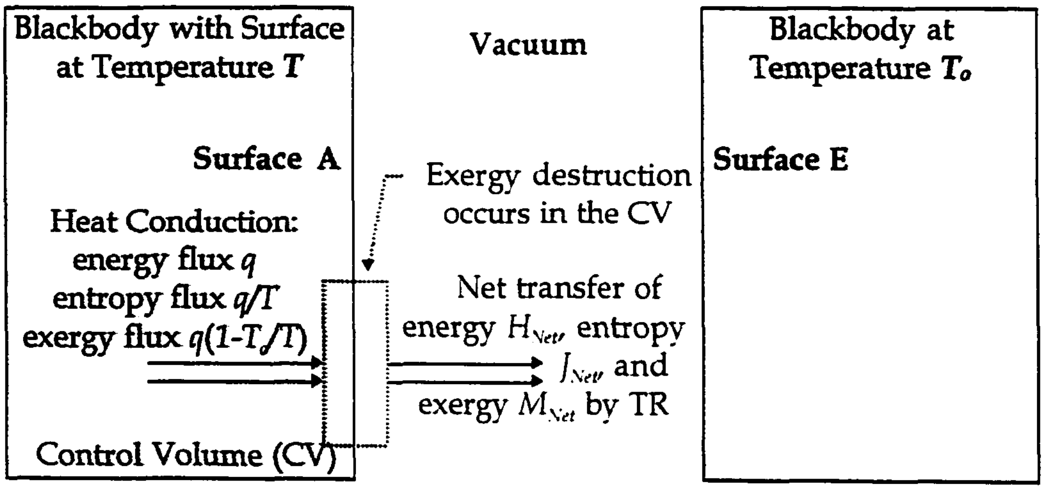


Figure 4-5: Exergy balance for the control volume.

Whenever there is heat transfer ($q \neq 0$) between the plates entropy production occurs due to radiation-matter interaction ($\dot{\Pi}_{RM}$), as can be determined by an entropy balance using Planck's spectral entropy radiance (3.2). This entropy production occurs in layer of material at each surface. This layer, referred to here as the interaction region, is defined as the region of material that contains TR that has or will travel into/from the region exterior to the solid material. This distinction between exterior and interior is required because all atoms including those within a solid continuously emit thermal radiation. For simplicity of discussion, the thermal conductivity is suficiently large so that the temperature[1] in the interaction region is approximately uniform. The control volume is defined such that it includes the radiation-matter interaction region.

The net exergy flux leaving the CV by TR transfer must be equal to the exergy flux entering by heat conduction at T minus the exergy destruction rate in the CV:

$$M_{Net} = \frac{1}{A}\left(\dot{\Xi}_{In} - \dot{I}\right) = q\left(1 - \frac{T_0}{T}\right) - T_0\frac{\dot{\Pi}_{CV}}{A} = q - T_0\left(\frac{q}{T} - \frac{\dot{\Pi}_{CV}}{A}\right) \tag{4.14}$$

The net energy flux of the TR is equal to that of the heat conduction ($H_{Net} = q$) and the net entropy flux by TR transfer is:

$$J_{Net} = \frac{q}{T} + \frac{\dot{\Pi}_{CV}}{A} \tag{4.15}$$

Thus, based on the Guoy-Stodola theorem the net exergy flux by TR is:

$$\overbrace{\left(M_{Net}\right)}^{\substack{\text{Net Exergy Flux towards} \\ \text{the Environment}}} = \overbrace{\left(H_{Net}\right)}^{\substack{\text{Net Energy Flux towards} \\ \text{the Environment}}} - T_o \overbrace{\left(J_{Net}\right)}^{\substack{\text{Net Entropy Flux towards} \\ \text{the Environment}}} \tag{4.16}$$

The net energy and entropy fluxes by TR are

$$H_{Net} = \sigma\left(T^4 - T_o^4\right) \qquad J_{Net} = \frac{4\sigma}{3}\left(T^3 - T_o^3\right) \tag{4.17}$$

---

[1] Strictly speaking the temperature in the interaction region is not uniform. So it may be argued that the emission temperature and the temperature at the inner boundary of the interaction region are not strictly equal. However, the temperature variation is very small because (1) the interaction region is usually very thin, e.g. on the order of a few micrometers for metals, and (2) the temperature gradient decreases to zero at the surface of the solid because heat conduction decreases to zero at the surface. Furthermore, in a theoretical sense the temperature difference can be made arbitrarily small by specifying a sufficiently large thermal conductivity.

respectively. Petela assumes that the exergy flux of BR at T_o is zero. So the exergy flux of BR at T is equal to the net exergy flux. Using (4.17) in (4.16) the exergy flux of BR at T becomes :

$$M_{BR} = \frac{\sigma}{3}\left\{3T^4 - 4T_oT^3 + T_o^4\right\} \tag{4.18}$$

or alternatively

$$M_{BR} = \sigma T^4\left\{1 - \frac{4}{3}x + \frac{1}{3}x^4\right\} \tag{4.19}$$

where x is the ratio of temperature T_o/T. This is the same as the result Petela obtained for the exergy of an enclosed BR system.

4.2.2 Karlsson's approach for the exergy of TR

Karlsson's [21] approach to determine the exergy of NBR is based on calculating the entropy production that occurs as a TR source flux is absorbed by a blackbody surface at T_o. The environment reference state selected is BR at temperature T_o. The geometry of Karlsson's approach is depicted in Figure 4-6. Monochromatic TR in the frequency interval ν,ν+dν is incident on a small area dY of a blackbody surface area (Y) at the environment temperature T_o. The monochromatic TR is contained in a solid angle dΩ with direction perpendicular to the blackbody surface.

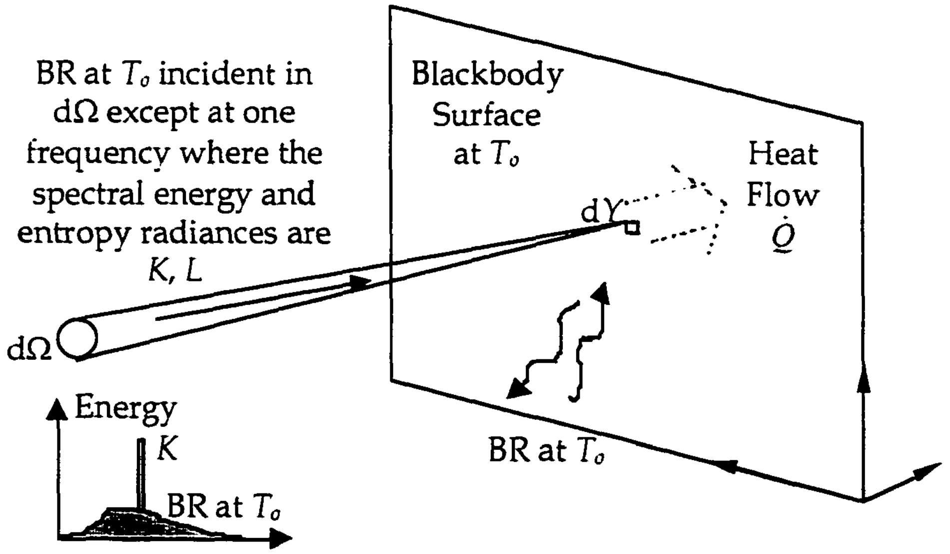


Figure 4-6: Monochromatic TR incident on a blackbody surface at T_o.

BR at T_o is emitted by the plate in every direction (over the solid angle 2π), including within the solid angle dΩ, and BR at T_o is incident from every direction (over the solid angle 2π) except in the solid angle dΩ. By energy conservation the heat flow into the plate is given as

$$\dot{Q} = K d\upsilon d\Omega dY - K_o d\upsilon d\Omega dY \tag{4.20}$$

where K and K_o are the spectral energy radiances of the incident monochromatic TR and the BR at T_o, respectively.

The entropy production is given as

$$\Delta\dot{S} = \dot{Q}/T_o + L_o d\upsilon d\Omega dY - L d\upsilon d\Omega dY \tag{4.21}$$

Karlsson states that the spectral exergy radiance of the incoming NBR is the entropy production rate times the environmental temperature:

$$B = T_o \Delta\dot{S} \tag{4.22}$$

After substituting for $\dot{Q}$ in Equation (4.21) using Equation (4.20), Karlsson then claims that the exergy of the monochromatic beam is

$$B = \left[\left(K - K_o\right) - T_o\left(L - L_o\right)\right] d\upsilon d\Omega dY \tag{4.23}$$

Note that the notation used in this section 4.2.2 is that of Karlsson [21].

4.3 Maximum Conversion Efficiencies in Solar Engineering

In the field of solar engineering a variety of conversion processes have been considered: thermal, quantum or hybrid thermal-quantum processes. In section 4.3.1 we consider pure thermal single-stage absorption systems with blackbody absorptivity. Inherently quantum systems operate with a threshold or cutoff frequency. By choosing special coatings thermal systems may operate with a threshold frequency as well, this is discussed at the end of section 4.3.1. In section 4.3.2 we consider pure quantum single-cell systems. Finally we will examine omnicolor multiple threshold systems (section 4.3.3).

4.3.1 Single-stage thermal conversion

In thermal conversion the TR source is absorbed by a receiver or collector as heat. The heat transfer rate from the collector is the difference between the absorbed and emitted TR energy flow rates. Figure 4-7 depicts a basic thermal conversion device for isotropic TR fluxes. The blackbody collector is thermally connected to the environment through a reversible Carnot heat engine (HE). The absorbing material has blackbody characteristics without threshold behaviour.

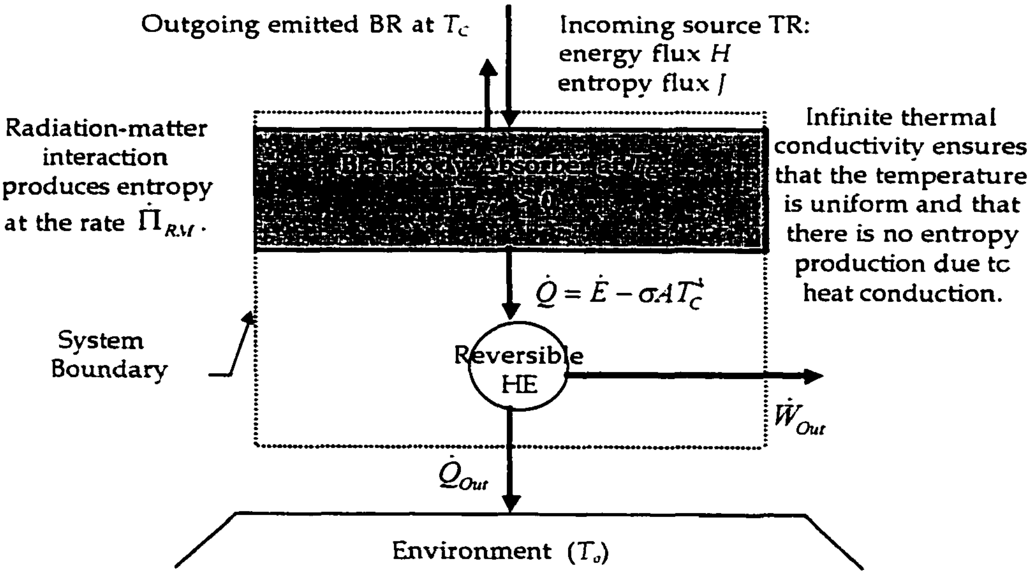


Figure 4-7: Single-stage thermal (SST) conversion device.

The incident TR is isotropic and uniform on the collector so the energy and entropy source fluxes that are incident on the collector are

$$\dot{E} = \int_{x-sect.} H dA = HA \qquad \dot{S} = \int_{x-sect.} J dA = JA \tag{4.25}$$

respectively, where A is the surface area of the collector. For simplicity a one dimensional geometry is ensured by specifying that the outer surface of the collector is perfectly isolating so that there is no heat conduction or TR transfer. Also, the thermal conductivity of the collector material is sufficiently large so that the temperature is uniform and entropy production due to heat conduction can be neglected. Outgoing radiation emitted by the collector must be included in the analysis because all matter that absorbs TR must also emit TR. The collector is a blackbody so all incident TR is absorbed and the emitted TR has blackbody characteristics.

The thermodynamic system is defined as the combination of the collector and the heat engine (HE), as shown in Figure 4-7. Applying the first law of thermodynamics to the collector and heat engine combination we have

$$\dot{W}_{out} = \dot{E} - \dot{Q}_{out} - \sigma A T_C^4 \tag{4.26}$$

where T_C is the temperature of the collector, $\dot{W}_{out}$ is the work output from the heat engine, and $\dot{Q}_{out}$ is the heat rejected to the environment. Application of the second law of thermodynamics to the collector and heat engine combination gives

$$\dot{\Pi}_{RM} = \frac{\dot{Q}_{out}}{T_o} + \frac{4\sigma}{3} A T_c^3 - \dot{S} \tag{4.27}$$

where $\dot{\Pi}_{RM}$ is the entropy production rate due to radiation-matter interaction in the collector. Upon eliminating the heat rejected to the environment ($\dot{Q}_{out}$) from equations (4.26) using (4.27) we have

$$\dot{W}_{out} = \left(\dot{E} - \sigma A T_C^4\right) - T_o\left(\dot{S} - \tfrac{4\sigma}{3} A T_C^3\right) - T_o \dot{\Pi}_{RM} \tag{4.28}$$

Note that Landsberg [13, p. R3] stated that if $\dot{\Pi}_{RM}$ and the radiation emitted from the collector are neglected the work output of the device is

$$\dot{W}_{out} = \dot{E} - T_o\dot{S} \tag{4.29}$$

Other researchers have found this type of reasoning confusing. Haught [3, p. 3] states that the "Thermodynamic treatments ... neglect the limitations (re-radiation, threshold absorption) that are inherent in the conversion process". DeVos [7, p. 124] states that it is confusing when Landsberg sets the entropy production rate to zero for the single-stage thermal converter because it suggests that at maximum efficiency the process of the solar cell is reversible.

Returning to the analysis, since there is no entropy production in a Carnot heat engine the entropy flow leaving the HE with Q_{out} must be equal to that entering with Q:

$$\frac{Q_{out}}{T_o} = \frac{\dot{E} - \sigma A T_C^4}{T_C} \tag{4.30}$$

Using Equation (4.30) to eliminate Q_{out} from equation (4.26) we have

$$\dot{W}_{out} = \left(\dot{E} - \sigma A T_C^4\right)\left(1 - \frac{T_o}{T_C}\right) \tag{4.31}$$

For a specified source radiation in a particular environment the only variable in the work output expression is the collector temperature T_C. Thus, to find the maximum work output rate the temperature of the collector must be optimized. As T_C increases the thermal efficiency $(1-T_o/T_c)$ increases yet the net energy flow rate into the converter $(\dot{E} - \sigma A T_C^4)$ decreases. So a balance must be reached such that the combination in efficiency and the net energy flow rate through the device results in the maximum work output rate. To find the optimum collector temperature we differentiate the work output rate (4.31) with respect to T_C and set the result to zero. This results in a fifth degree polynomial for the optimum temperature of the collector

$$T^5 - \tfrac{3}{4}T_oT^4 - \tfrac{1}{4}\left(\dot{E}/\sigma A\right)T_o = 0 \tag{4.32}$$

For blackbody source radiation, upon introducing the non-dimensional temperature ratios $\theta = T/T_o$ and $\theta_s = T_s/T_o$ (see for example Bejan [11, p. 503]), this becomes

$$4\theta^5 - 3\theta^4 - \theta_s^4 = 0 \tag{4.33}$$

The expression for the optimum temperature is a fifth degree polynomial equation that cannot be solved analytically for arbitrary values of θ_s. To find the roots of (4.33) the temperature ratio θ_s must be specified, that is the ratio of T_s to T_o. Note that there is only one real root for the optimum temperature because the sign of the coefficients in the polynomial only changes once (4 of the roots are pairs of imaginary complex conjugates). For solar radiation, approximated as BR with an emission temperature of 5762 K, in an environment with a temperature of 300 K, the optimum collector temperature is 2464.80 K. The corresponding first-law energy efficiency is 84.9% and is defined as the work output in Equation (4.31) divided by $\dot{E} = \sigma A T_s^4$:

$$\eta \equiv \frac{\dot{W}_{out}}{\dot{E}} = \left(1 - \frac{\theta^4}{\theta_s^4}\right)\left(1 - \frac{1}{\theta}\right) \tag{4.34}$$

This high efficiency is a result of the large temperature difference between the material emission temperature of the SR and the environment temperature T_o.

Rather than isotropic solar radiation, Haught [3] considers the case where the solar radiation is contained in a small solid angle determined by the Earth's distance from the Sun. Dispersion and attenuation are avoided by considering solar radiation at the top of the atmosphere (TOA). Haught's analysis is also different because he (1) uses a slightly different temperature for the solar radiation, 6000 K rather than 5762 K, and (2) he introduces a cutoff frequency for the absorber as is the case in quantum conversion, see section 4.3.2.

Selective absorption can be achived for thermal conversion with the use of the proper coating material. For example, see De Vos' text [22, p. 81]. Selective absorption is beneficial because it favors the absorption of high frequency SR while reducing the emission of low frequency outgoing TR. That is, the cutoff frequency may be chosen to favour the absorption of SR while reducing the emission of TR.

Haught reports a maximum conversion efficiency for unconcentrated SR of 54.0% at a collector temperature of 863 K and a cutoff frequency of $2.22(10)^{14}$ hz. Haught [3] also considers the conversion of highly concentrated SR.

Note that the case of isotropic SR discussed here represents the case of ideal concentration (factor of 43,600). For a concentration factor of 10,000 Haught reports that the maximum conversion efficiency is 80.0% at a collector temperature of 1900 K and a cutoff frequency of zero. It is important to note that for emission and absorption over the same solid angle, represented by the isotropic case here, the usefulness of the cutoff frequency becomes negligible (thermal systems do not normally exhibit threshold behavior).

4.3.2 Single-cell quantum conversion

Quantum conversion involves a fundamentally different mechanism than thermal conversion. In quantum conversion photon absorption excites the receiver medium causing atomic transitions such as electron-hole excitation. Quantum processes include photovoltaic conversion, photochemical processes, and photosynthesis.

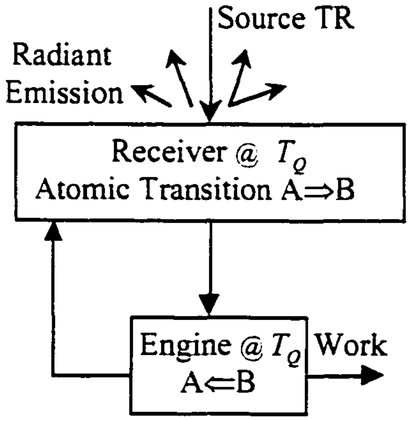


Figure 4-8: Single-cell quantum (SCQ) conversion.

The atomic transition to the excited state requires the absorption of a photon with energy greater than or equal to the excitation energy μ. As a result, only a fraction of the stream of incoming photons may be absorbed. This is because the photons with frequency below the cutoff (threshold) frequency ν_0 have an energy level $h\nu$ less than the excitation energy level μ. Thus, the quantum system always exhibits a step function excitation that depends on the quantum system temperature T_Q and the excitation energy μ,

$$\alpha(\nu,\mu,T_Q) = \begin{cases} 0 & \nu < \nu_0 \\ 1 & \nu \geq \nu_0 \end{cases} \tag{4.35}$$

Although thermal systems can exhibit a threshold behavior as well, the quantum system is different in that only the energy μ is utilized even though the photon may have a much higher energy $h\nu$ above the threshold.

In general the production of work through quantum conversion requires an 'engine' to perform the reverse transition, as depicted in Figure 4-8. However, in photovoltaic conversion work is produced directly through electric current flow and no 'engine' as such is required. The absorption of photons results in an electric current, and thus electrical work output, in the external circuit or load.

For isotropic source radiation incident on the collector the work output rate is

$$\dot{W} = \int_0^\infty \left[H_\nu(T_S) - H_\nu(\mu,T_Q)\right]\mu\alpha d\nu \tag{4.36}$$

where $H_\nu(T_S)$ and $H_\nu(\mu,T_Q)$ are the spectral energy irradiance of the source radiation and the quantum emission radiation, respectively.

For BR source radiation the spectral energy irradiance is

$$H_\nu(T_S) = \frac{2h\pi}{c^2}\frac{\nu^3}{e^{\frac{h\nu}{kT_s}} - 1} \tag{4.37}$$

and for quantum emission the spectral energy irradiance is given by

$$H_\nu(\mu,T_Q)=\frac{2h\pi}{c^2}\frac{\nu^3}{e^{\frac{h\nu-\mu}{kT_Q}}-1} \tag{4.38}$$

For photon emission to remain finite the absorption threshold (ν_o) must be greater than the quantum emission threshold (μ/h). Figure 4-9 illustrates a typical quantum emission spectrum and the incident solar spectrum.

Using equations (4.37) and (4.38) the work output may be expressed as

$$\dot{W}=\int_{\nu_o}^{\infty}\frac{2h\pi\mu}{c^2}\nu^3\left\{\frac{1}{e^{\frac{h\nu}{kT_S}}-1}-\frac{1}{e^{\frac{h\nu-\mu}{kT_Q}}-1}\right\}d\nu \tag{4.39}$$

To find the maximum work output the optimum value of the excitation energy μ must be found such that μ/h is less than the cutoff frequency ν_o. A balanced must be obtained to achieve maximum work because a high cutoff frequency reduces emission and increases the fraction of absorbed energy that is utilized but at the same time reduces the number of photons absorbed.

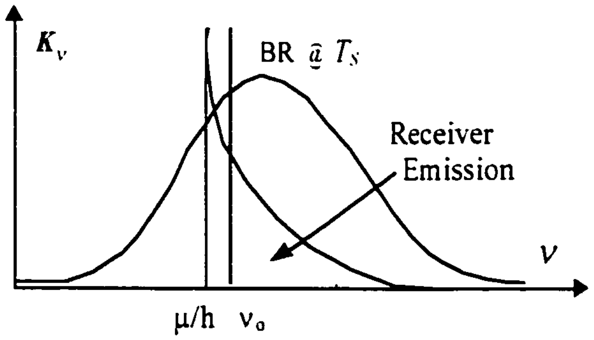


Figure 4-9: Qualitative single-cell quantum emission and incident BR.

For isotropic BR De Vos reports a maximum conversion efficiency of 85.4% [22]. The conversion of isotropic BR represents the case of ideal concentration (C = 43,600). For unconcentrated BR Haught [3] reports that the maximum conversion efficiency of 30.9% occurs when $T_Q = T_o$, $\mu = 1.54(10)^{-19}$J, and $\nu_o = 3.16(10)^{14}$ hz.

For a concentration factor of 10^4 Haught states that the maximum obtainable conversion efficiency is 40.0%.

The maximum possible conversion efficiencies for the single-cell quantum device are lower than that of single-stage thermal conversion. Haught [3, p. 15] explains this result by stating that the lower quantum efficiency is due to the fact that the quantum system responds, not to the total energy, but only to the number of photons above the threshold energy and is therefore less energy efficient than a thermal system which integrates the energy contribution of all photons above the cutoff minimum. It is interesting to note that in the case of ideal concentration (isotropic solar radiation) there is no cutoff frequency and thus the thermal device responds to the total energy of incident photons at all frequencies.

4.3.3 Omnicolor multiple threshold system

The use of multiple collectors individually optimized over different frequency ranges increase the overall conversion efficiency. For example, the quantum conversion efficiency is increased when a second collector is introduced that absorbs the radiation with frequencies below the first cutoff frequency. The maximum efficiency is achieved in the limit of an infinite number of collectors each absorbing and effectively emitting at a single frequency and individually optimized at that frequency. Figure 4-10 illustrates an infinite tandem of quantum conversion cells (without electroluminescence).

The omnicolor photothermal device was first introduced by Haught [3] and the photovoltaic device was presented by DeVos [23]. Haught [3, p. 3] states that the "results obtained are independent of the specific form of the thermal and quantum radiation conversion device and serve as an upper bound on the efficiency with which radiant energy can be converted to useful work in any actual device". In agreement with Haught, De Vos [24, p. 2006] says that the efficiency expression that he presents is "not only the highest conversion efficiency that can be achieved with the solar cell structure we have described in the introduction, but also the highest conversion efficiency achievable with any photovoltaic solar energy converter". DeVos and Vyncke [25] also state that the infinite series of optimized omnicolor collectors is "the thermodynamically optimal device for converting solar energy into work".

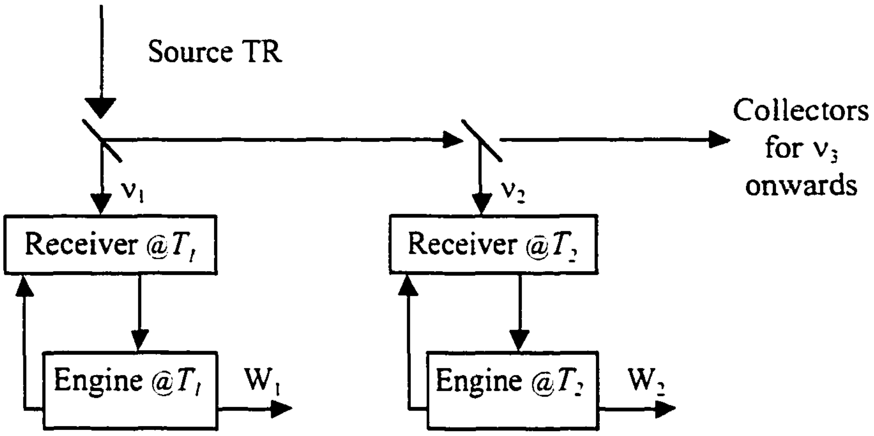


Figure 4-10 Infinite tandem of quantum cells.

Haught [3] has shown that omnicolor quantum and thermal systems with threshold behaviour have the same maximum efficiency. Haught also examines hybrid (cascaded) quantum-thermal conversion to show that pure thermal and pure quantum conversion are the two extremes in a range of possible conversion processes.

The motivation for considering a hybrid quantum-thermal device can be seen by examining the pure quantum conversion process. The energy of an absorbed photon $h\nu$ in excess of the excitation energy μ results in heat flow at the quantum system temperature T_Q. This rejected heat can be used in a bottoming cycle to form cascaded (hybrid) quantum-thermal conversion.

Haught shows that for the limiting case $T_Q = T_o$ the work output for the thermal portion is zero and the conversion is purely quantum. At the other extreme, purely thermal conversion results when the excitation energy is zero and the quantum portion does not produce work. Figure 4-11 shows the conversion efficiency versus quantum system temperature for a single-stage cascaded system (not omnicolor) with concentrated sunlight (factor of 10^4). The conversion efficiency increases as the system becomes more thermally oriented. However, in the case of an infinite series of omnicolor devices the upper limit to the conversion of BR is the same for purely quantum, cascaded (hybrid) quantum-thermal, and purely thermal conversion.

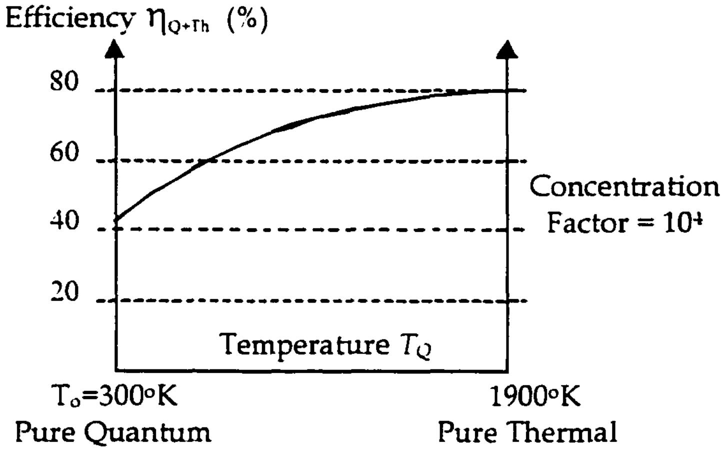


Figure 4-11 Conversion efficiency versus system temperature for a single collector cascaded quantum-thermal converter.

Table 4-1 summarizes the maximum SR energy conversion efficiencies for pure thermal and pure quantum single collector systems, and infinite-series omnicolor devices, for different levels of concentration. Lower concentration factors result in lower maximum conversion efficiencies. Unconcentrated SR occurs in a very small solid angle. The entry for isotropic SR may be viewed as the case of ideal concentration (C=43,600); incoming radiation is independent of direction over a solid angle of 2π (hemisphere of directions). Note that thermal and quantum omnicolor conversion have the same maximum ideal efficiency so there is only a single entry made for omnicolor in Table 4-1 for each level of concentration.

For all levels of concentration the single-cell quantum system has a lower efficiency than the corresponding single-stage thermal system. As mentioned in section 4.3.2, Haught [3, p. 15] explains that thermal conversion with selective absorption is more efficient than the equivalent quantum conversion because quantum converters only respond to the number of photons above the threshold while a thermal converter utilizes all the energy absorbed above the cutoff.

Table 4-1: Maximum first-law energy conversion efficiencies (in %) for SR.

Conversion Process	Unconcentrated, C = 1 (Haught [3])	Concentration, C = 10,000 (Haught [3])	Isotropic Solar * C = 43,600	
			Bejan [11]	De Vos [22]
Single-Stage Thermal	54.0	80.0	84.9	85.4
Single-Cell Quantum	30.9	40.0	------	40.8
Omnicolor Series	68.3	84.1	86.1	86.8**

* Bejan and De Vos use different values for T_o and T_S (Sun).

** De Vos reports another value of 85.4% for the case that emission is at a uniform quantum system temperature over the whole stack or series of cells.

Chapter 5 Exergy of Blackbody Radiation (BR)

5.1 Exergy of an Enclosed BR System

Three different conversion efficiencies were presented in section 4.1 for the maximum work obtainable from an enclosed BR system. Bejan states that the following questions must be addressed: (1) what is the origin (source) of the BR including how it got into the enclosure, and (2) what is the ultimate fate of the equilibriated BR because clearly there is no such thing as an environment of isotropic BR. While Spanner's (4.12) and Jeter's (4.13) definitions of efficiency may be useful in some respect, Petela's efficiency (4.6) represents the exergy of the enclosed BR system:

$$\Xi_{BR} = W_{\substack{Max\\out}} = U_{BR}\left[1-\frac{4}{3}\frac{T_o}{T}+\frac{1}{3}\left(\frac{T_o}{T}\right)^4\right] = aT^4V\left[1-\frac{4}{3}\frac{T_o}{T}+\frac{1}{3}\left(\frac{T_o}{T}\right)^4\right] \tag{5.1}$$

This is because the exergy of the BR system does not depend upon how the system originated or what happens to it after it has reached equilibrium with its environment. In other words, the exergy of BR is determined by considering step #2 alone of Bejan's 3 step cyclic process: filling with source radiation, equilibriating with the environment, and emptying.

Reversible extraction of work from the enclosed BR system is theoretically possible simply because equilibrium can exist between a BR system and its material enclosure. Without defining a temperature for the radiation system, equilibrium between the TR system and its enclosure signifies a state of maximum entropy for the combined system: the TR system plus its enclosure.

The Carnot heat engine and the special enclosure depicted in Figure 5-1 provide the physical components and geometry for obtaining reversible conversion. The enclosure is of a special nature in that (1) it is totally reflecting everywhere except in a small thermally conducting region thus allowing the internal energy and entropy of the enclosure to be neglected, and (2) the thermal conductivity in this region is infinite thereby eliminating the need to consider entropy production due to heat conduction.

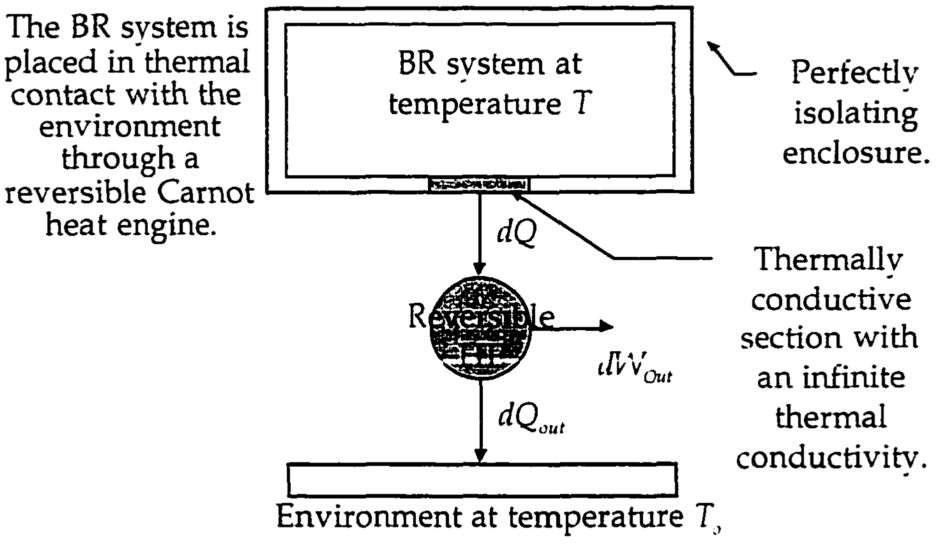


Figure 5-1: BR system connected to a reversible Carnot heat engine.

Bejan [11, pp. 490-496] agrees that Petela's result represents the exergy of the enclosed TR system yet he questions its physical significance with respect to the conversion of solar fluxes (approximated as BR fluxes). Bejan states that in "the narrow context in which the Petela problem was formulated, the η_p ratio ... is not a 'conversion efficiency'". However, in sections 5.2 to 5.4 it is shown that Petela's result does represent the exergy *flux* of BR and the true upper limit for the conversion of BR fluxes.

5.2 Definition of the Environment for the Exergy of TR

The unusual nature of TR transfer in the context of exergy analysis raises the question as to the appropriate definition of the environment for the exergy flux of TR. In questioning the significance of Petela's result Bejan [11, p. 492] states that "there is no such thing as an environment of isotropic blackbody radiation as is assumed most visibly in the availability type derivation". In Petela's [5] original derivation involving a deformable reflecting enclosure, the specified environment is strictly isotropic BR in a vacuum (as depicted in Figure 4-1). This unusual environment specification has lead to doubt regarding the general applicability of Petela's result to engineering systems.

In this section it will be shown that the specification of the 'pseudo' environment of strictly BR in a vacuum is only necessary to determine the exergy of BR and thus does not represent any practical restrictions on the environment in exergy analysis. The definition of the environment in conventional exergy analysis completely suffices for TR exergy analysis. Also, it will be explained why only the environment temperature is required for exergy analysis involving TR heat fluxes.

The pseudo environment of BR in a vacuum is required to isolate the exergy of TR from other forms of exergy. To isolate TR exergy from material exergy the enclosed BR system is contained in a vacuum. But, as a result of specifying a vacuum the system has mechanical exergy in an environment with gas pressure. This can be clearly seen if we consider Petela's piston cylinder device with an environment of normal gas pressures (BR pressure is orders of magnitude less than 1 atm). To completely isolate TR exergy it is necessary to consider a BR system in a vacuum and a pseudo environment of strictly BR in a vacuum at environment conditions. Thus, the specification of a special environment of strictly BR at T_o does not cause any restrictions on the environment for TR exergy analysis. Note that the environment in conventional exergy analysis by definition is in internal equilibrium and thus any non-solid regions (such as a region of gas or a vacuum) would contain isotropic BR at T_o.

The environment temperature T_o is the only relevant parameter of the environment for TR exergy. In Petela's mechanical piston-cylinder approach, and the heat engine approach of section 5.1, the final dead-state equilibrium radiation pressure is that of BR at T_o rather than that of the environment gas pressure P_o. In the TR exergy calculation the BR system may be said to simultaneously achieve thermal and mechanical equilibrium with the pseudo environment, because there is only one independent intensive parameter for the BR system. For Petela's piston-cylinder approach the simplest choice of parameter to specify the dead state is the pressure of BR in the pseudo environment. However, this BR pressure can only be related to the temperature T_o of the real environment but not to its gas pressure P_o. Therefore the only relevant parameter of the environment is T_o.

The exergy of an enclosed BR system is the theoretical maximum work output that can be obtained by bringing the BR into equilibrium with its environment. The TR has both energy and entropy whereas work output has zero entropy. During the ideal production of work from the BR system all the entropy leaving the system enters the environment. Yet, this transfer of entropy must be accompanied by an increase of the internal energy of the environment. The environmental temperature T_o determines the magnitude of the required energy change. This temperature is defined as the slope of internal energy U versus entropy S when volume V and mole numbers N_i are fixed, as shown in figure 5-2. The extensive properties can change but the relative changes are small enough that the intensive properties such as temperature do not change.

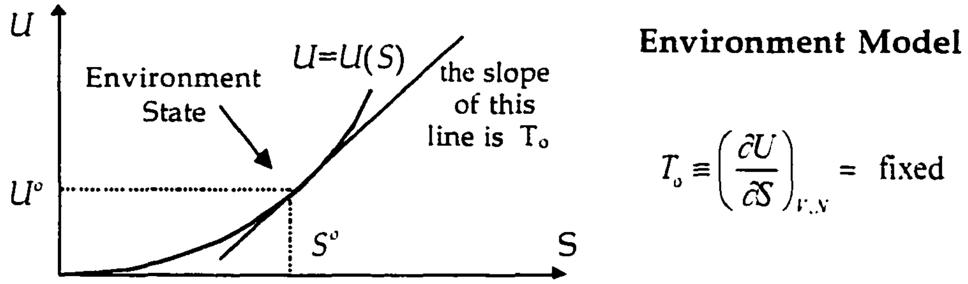


Figure 5-2: Temperature of the environment; the slope of *U=U(S)*.

When the entropy of the environment is increased at the rate $\dot{S}$ by BR conversion the energy must be increased at a rate of $T_o\dot{S}$. Note that for TR conversion $\dot{E}$ and $\dot{S}$ are net quantities due to absorption of solar radiation (SR) and inherent emission, see section 6.2. This relation between the energy and entropy transfer to the environment is analogous to the production of work by the Carnot heat engine, as depicted in Figure 5-3. The entropy flux ($\dot{S}$) due to heat conduction must be completely diverted to the environment with an energy flux $T_o\dot{S}$.

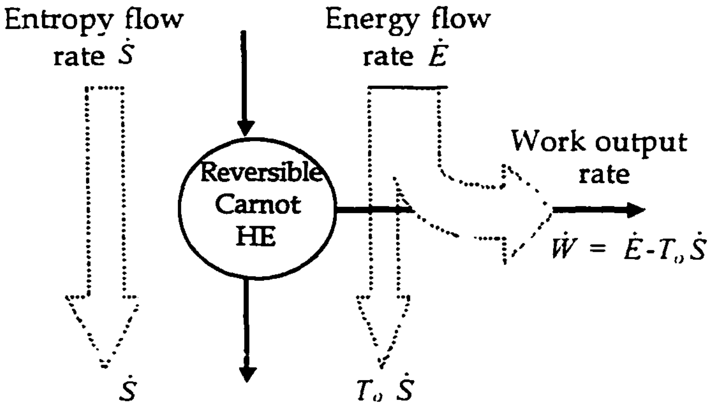


Figure 5-3: Energy and entropy flow rates for the reversible Carnot heat engine.

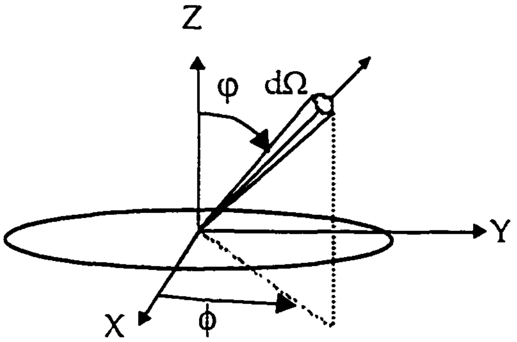
5.3 Reversible Conversion of BR Fluxes

From a solar engineering perspective it appears that the conversion of BR is inherently irreversible and consequently that Petela's BR exergy result for the enclosed system is not relevant. For example, Jeter [26, p. 79] feels that Petela's exergy is not representative of an actual utilization (conversion) process and states that Petela's result "is the correct formulation for the availability of cavity radiation ... however, it is not the result applicable to the collection and conversion of solar energy." Expressing a similar view, Bejan [11, pp. 495–496] states his viewpoint that "η_P (Petela's efficiency) is no more than a convenient albeit artificial way of non-dimensionalizing the calculated work output" and that Petela's efficiency "is not a 'conversion efficiency.' "

Petela's parallel-plate approach for determining the exergy flux of BR offers no insight in resolving the question of inherent irreversibility for BR conversion. This is because the parallel-plate approach is only valid if it is assumed that reversible BR conversion is possible. Reversible conversion is implied because it is assumed that no part of the entropy production rate is inherent and thus the entropy production rate is directly proportional to the exergy destruction rate (Gouy-Stodola theorem applied to TR).

However, the fact that reversible conversion of an enclosed BR system is theoretically possible requires that reversible conversion of BR fluxes is theoretically possible as well. This is a consequence of the fact that the exergy radiance of BR at any point in the enclosed system is geometrically related to the internal exergy of the system. Also, the exergy radiance of BR must be independent of whether it is incident on a conversion device or inside an enclosure. Thus, Petela's BR exergy result for the enclosed system does represent the theoretical upper limit for the conversion of BR fluxes. After considering the geometric relationship between the internal exergy of the enclosed system and the BR exergy radiance, we will consider how reversible conversion of BR fluxes might be achieved.

At any location within the enclosed BR system discussed in section 5.1 there are BR fluxes travelling in every direction. Figure 5-4 depicts a small pencil of rays (*dΩ*) at an arbitrary location in the BR system centered about an arbitrary direction.



An infitesimal cone of directions with solid angle dΩ, at an arbitrary location in the BR system, centered about an arbitrary direction.

Figure 5-4: Infinitesimal pencil of rays of isotropic radiation.

The BR in the cavity is isotropic and uniform so the energy and entropy radiances at any point are geometrically related to the specific (per volume) internal energy and entropy, respectively:

$$K = \frac{c}{4\pi}\frac{U}{V} = \frac{uc}{4\pi} \qquad \text{and} \qquad L = \frac{c}{4\pi}\frac{S}{V} = \frac{sc}{4\pi} \tag{5.2}$$

Further explanation of this geometric relationship for isotropic TR is provided elsewhere (e.g., Planck [12, p. 21] and Jakob [27, p. 29]). Exergy is a fundamental quantity like energy so the *exergy radiance* (N) of BR is likewise related to the *specific internal exergy* (Ξ_{BR}/V) of the enclosed BR system. Thus, using equation (4.5) we have

$$N_{BR} = \frac{c}{4\pi}\frac{\Xi_{BR}}{V} = \frac{\sigma}{a\pi}\frac{\Xi_{BR}}{V} = \frac{\sigma}{\pi}T^4\left[1 - \frac{4}{3}\frac{T_o}{T} + \frac{1}{3}\left(\frac{T_o}{T}\right)^4\right] \tag{5.3}$$

To support the validity of reversible conversion of BR fluxes consider the thermal conversion device depicted in Figure 5-5. The BB material is isolated from its surroundings except that it is thermally connected to the environment through a reversible Carnot heat engine. The conversion device is thus a combination of the BB material and the Carnot heat engine (HE).

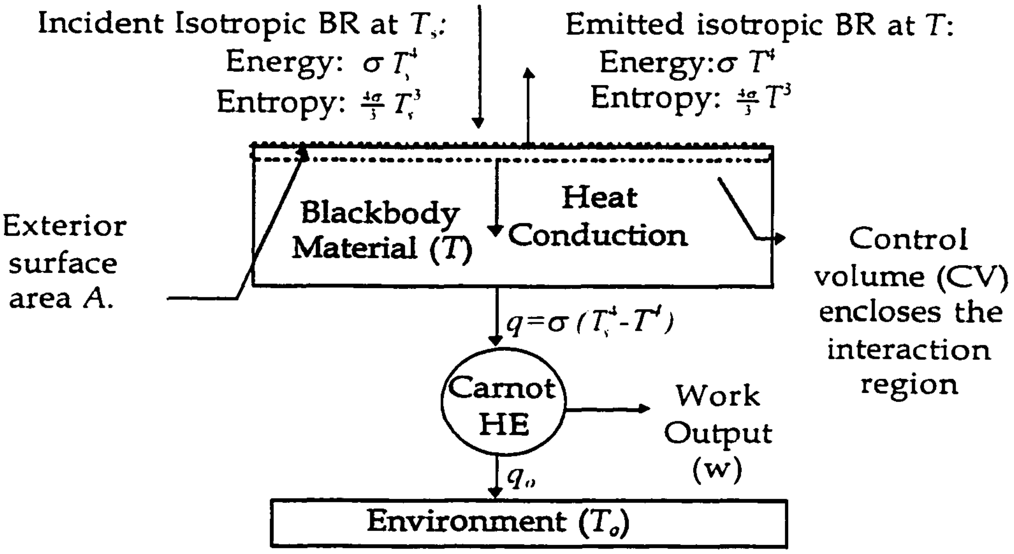


Figure 5-5: Blackbody thermal conversion device.

The incident isotropic and uniform BR was emitted by a material at temperature T_S (source) and the collector is at temperature T. The material of the collector has infinite thermal conductivity to ensure that the temperature is uniform and that there is no entropy production associated with heat conduction. The entropy production ($\dot{\Pi}_{RM}$) rate in the CV per unit area is

$$\frac{\dot{\Pi}_{RM}}{A} = \left(\frac{q}{T} + \frac{4\sigma}{3}T^3\right) - \frac{4\sigma}{3}T_s^3 = \frac{4\sigma}{3}\left(T^3 - T_s^3\right) + \frac{\sigma\left(T_s^4 - T^4\right)}{T} \tag{5.4}$$

where A is the area of the upper surface of the CV. This may be re-arranged as

$$\frac{\dot{\Pi}_{RM}}{A} = \frac{\sigma}{T}\left[T_s^4 - \frac{4}{3}TT_s^3 + \frac{1}{3}T^4\right] \qquad (5.5)$$

The work output per unit area of the collector is

$$\frac{W}{A} = q\left(1 - \frac{T_o}{T}\right) = \frac{\sigma}{T}\left(T_s^4 - T^4\right)\left(T - T_o\right) \qquad (5.6)$$

When $T_s > T$ the entropy production rate in equation (5.5) is non-zero and the converter operation is irreversible. However, when the source and collector temperature have an infinitesimal difference, the work output rate is infinitesimal, and the converter operation is reversible. This can be seen by considering the limit as T approaches T_s of the ratio of the entropy production rate (Eq. 5.5) to the work output rate (Eq. 5.6):

$$L = \underset{T \to T_s}{\mathit{Limit}}\left(\frac{\dot{\Pi}_{RM}}{W}\right) = \underset{T \to T_s}{\mathit{Limit}}\left[\frac{\frac{1}{3}T^4 - \frac{4}{3}TT_s^3 + T_s^4}{\left(T - T_o\right)\left(T_s^4 - T^4\right)}\right] \qquad (5.7)$$

The numerator and denominator both approach zero. Using L'Hopital's rule this is equivalent to the limit as T approaches T_s of the ratio of the independently differentiated numerator and denominator:

$$L = \underset{T \to T_s}{\mathit{Limit}}\left[\frac{\frac{4}{3}\left(T^3 - T_s^3\right)}{-5T^4 + 4T_oT^3 + T_s^4}\right] = \frac{\mathit{zero}}{\mathit{non-zero}} = 0 \qquad (5.8)$$

Thus, in the limit T approaches T_s the entropy production rate approaches zero faster than the work production rate. Figure 5-6 shows a qualitative plot of the work production rate versus the entropy production rate. At the point (0,0), that is at $T=T_s$, the slope is zero.

This result is analogous to De Vos' [7] conclusion for quantum conversion in which he stated that at near open circuit condition (absorbed radiation equal to emitted radiation) for the photovoltaic converter the "photon transfer goes to zero in the 1st order while entropy production rate in the 2nd order". This result for thermal and quantum conversion of TR is analogous to the reversible operation of the Carnot heat engine. To obtain reversible heat conduction to and from the Carnot heat engine the temperature differences must be infinitesimal. With respect to practical operation the reversible Carnot heat engine is a zero power device. Thus, for both TR conversion and the production of work from heat conduction, reversible work production is only achieved with heat transfer across an infinitesimal temperature difference.

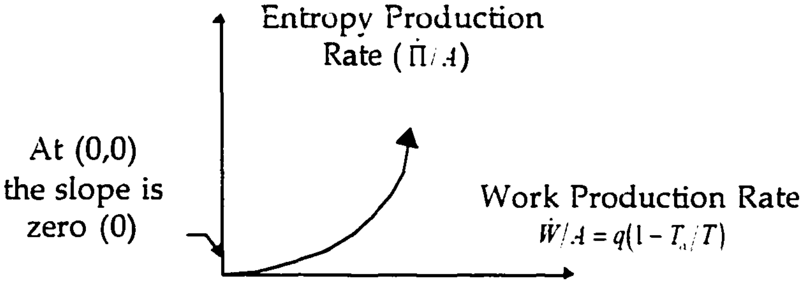


Figure 5-6: Entropy production rate versus work production rate.

So BR conversion is reversible when there is an infinitesimal difference between the converter temperature and the BR source temperature. In fact this reversible conversion of BR fluxes is exactly what happens in the small thermally conducting region of the enclosed BR system in Figure 5-1 during ideal conversion.

From a statistical thermodynamics perspective one might ask what the physical source of irreversibility is in non-ideal BR conversion, such as the single-stage thermal device discussed in section 4.3.1. Net energy transfer in the absorbing material of this device is from photons (bosons) to electrons (fermions) to the lattice phonons or quantized lattice vibrations (bosons). One possibility[1] is that irreversibility occurs because the energy is transferred between groups of statistical particles with different statistical behaviour (Fermi-Dirac and Bose-Einstein). However, this process occurs in infinitesimal BR conversion, as occurs in the system of Figure 5-1, and is reversible.

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[1] This explanation originated when Dr. Whale introduced this idea in research meetings with Dr. Scott. Dr. Whale and Dr. Haddow.

Thus, it is more likely that irreversibility occurs in non-ideal BR conversion due to energy transfer between groups of statistical particles that are in dis-equilibrium with each other. For example, when dis-equilibrium exists between the fermions (electrons) and the phonons this results in heat transfer across a finite temperature difference and entropy production. This occurs, for example, when the magnetic field is suddenly reversed in a magnetic spin system: the electrons quickly establish equilibrium with each other but are in dis-equilibrium with the lattice.

The fact that reversible conversion can occur when the temperature difference is infinitesimal means that thermal conversion of a BR source flux would be reversible if there were an infinite series of absorption/emission stages with infinitesimal temperature differences between each stage. As an example of how such a multiple-stage absorption/emission device might physically operate consider the two-stage device in Figure 5-7. The incoming source flux enters stage 1 of the device and outgoing BR leaves the final stage at temperature T_N. Each consecutive stage is at a lower temperature, receiving BR from the previous stage and emitting BR to the following stage.

The physical aspect of directing the thermal radiation fluxes has been isolated to "black box" devices. Consider stage 2 as an example. The incoming BR flux from stage 1 is re-directed into stage 2 while the outgoing BR is re-directed to stage 3. From a theoretical perspective the black-box is acceptable because simply re-orientating the TR does not necessarily change its energy or entropy.

In a practical sense an infinite stage device is not possible. However, the use of even two stages is a practical possibility and results in a substantial increase in efficiency. Consider the two-stage thermal (TST) device depicted in Figure 5-8.

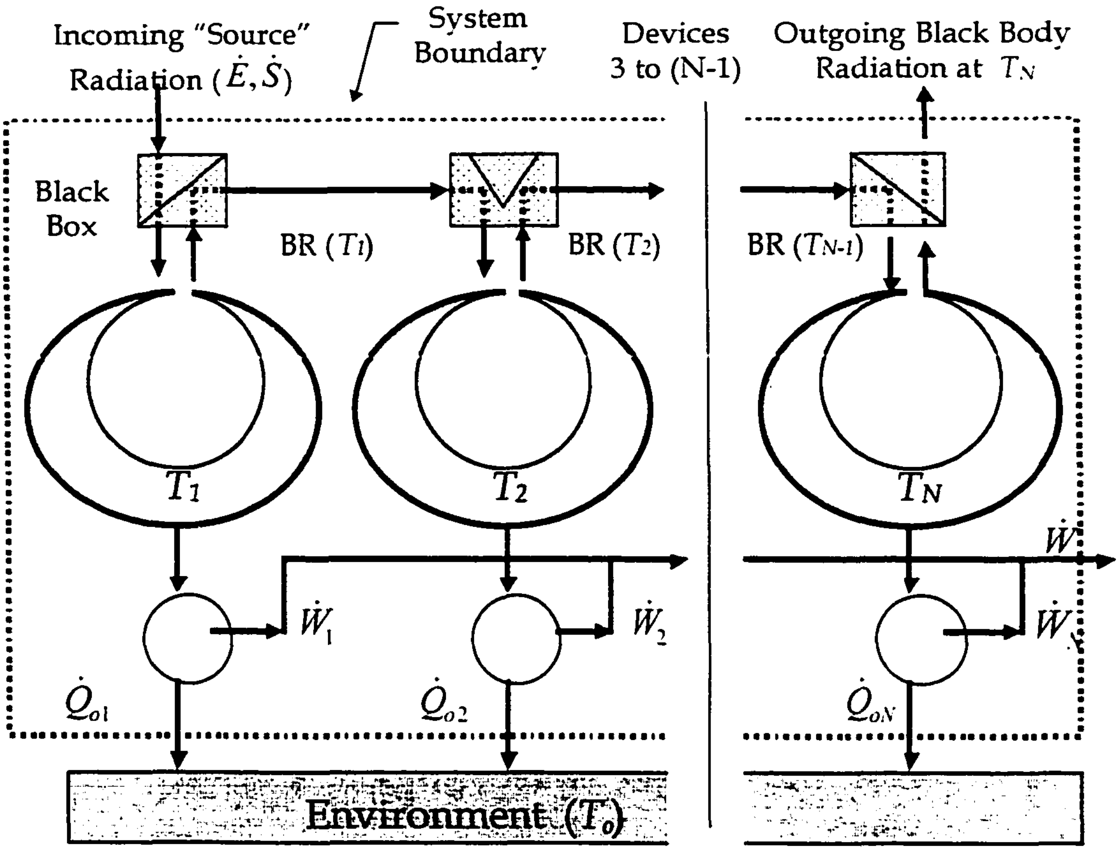

Figure 5-7: Multistage thermal conversion device.

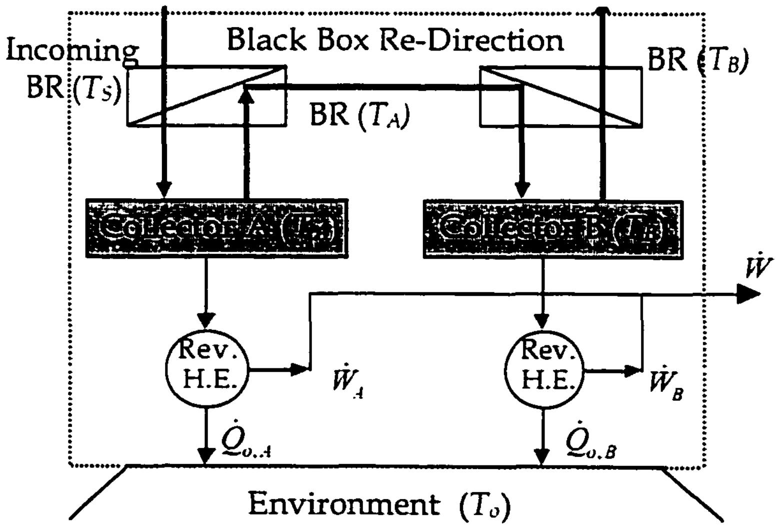

Figure 5-8: Two-stage thermal (TST) conversion device.

For simplicity a flat blackbody absorber is specified in Figure 5-8 rather than the collection device that could be made of non-blackbody absorbing material in Figure 5-7.

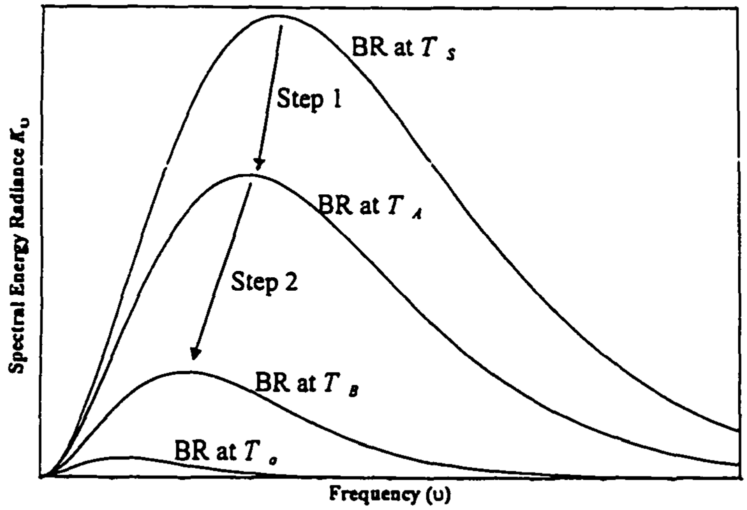

Figure 5-9: Energy spectrums for two-stage thermal (TST) conversion of BR.

In collector A the BR at T_S is absorbed and BR at T_A is emitted (step 1). In collector B, BR at T_A is absorbed and BR at T_B is emitted (step 2). The BR energy spectrums for this two-stage conversion process are depicted in Figure 5-9.

The total work output from the two stages is

$$W = \sigma A\{(T_S^4 - T_A^4)(1 - T_o/T_A) + (T_A^4 - T_B^4)(1 - T_o/T_B)\} \tag{5.9}$$

and upon introducing dimensionless temperature ratios $\theta = T/T_o$ we have

$$W = \sigma A T_o^4\{(\theta_S^4 - \theta_A^4)(1 - 1/\theta_A) + (\theta_A^4 - \theta_B^4)(1 - 1/\theta_B)\} \tag{5.10}$$

The first law efficiency is thus

$$\eta = \frac{W}{\sigma A T_S^4} = \theta_S^{-4}\left\{(\theta_S^4 - \theta_A^4)\left(1 - \frac{1}{\theta_A}\right) + (\theta_A^4 - \theta_B^4)\left(1 - \frac{1}{\theta_B}\right)\right\} \tag{5.11}$$

The maximum power, or maximum energy efficiency, was determined by finding optimum values for θ_A and θ_B for a particular value of θ_S subject to the constraint:

$$1 \le \theta_B \le \theta_A \le \theta_S \tag{5.12}$$

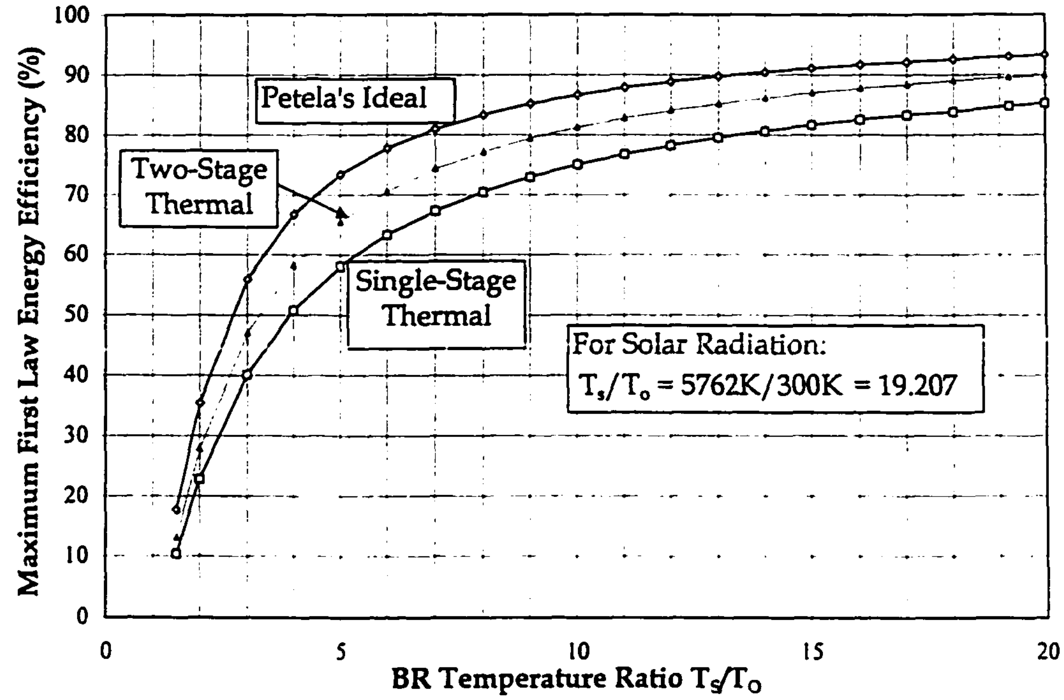

Figure 5-10: Maximum first-law energy conversion efficiencies for BR; Petela's ideal efficiency, single (SST) and two-stage thermal (TST) processes.

The maximum first law energy efficiencies for ideal conversion (Petela's BR exergy), single-stage and two-stage thermal conversion are presented in Table 5-1 and Figure 5-10 as a function of the BR source temperature ratio θ_S. The second-law exergetic efficiencies will be considered in section 8.2.

For SR approximated as BR with emission temperature of 5762 K, and an environment temperature of 300 K, the temperature ratio θ_S is equal to 19.21. For this condition Petela's efficiency (using equation (4.6)) is 93.1% compared to the single-stage thermal efficiency of 84.9% and the two-stage thermal efficiency of 89.7% (from equation (5.11) when θ_A =12.5 and θ_B =5.9).

Table 5-1: Maximum first-law energy conversion efficiencies for BR conversion

θ_S	Energy Efficiency (%)			Optimum Temperature Ratios		
	Petela's	Two-Stage Thermal	Single-Stage Thermal	θ	θ_A	θ_B
1.5	17.70	13.09	10.36	1.257	1.341	1.175
2	35.42	27.85	22.80	1.513	1.685	1.353
3	55.97	47.08	40.12	2.004	2.367	1.697
4	66.80	58.28	50.86	2.470	3.037	2.022
5	73.39	65.52	58.11	2.915	3.698	2.331
6	77.80	70.57	63.33	3.343	4.349	2.627
7	80.97	74.30	67.29	3.758	4.994	2.912
8	83.34	77.17	70.41	4.162	5.633	3.188
9	85.19	79.45	72.93	4.556	6.266	3.455
10	86.67	81.30	75.01	4.942	6.895	3.716
11	87.88	82.84	76.76	5.320	7.520	3.970
12	88.89	84.13	78.26	5.691	8.141	4.218
13	89.74	85.24	79.56	6.057	8.759	4.462
14	90.48	86.20	80.69	6.416	9.374	4.701
15	91.11	87.04	81.69	6.771	9.986	4.936
16	91.67	87.78	82.58	7.121	10.595	5.168
17	92.16	88.44	83.38	7.467	11.202	5.395
18	92.59	89.02	83.86	7.809	11.806	5.619
19.207	**93.06**	**89.66**	**84.89**	**8.216**	**12.533**	**5.887**
20	93.33%	90.03%	85.36%	8.481	13.009	6.060

The physical re-direction of the BR emitted from stage 1 has been represented by 'black-box' devices. One possibility for the inner workings of the black box re-direction device is that the material used has directionally dependent absorption, reflection and transmission properties. The material in the re-direction device would transmit the relatively high-frequency incoming solar radiation while reflecting the emitted BR from stage 1. Regardless, the use of the black-box re-direction device in Figures 5-7 and 5-8 is acceptable from a theoretical perspective because, as pointed out earlier, simply re-orientating the TR does not necessarily change its energy or entropy.

5.4 General Balance Equations for a Control Volume Corrected for TR Heat Transfer

Thermodynamic texts are often misleading because they state that heat transfer has three forms, conduction, convection and radiative transfer, and then proceed to evaluate the entropy and exergy flux of heat transfer in a way that does not apply to TR transfer. The balance equations for a control volume that are stated in thermodynamic texts were discussed in section 2.6. Correct evaluation of the entropy and exergy flux (irradiance) of TR allows these general balance equations to be more accurately re-stated. The energy balance equation for a control volume is the same when TR transfer is involved:

$$\frac{dE_{CV}}{dt} = \int_{CV\ boundary} q\ dA - \left(\dot{W}_{CV} - P_o \frac{dV_{CV}}{dt}\right) + \sum_i \dot{m}_i h_i \tag{5.13}$$

where q is the summation of all three forms of heat transfer: conduction, convection, and TR transfer. However, the entropy balance equation must be stated as

$$\frac{dS_{CV}}{dt} = \int_{CV\ boundary} \left[\frac{q_{cc}}{T_b} + J_{Net}\right] dA + \sum_i \dot{m}_i s_i + \dot{\Pi}_{CV} \tag{5.14}$$

where J_{Net} is the net entropy flux (irradiance) of TR and q_{cc} is the heat transfer not due to TR transfer ($q_{cc} = q - H_{Net}$ where H_{Net} is the net energy flux of TR). The thermal-mechanical exergy balance equation is likewise

$$\frac{d\Xi_{CV}}{dt} = \int_{CV\ boundary} \left[q_{cc}\left(1 - \frac{T_o}{T_b}\right) + M_{Net}\right] dA - \left(\dot{W}_{CV} - P_o \frac{dV_{CV}}{dt}\right) + \sum_i \dot{m}_i (h_i - T_o s_i) - \dot{I}_{CV} \tag{5.15}$$

where M_{Net} is the net exergy flux (irradiance) of TR. Note that chemical exergy, kinetic energy, and gravitational potential energy have not been included in the above equations. Also, the subscript i is used to indicate flows into the system so any outgoing mass flows would have a negative sign.

Chapter 6 The Effect of Inherent Emission on TR Conversion

All material that absorbs TR must also emit TR. Thus, any TR conversion device inherently emits TR. Researchers in solar engineering usually feel that inherent emission cannot be ignored while other researchers state that inherent emission can be ignored to determine the maximum work output for TR conversion. For example, Landsberg [28, p. 2786] gives the impression that inherent emission can be ignored by presenting the photon exergy flux as the energy flux minus the product of the environmental temperature and the entropy flux ($H - T_o J$), with no term for inherent emission. Further, some researchers indicate that inherent emission by the conversion device would reduce the maximum ideal work output.

In section 6.1 it is shown that the analysis of Petela's parallel-plate approach gives the impression that the exergy irradiance of BR is $H - T_o J$ with no inherent emission term. However, this is a misunderstanding that arises because the Guoy-Stodola theorem, used in Petela's approach, can only give the *net* exergy flux of TR while the inherent emission terms cancel out in a net exergy flux calculation.

In section 6.2 it is shown that inherent emission is a fundamental issue that cannot be ignored in determining the maximum work obtainable from TR fluxes. The requirements for ideal conversion of BR fluxes are illustrated using a black-box conversion device and the effect of inherent emission on the work output from this ideal device is discussed.

6.1 Comparison of Petela's Approaches

An analysis of Petela's parallel-plate approach gives the impression that the TR exergy flux is the energy flux minus the product of the environmental temperature and the entropy flux, thereby indicating that there is no inherent emission term.

Consider Petela's one-dimensional parallel-plate method, depicted in Figure 6-1. One BB surface is at temperature T while the other is at T_o. Steady-state TR transfer occurs in the vacuum region between the two plates. The exergy transfer rate by TR is calculated as the incoming exergy flux by heat conduction minus the exergy destruction rate in the control volume (CV). The CV is chosen such that only heat conduction occurs at its inner boundary.

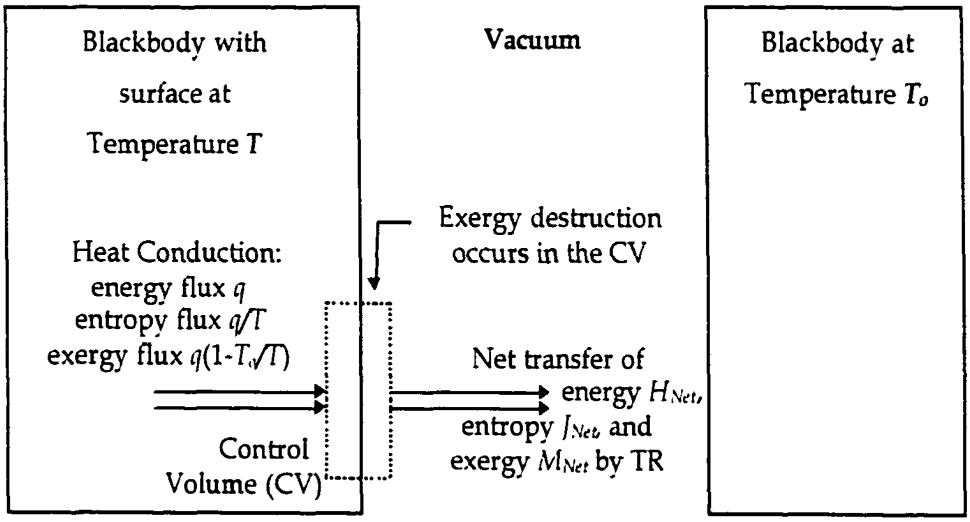

Figure 6-1: Petela's parallel-plate approach.

Based on the Gouy-Stodola theorem the net exergy flux by TR is equal to the incoming exergy flux by heat conduction minus the exergy destruction rate in the CV. In section 4.2.1 it was shown that this results in a net exergy flux by TR given by

$$M_{Net} = H_{Net} - T_o J_{Net} \qquad (6.1)$$

or, in an equivalent expression,

$$M_{Net} = \left(H - T_o J\right)^{BR}_{at\ T} - \left(H - T_o J\right)^{BR}_{at\ T_o} \qquad (6.2)$$

Upon using equation (3.3) for BR at T and T_o we have

$$M_{Net} = \sigma\left(T^4 - \tfrac{4}{3} T_o T^3\right) - \left(-\tfrac{1}{3}\sigma T_o^4\right) \qquad (6.3)$$

If instead one surface is at temperature T_1 while the other is at $T_2 > T_1$ then the net exergy flux is

$$M_{Net} = \left(H - T_o J\right)_{\substack{BR \\ at\ T_2}} - \left(H - T_o J\right)_{\substack{BR \\ at\ T_1}} \tag{6.4}$$

In equations (6.2) and (6.4) it appears that the exergy flux of any BR (whether at T, T_1, T_2, or T_o) is $H - T_o J$, with no inherent emission term. However, this appearance is not the case. The misunderstanding arises because the Guoy-Stodola theorem can only give the *net* exergy flux by TR while the inherent emission terms cancel out in the net exergy flux expression.

To emphasize the fact that $H - T_o J$ is not the exergy flux of BR consider the following. The exergy of the enclosed BR system in the dead state is zero. Inherent emission causes the final dead state of the system to be BR at T_o. Thus, the exergy flux of BR at T_o is zero because the exergy flux of BR, within the same environment, must be the same regardless of where it is located; whether in the enclosed system of section 5.1 or between the parallel plates of section 4.2.1. However, the expression $H - T_o J$ gives a non-zero negative value for the exergy of BR at T_o and therefore is not the correct expression for the exergy flux of BR.

Since the exergy flux of BR at T_o is zero, Equation (6.3) represents the exergy of BR at T alone. The second term in equation (6.3) is determined by the energy and entropy flux of BR at T_o, yet it represents the effect of inherent emission on the exergy of BR at T. Note that if instead absorption was not accompanied by inherent emission, then the dead state of the enclosed system would be a state devoid of TR and the expression $H - T_o J$ would represent the exergy flux of BR.

It is logical to expect that inherent emission would always tend to reduce the work output obtainable from BR conversion. However, this is not the case as is explained in the following section.

6.2 An Additive Inherent Emission Term for the Exergy Flux of TR

It is true that inherent emission by a non-ideal thermal conversion device reduces the work output because the TR emitted by the converter is well above T_o. Also, inherent emission by common conversion devices results in substantial irreversibility. For example, see section 8.3 for omnicolor conversion. Researchers have indicated that inherent emission has a negative effect on ideal conversion as well. For example, Landsberg [8, p. 563] states that Petela's efficiency is "pulled down below the Carnot efficiency because of the black-body emission from the converter which does not contribute to the useful work output."

However, the reverse is true for ideal conversion because inherent emission has a beneficial effect. The reason for this reversal can be seen by considering the reversible black-box conversion device depicted in Figure 6-2. The device absorbs the incoming isotropic BR with emission temperature T and emits BR at T_o with zero exergy flux.

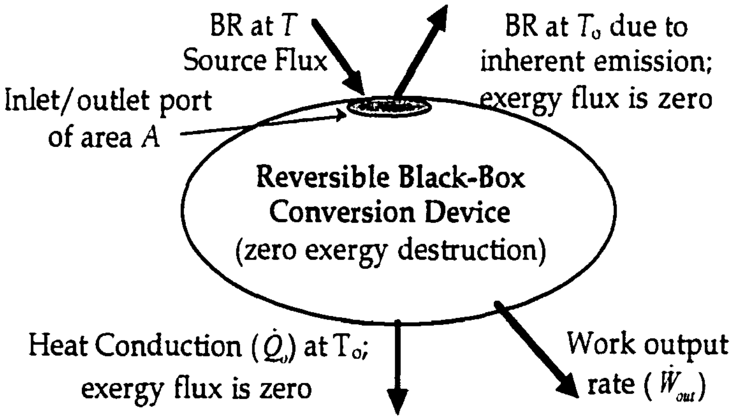

Figure 6-2: Black-box model for ideal BR conversion.

There is no entropy flow with work transfer so the entropy of the source radiation can leave the device by only two paths; BR at T_o and heat conduction at T_o. Note that for the Carnot heat engine there is only one path by which entropy leaves the device, by heat conduction at T_o (see Figure 5-3). The entropy-to-energy ratio of heat conduction at T_o is equal to $1/T_o$ while that of BR at T_o is equal to $(4/3)/T_o$. Although BR at T_o and heat conduction at T_o both have a zero exergy flux, BR at T_o is a better means of rejecting entropy to the environment than heat conduction at T_o because the required energy flow rate to the environment is lower. As a result, inherent emission results in an additive term ($+\frac{1}{3}x^4$) in the exergy expression for ideal reversible conversion:

$$W_{out} = \sigma A T^4\left(1 - \tfrac{4}{3}x + \tfrac{1}{3}x^4\right) \tag{6.4}$$

The reason that the Petela efficiency ($W_{out}/\sigma A T^4$) is less than the Carnot efficiency ($1 - x$) is not due to inherent emission, but rather to the fact that the source flux has a high ratio of entropy to energy resulting in the 4/3 factor in the second term of (6.4). That is, the entropy flux of BR at T is a factor of 4/3 higher than that of heat conduction at T with the same energy flux.

When calculating the exergy flux care must be taken not to count the inherent emission term more than once. Confusion in this regard may occur when there are multiple TR spectrums, such as emitted and reflected, travelling in the same direction. Also, when calculating the net exergy flux from a surface the inherent emission term will cancel out. However, leaving the inherent emission term in the exergy flux expression allows one to understand the contribution of each TR flux to the net exergy flux. This is particularly important in some cases such as when there is virtually no TR travelling in a certain direction (see section 6.3). Keeping in mind that the presence of the inherent emission term is essential in determining the maximum work output obtainable for TR conversion.

Inherent emission is a benefit in ideal conversion yet it is considered a hindrance when relatively high temperature TR is emitted by a conversion device in practice. One may argue that a thermal conversion device could absorb a BR source without emitting TR if its temperature was near absolute zero. However, such a device could not operate in a work producing mode because the converter temperature must be between the source and environment temperatures. The net effect of the absorption of source radiation would simply be to cause exergy destruction in the device. The absorption of the source TR would have the same effect as any heat load on such a cryogenic device.

6.3 Non-zero exergy flux when there is no TR Present

An interesting implication of Petela's result for the exergy flux of BR is that when the emission temperature of the BR approaches absolute zero, the condition when there is no TR, the exergy irradiance approaches a non-zero value. This can be explained as follows. First recall that by definition the environment is in an equilibrium state and thus filled with BR at T_0. Now consider a system consisting of an evacuated cavity with perfectly isolating walls and devoid of any TR. The system is not in equilibrium with its environment, as there is a spontaneous tendency for the system to be filled with BR at T_0 upon the removal of the thermal restraint. Thus, the system has a non-zero exergy. Similarly, the exergy irradiance at any location in the system is non-zero because it is geometrically related to the specific internal exergy of the enclosed system.

Chapter 7 Inherent Irreversibility and Non-Blackbody Radiation (NBR) Exergy

In chapter 5 it was shown that reversible conversion of BR is theoretically possible. However, in this chapter evidence will be presented that suggests that the conversion of NBR is inherently irreversible. Petela's parallel plate approach for determining exergy will be re-worked for NBR fluxes and it will be shown that it is equivalent to Karlsson's result for NBR exergy. Using an enclosed system approach for NBR exergy a new expression for NBR exergy flux will be presented and compared to Karlsson's result.

7.1 Petela's Approach Extended for NBR Fluxes

Petela's [5] parallel-plate approach can be extended to consider NBR fluxes. In Figure 7-1[1] one surface is a GB at T with emissivity ε, while the other surface is a BB at T_o. The BR at T_o is partially reflected by the GB surface A so it has GR character at temperature T_o and an emissivity of 1-ε. The TR emitted from surface A is GR with emission temperature T and emissivity ε. The reflected and emitted GR is incident on and completely absorbed by the BB surface E at T_o.

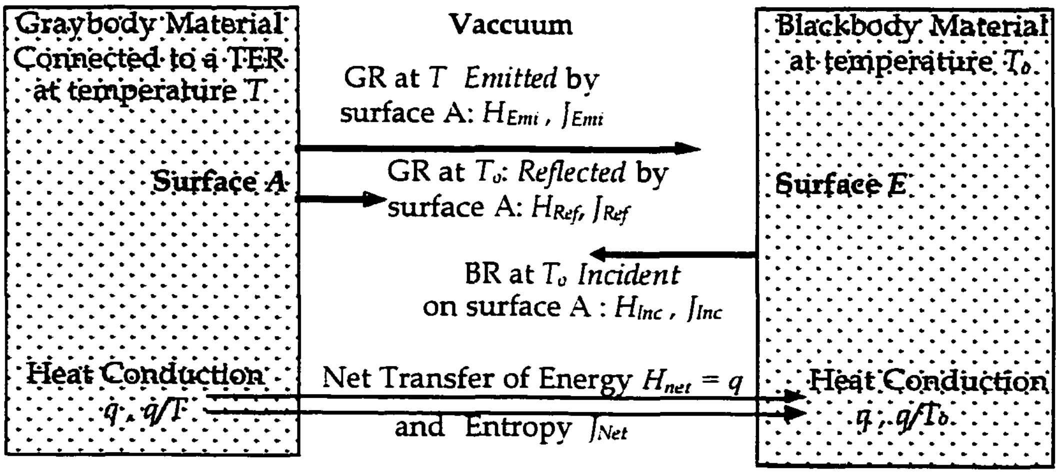

Figure 7-1: TR exchange between two parallel surfaces.

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[1] Note that for each flux in Figure 7-1 the energy and entropy fluxes are separated by a comma, for example (q, q/T).

At steady state the net energy flux by heat conduction (q) in the solid is equal to the net energy transfer rate by TR across the vacuum,

$$q = H_{\text{Net}} = H_{\substack{\text{Ref}\\ +\text{Emi}}} - H_{\text{Inc}} = H_{\substack{\text{Ref}\\ +\text{Emi}}} - \sigma T_o^4 \tag{7.1}$$

where the subscript 'Ref + Emi' refers to the combination of emitted and reflected TR. The entropy production rate per unit surface area at surface A is simply the difference between the entropy transfer rates:

$$\frac{\dot{\Pi}_{CV}}{A} = J_{\text{Net}} - \frac{q}{T} = \left(J_{\substack{\text{Ref}\\ +\text{Emi}}} - \tfrac{4}{3}\sigma T_o^3 \right) - \frac{q}{T} \tag{7.2}$$

The net transfer of exergy by TR (M_{Net}) away from surface A is equal to the incoming exergy of heat conduction q minus the irreversibility in the control volume at surface A. The net exergy flux by TR is equal to the exergy flux of the combined emitted and reflected TR alone because the exergy flux of the incident BR at T_o is zero:

$$M_{\substack{\text{Ref}\\ +\text{Emi}}} = M_{\text{Net}} = q\left(1 - \frac{T_o}{T}\right) - T_o \frac{\dot{\Pi}_{CV}}{A} = q - T_o J_{\substack{\text{Ref}\\ +\text{Emi}}} + \tfrac{1}{3}\sigma T_o^4 \tag{7.3}$$

After substituting for q using Equation (7.1) we have

$$M_{\substack{\text{Ref}\\ +\text{Emi}}} = H_{\substack{\text{Ref}\\ +\text{Emi}}} - T_o J_{\substack{\text{Ref}\\ +\text{Emi}}} + \tfrac{1}{3}\sigma T_o^4 \tag{7.4}$$

The combined emitted and reflected energy spectrum is arbitrary so clearly this result applies to TR with any spectrum. For GR at T alone we have

$$M_{GR} = H_{GR} - T_o J_{GR} + \tfrac{1}{3}\sigma T_o^4 \tag{7.5}$$

where the energy and entropy flux of GR is given in section 3.1. For any NBR the exergy flux is

$$M_{NBR} = H_{NBR} - T_o J_{NBR} + \tfrac{1}{3}\sigma T_o^4 \tag{7.6}$$

7.2 Review of Karlsson's Approach for NBR Exergy and Comparison to Petela's Approach Extended for NBR Fluxes

Karlsson's [21] result (4.23) for monochromatic radiation applied to NBR is equivalent to the result from Petela's approach extended to NBR fluxes, Equation (7.6). These approaches are based on the Guoy-Stodola theorem and assume that reversible conversion of NBR is theoretically possible. The difference in these approaches is that Karlsson's approach eliminates the NBR emitting surface present in Petela's approach and thus the need to consider reflected radiation.

With reference to the definition of the environment, in Petela's and Karlsson's approach a BB surface at T_0 with a vacuum is specified. As discussed in section 5.2, these specifications, as they are stated, give a misleading impression regarding the definition of the environment for TR exergy.

Note that Karlsson uses K and L for spectral radiances contrary to the convention employed in this thesis and introduced by Max Planck of using K and L for radiances and K_ν and L_ν for spectral radiances. Also, note that Karlsson uses other notation contrary to what is used in this thesis, Karlsson uses respectively Y, $\Delta\dot{S}$, b and B in place of A, $\dot{\Pi}$, N_ν and $\dot{\Xi}$. More importantly, Karlsson's Equations (4.20, 4.21, and 4.23) are mathematically inconsistent because they have differential intervals of frequency (dν), solid angle (dΩ), and surface area (dY) on one side of the Equation only rather than finite intervals $\Delta\nu$, $\Delta\Omega$, and ΔY, respectively.

In Karlsson's analysis the incident TR is everywhere BR at T_0 except in the small solid angle $\Delta\Omega$ and in the small frequency range $\Delta\nu$, incident on the small area ΔY. In other words, the incident energy spectrum in $\Delta\Omega$ is BR at T_0 except with an arbitrary spectral energy radiance K_ν in some small frequency interval $\Delta\nu$. Karlsson takes the exergy of the incident TR as that of the monochromatic radiation in $\Delta\nu$, implying that the exergy of the BR at T_0 in the same solid angle, in the frequency intervals excluding $\Delta\nu$, is zero at each frequency. Then the exergy of arbitrary NBR is simply the integral over frequency of Karlsson's expression for monochromatic radiation.

Also, note that the character of TR incident in other directions outside of $\Delta\Omega$ has no effect on the analysis of radiation incident in $\Delta\Omega$. This is because the entropy production rate due to TR transfer in any direction is independent of what is happening at other directions. Thus, Karlsson's specification of only BR at T_o incident and emitted in all other directions simplifies the analysis but is not a necessity. However, note that the entropy production rate due to emission in $\Delta\Omega$ can only be isolated from that due to absorption in $\Delta\Omega$ if the energy spectrums do not overlap.

Karlsson's expressions for heat flow and entropy production rate per unit area can be expressed for arbitrary incident TR as

$$q = \int_0^{\infty}\int_0^{2\pi}\int_0^{\pi/2}\left(K_\nu - K_\nu^{BR\ at\ To}\right)\sin\vartheta\cos\vartheta\, d\vartheta\, d\varphi\, d\upsilon \qquad (7.7)$$

and

$$\dot{\sigma} = \int_0^{\infty}\int_0^{2\pi}\int_0^{\pi/2}\left[\overbrace{\left(K_\nu - K_\nu^{BR\ at\ To}\right)/T_o}^{\substack{\text{Entropy transfer by}\\ \text{heat conduction}}} - \overbrace{\left(L_\nu - L_\nu^{BR\ at\ To}\right)}^{\substack{\text{Net entropy transfer}\\ \text{by TR}}}\right]\sin\vartheta\cos\vartheta\, d\vartheta\, d\varphi\, d\upsilon \qquad (7.8)$$

were the integrand of the heat flow integral is $q_{\nu\Omega}$ and that of Equation (7.8) for entropy production rate is $\dot{S}_{\nu\Omega}$. It can be straightforwardly shown that the integrand $\dot{S}_{\nu\Omega}$ is positive for any value of the emission temperature including $T<T_o$. The entropy production rate is positive regardless of whether there is a net transfer of energy by TR towards or away from the surface. The first term in the integrand $\dot{S}_{\nu\Omega}$ is the entropy transfer rate away from the surface by heat conduction and the second term is the net entropy transfer rate by TR toward the surface.

7.3 NBR Exergy Flux based on the Analysis of an Enclosed NBR System

The exergy flux of NBR can be determined by simply considering the exergy of an enclosed NBR system. As with BR discussed in section 5.3, this is possible because the exergy radiance (*N*) of isotropic TR is geometrically related to the specific (per volume) internal exergy:

$$N = \frac{c}{4\pi}\frac{\Xi}{V} \tag{7.9}$$

Consider a uniform and isotropic NBR system contained in an evacuated perfectly reflecting enclosure (Figure 7-2). The enclosure is perfectly reflecting so that the NBR does not spontaneously equilibrate to BR with the same energy. This is a necessary condition because a NBR system cannot exist in equilibrium with its emitting material. However, the NBR must interact with matter in order to be absorbed and produce work. Interaction of the NBR with a material conversion (work producing) device is unavoidable. Thus, it appears that the conversion of NBR is inherently irreversible and thus the exergy of NBR is the *maximum* work not the *reversible* work.

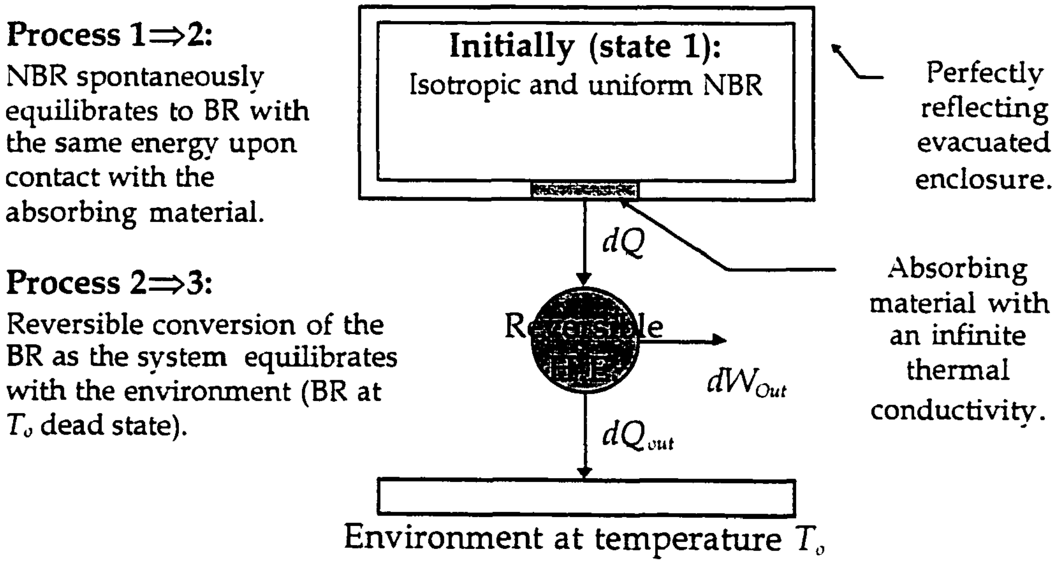

Figure 7-2: Conversion of an enclosed NBR system.

The energy of the enclosed system is fixed (U_1=U_2) during the spontaneous transition to BR while the entropy becomes

$$S_2 = \tfrac{4}{3} a^{1/4} V^{1/4} U_1^{3/4} \tag{7.10}$$

Reversible conversion of the BR is theoretically possible so the exergy of the enclosed system is that of BR with the same energy. Figure 7-3 depicts the ideal conversion for the NBR system:

Process 1⇒2:	Spontaneous irreversible transition of NBR to BR with the same energy but higher entropy (upon contact with absorbing material).
Process 2⇒3:	Reversible conversion of the BR as the system equilibrates with the environment (BR at T_o dead state).

Using Equation (5.1) the exergy of an enclosed BR system is

$$\Xi = U - T_o S + \tfrac{a}{3} T_o^4 V \qquad (7.11)$$

and after substituting for the final entropy S_2 from Equation (7.10) we have the internal exergy of the enclosed NBR system:

$$\Xi = U - T_o \left\{ \tfrac{4}{3} a^{1/4} V^{1/4} U^{3/4} \right\} + \tfrac{a}{3} T_o^4 V \qquad (7.12)$$

where the subscript for U_1 has been dropped.

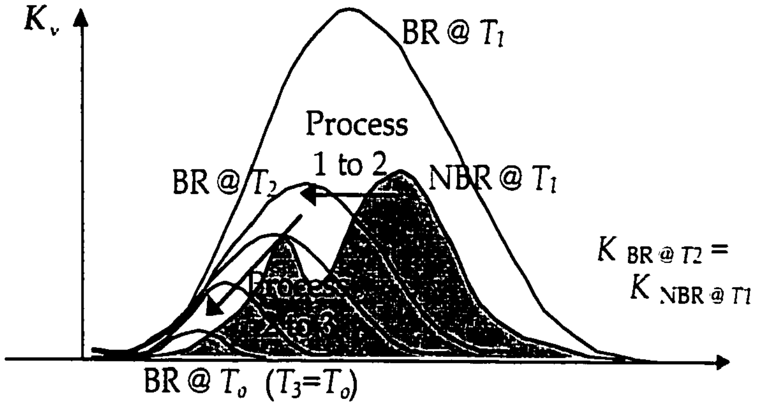

Figure 7-3: Energy spectrums for the conversion of an enclosed NBR system.

The TR system is isotropic and uniform, so by using the geometric relations in Equations (5.2) and (7.9), we arrive at the exergy radiance of NBR:

$$\boxed{N = K - T_o \left\{ \tfrac{4}{3} \left(\tfrac{\sigma}{\pi} \right)^{1/4} K^{3/4} \right\} + \tfrac{\sigma}{3\pi} T_o^4} \qquad (7.13)$$

The exergy radiance N in Equation (7.13) is a function of only the NBR energy radiance K and the environment temperature T_o: it is independent of the NBR entropy radiance L. The spectral entropy radiance L_ν spectrum of NBR is completely determined by the spectral energy radiance spectrum K_ν. This means that the exergy radiance N in (7.13) is dependent on the area (K), but independent of the shape, of the K_ν spectrum. As one would expect, Equation (7.13) for the exergy radiance of NBR reduces to Petela's result for BR.

In general, the energy radiance K of NBR must be left variable except for GR where the exergy radiance, using Equation (3.5) for the energy radiance, is

$$N = \frac{\sigma}{\pi} T^4 \left\{ \varepsilon - \frac{4}{3} \varepsilon^{3/4} x + \frac{1}{3} x^4 \right\} \tag{7.14}$$

were x is the dimensionless temperature ratio T_o/T. Table 7-1 shows the exergy of an enclosed system, exergy flow rate, exergy irradiance, and exergy radiance for general isotropic NBR and the special cases of BR and GR.

Table 7-1: Exergy Quantities for Isotropic TR.

Exergy Quantity	TR Spectrum Type		
	NBR	BR	GR
Exergy Ξ (J)	$\Xi = U - T_o \left\{ \frac{4}{3} (aV)^{1/4} U^{3/4} \right\} + \frac{1}{3} aVT_o^4$	$aVT^4 \left\{ 1 - \frac{4}{3} x + \frac{1}{3} x^4 \right\}$	$aVT^4 \left\{ \varepsilon - \frac{4}{3} \varepsilon^{3/4} x + \frac{1}{3} x^4 \right\}$
Flow Rate $\dot{\Xi}$ (W)	$\dot{\Xi} = \dot{E} - T_o \left\{ \frac{4}{3} (A\sigma)^{1/4} \dot{E}^{3/4} \right\} + \frac{1}{3} \sigma A T_o^4$	$\sigma A T^4 \left\{ 1 - \frac{4}{3} x + \frac{1}{3} x^4 \right\}$	$\sigma A T^4 \left\{ \varepsilon - \frac{4}{3} \varepsilon^{3/4} x + \frac{1}{3} x^4 \right\}$
Irradiance M (W/m^2)	$M = H - T_o \left\{ \frac{4}{3} \sigma^{1/4} H^{3/4} \right\} + \frac{1}{3} \sigma T_o^4$	$\sigma T^4 \left\{ 1 - \frac{4}{3} x + \frac{1}{3} x^4 \right\}$	$\sigma T^4 \left\{ \varepsilon - \frac{4}{3} \varepsilon^{3/4} x + \frac{1}{3} x^4 \right\}$
Radiance N (W/m^{2}sr)	$N = K - T_o \left\{ \frac{4}{3} \left(\frac{\sigma}{\pi} \right)^{1/4} K^{3/4} \right\} + \frac{\sigma}{3\pi} T_o^4$	$\frac{\sigma}{\pi} T^4 \left\{ 1 - \frac{4}{3} x + \frac{1}{3} x^4 \right\}$	$\frac{\sigma}{\pi} T^4 \left\{ \varepsilon - \frac{4}{3} \varepsilon^{3/4} x + \frac{1}{3} x^4 \right\}$

The ideal (irreversible) conversion of NBR may be illustrated by the black-box model shown in Figure 7-4. This black-box conversion is identical to that for BR conversion (Figure 6-2) apart from the fact that NBR conversion is inherently irreversible.

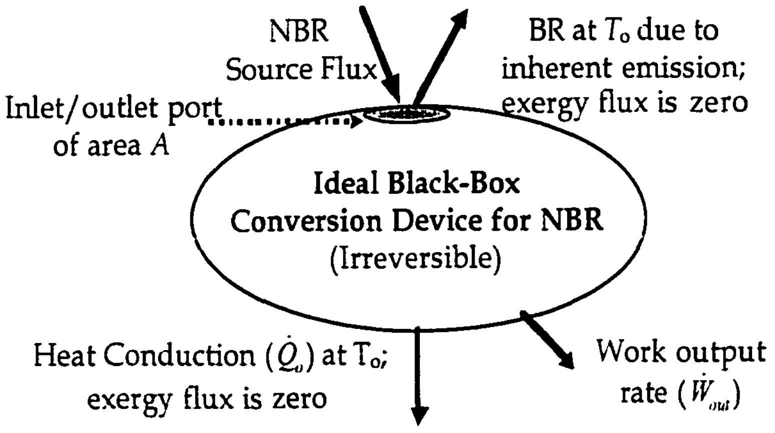

Figure 7-4: Black-box model for ideal NBR conversion.

In the following section we will compare this result to the result using Karlsson's or Petela's approach based on the Guoy-Stodola theorem.

7.4 Inherent Irreversibility and the Exergy of NBR

The production of work from NBR appears to be inherently irreversible. This is because NBR must interact with matter to produce work but the interaction of NBR with matter, including its own emitting material, appears to be an inherently irreversible entropy producing process. As seen from the analysis in section 5.1, reversible conversion of a BR system requires that equilibrium can exist between the radiation and the material of the conversion device. An enclosed NBR system will spontaneously equilibriate to BR with the same energy unless the enclosure is perfectly reflecting. Perfectly reflecting means that the NBR is not in thermal contact with its enclosure. A cavity devoid of TR inside a non-blackbody material will spontaneously and rapidly become filled with BR rather than NBR at the local temperature of the material.

Petela's and Karlsson's approaches avoid this issue in that they are based on the Guoy-Stodola theorem meaning that all entropy production is directly associated with exergy destruction. If the conversion of NBR is inherently irreversible then part of the entropy production calculated in these approaches is theoretically inherent and cannot be avoided. In this case the result using Petela's or Karlsson's approach gives a level of work output that cannot be theoretically achieved.

The only possibility for the reversible conversion of a NBR system, and the possibility of equilibrium existing between matter and a NBR system, requires that material can at least theoretically exist that absorbs and emits radiation only within an infinitesimal frequency range. In this case reversible conversion of an NBR system would be theoretically possible with an infinite series of single-frequency materials covering the whole range of frequencies of the NBR. For thermal conversion, each single-frequency material would have an initial temperature such that absorption was equal to emission and the temperature would be quasi-statically reduced to T_o producing work reversibly for each frequency of the NBR.

However, the theoretical possibility of single-frequency material is questionable. Quantum systems inherently exhibit threshold behaviour while thermal systems can do so with the proper coating materials. In omnicolor conversion the TR emission from the stack gives the impression that each cell is behaving in a single-frequency manner but this is not the case. Each cell is emitting TR with frequencies in a range above its cutoff frequency to the two cells adjacent to it, one at lower temperature and threshold frequency and the other at higher temperature and threshold frequency (see section 8.3). The geometry of the omnicolor configuration results in the emission from the stack of BR with a frequency dependent emission temperature $T(\nu)$ but the individual cells are not absorbing and emitting at a single frequency. So omnicolor conversion may emulate a series of single frequency emissions but it is important to note that the omnicolor conversion process is theoretically irreversible even for BR.

Furthermore a single frequency thermal device does not seem physically possible. Thermal vibrations in the material are by nature not confined to a single frequency. Energy is transferred from the lattice vibrations to the electrons where there is an unlimited number of possible energy level jumps above a certain minimum energy. Thus, there are a large number of possible photon energies that can occur when an electron drops to a lower energy level. Operation of a thermal conversion device requires heat transfer through the lattice. So even in the unlikely case that radiant emission could be confined to a single frequency, the associated energy transfer from the electrons (fermions) to the lattice (phonons) and then heat transfer between phonons in the lattice would be irreversible. This is because in hypothetical single-frequency operation only phonons at that particular frequency would be excited.

Evidence has been presented that suggests that NBR conversion is inherently irreversible. However, this issue of inherent irreversibility has not been definitively resolved. The following is a list of statements that are either all true if the conversion of NBR is inherently irreversible or all false if it is not:

1) Materials that emit and absorb only within an infinitesimal frequency range are not theoretically possible.
2) The exergy of NBR is the maximum ideal work but not the reversible work (based on non-equilibrium NBR entropy).
3) Petela's and Karlsson's approaches give an upper limit to the work output that is not even theoretically obtainable. Part of the entropy production rate calculated in these approaches, based on the non-equilibrium NBR entropy, cannot even be theoretically avoided.
4) The Guoy-Stodola theorem using the non-equilibrium NBR entropy is invalid or not applicable to NBR conversion.
5) The NBR exergy is a function of the area of the energy spectrum and not its shape.
6) The exergy-to-energy ratio (N/K) is the same for NBR and BR with the same energy, rather than BR having a minimum ratio for all TR with the same energy.
7) Spectral exergy radiance is not admissible and the exergy of BR at T_o cannot be said to be zero at each frequency (spectral basis).

7.4.1 Non-Equilibrium NBR Entropy

In the case that the NBR conversion is inherently irreversible it appears that the GS theorem is violated. However, it may be that the GS theorem is not applicable to NBR conversion due to the non-equilibrium nature of NBR entropy. The first issue considered in this section is whether non-equilibrium entropy of monochromatic radiation or NBR is admissible. The second question is whether exergy can be determined from non-equilibrium entropy.

Planck and Landsberg state that monochromatic radiation and NBR has a definite entropy. Planck [12, p. 92,] states that "every separate, plane polarized, monochromatic pencil has its definite entropy". This is in agreement with the fact that TR at different frequencies is propagated independently. Lansberg [8] considered a gas of bosons not necessarily in equilibrium and concluded that the result obtained from equilibrium statistical mechanics is of wider significance and represents a non-equilibrium entropy. Landsberg also concluded that Planck's result for monochromatic radiation applies to gray radiation (diluted blackbody radiation (DBR)) and that the mean occupation number is simply equal to that for BR times the emissivity. Also, Planck's result applied to NBR is consistent with the observed behaviour of TR in that the calculated entropy of NBR is always lower than that for BR with the same energy. This is a necessary condition because an isolated NBR system is unstable and will spontaneously equilibriate to BR with the same energy upon the addition of a particle of matter, meaning that the final state (BR) must have higher entropy.

Entropy is a statistical quantity so it is important to realize that monochromatic radiation travelling in a certain direction does not consist simply of a single electromagnetic wave or photon. Monochromatic radiation travelling in a certain direction is a superposition of a large number of simple periodic waves which have an arbitrary plane of polarization (for unpolarized). Viewing the radiation as a stream of photons is a useful viewpoint in many situations but it does not reveal the entire character of radiative transfer. The thermodynamic quantities of energy and entropy are mean values of the electromagnetic quantities.

The second question stated at the beginning of the section is whether exergy can be determined using a non-equilibrium entropy. Non-equilibrium NBR certainly can have a potential to do work and thus a non-zero exergy. However, the magnitude of this work for NBR conversion appears to be lower than what is calculated using the non-equilibrium NBR entropy. So the Guoy-Stodola theorem may not be applicable, rather than being viewed as violated, in the case that the conversion of NBR is inherently irreversible based on the non-equilibrium NBR entropy.

7.5 Comparison of the Result of this Study to Karlsson's Result for NBR Exergy

Based on the analysis of an enclosed NBR system the exergy radiance of NBR is

$$N = K - T_o\left\{\tfrac{4}{3}\left(\tfrac{\sigma}{\pi}\right)^{\frac{1}{4}} K^{\frac{3}{4}}\right\} + \tfrac{\sigma}{3\pi} T_o^4 \tag{7.15}$$

From Karlsson's approach (section 4.2.2), or Petela's approach extended for NBR fluxes (section 7.1), the exergy of NBR was given as

$$N_{Karl} = K - T_o\{L\} + \tfrac{\sigma}{3\pi} T_o^4 \tag{7.16}$$

The numerical difference between the present result and Karlsson's result is often relatively small. This is because the difference between the entropy of NBR (L) and the entropy of BR with the same energy can be relatively small. For example, the difference in entropy between GR and BR with same energy is within 1% for $\varepsilon > 0.5$ (see Figure 3-1). The corresponding percent difference between the enclosed system result and Karlsson's approach may be defined as

$$NPD = \frac{N_{Karl} - N}{N_{Karl}} = \frac{T_o\left\{\tfrac{4}{3}\left(\tfrac{\sigma}{\pi}\right)^{\frac{1}{4}} K^{\frac{3}{4}} - L\right\}}{N_{Karl}} \tag{7.17}$$

and for GR this becomes

$$NPD = \frac{\frac{4}{3}x\left\{\varepsilon^{\frac{3}{4}} - \frac{45}{4\pi^4}I(\varepsilon)\right\}}{\varepsilon - \frac{4}{3}\frac{45}{4\pi^4}I(\varepsilon)x + \frac{1}{3}x^4} \qquad (7.18)$$

were x is the dimensionless temperature ratio T_o/T and where NPD stands for the Percent Difference in exergy radiance N. Note that NPD is always positive, that is Karlsson's exergy result is always higher than the present result, because the entropy of NBR is always lower than the entropy of BR with the same energy. Figure 7-5 shows the percent difference in the exergy expressions versus the inverse of x for various emissivities, when $T > T_o$, using the approximation for the entropy of GR (3.9) with $C_2 = 2.311$ and $C_3 = 0.175$ (accurate to 0.16% of the actual value for $\varepsilon > 0.05$).

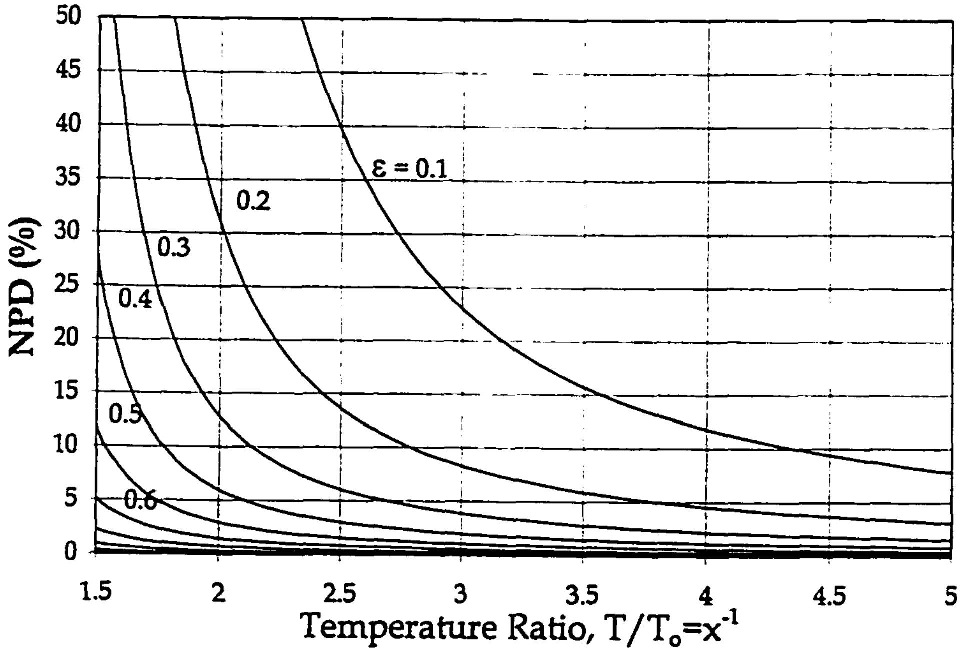

Figure 7-5: NPD versus $T/T_o = x^{-1}$, for $T > T_o$ ($x<1$).

Figure 7-6 depicts NPD versus x^{-1} for various emissivities for $T < 2.5T_o$.

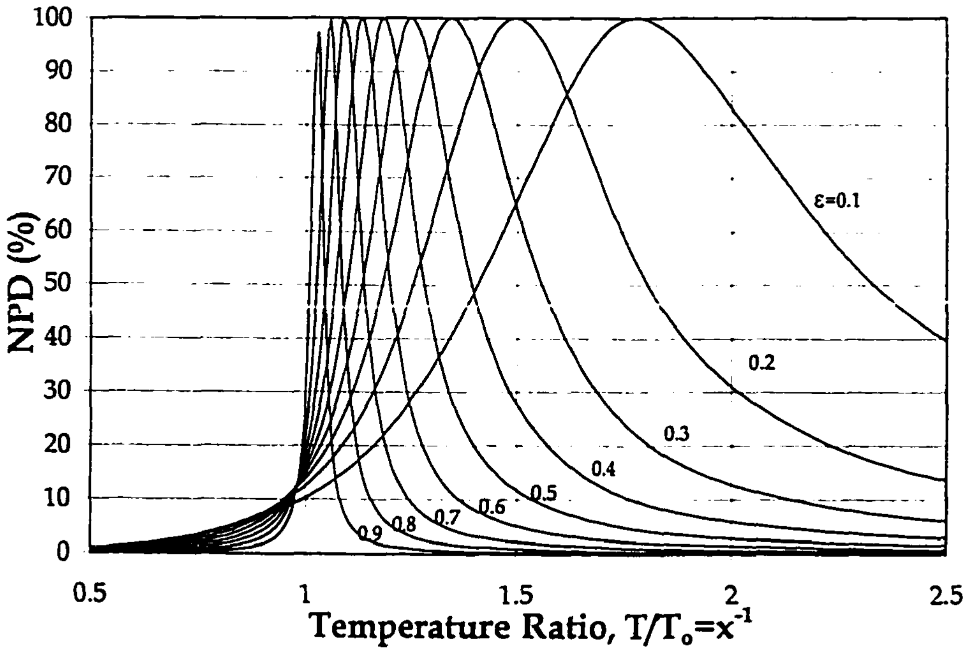

Figure 7-6: NPD versus $T/T_o = x^{-1}$, for $0.5\ T_o < T < 2.5\ T_o$.

The percent difference is generally highest for small emissivities and temperatures close to T_o (x close to unity). NPD is high for small emissivities because the percent difference between the entropy of GR and BR with the same energy increases as emissivity decreases (see Figure 3-1). For high emissivities the present result and Karlsson's result merge together and become Petela's result for BR when $\varepsilon=1$. NPD is high for temperatures close to T_o because the second term in the exergy expressions, the only term that differs between the two results, becomes more significant as x approaches unity ($T=T_o$). Quantitatively we have for any emissivities greater than 0.10 the percent difference NPD is:

- within 10% for $T > 4.36\ T_o$ and $T < 0.95\ T_o$
- within 5% for $T > 6.62\ T_o$ and $T < 0.83\ T_o$
- within 1% for $T > 24.6\ T_o$ and $T < 0.51\ T_o$

Chapter 8 Significance of TR Exergy in Solar Energy Conversion

8.1 TR Exergy - The Upper Limit to SR Conversion

In the field of solar engineering it is widely accepted that omnicolor conversion is the ideal theoretical process for solar energy conversion. For example, Haught [3] states regarding omnicolor conversion that the "results obtained are independent of the specific form of the thermal and quantum radiation conversion device and serve as an upper bound on the efficiency with which radiant energy can be converted to useful work in any actual device." In agreement with Haught, De Vos and Pauwels [4] also state that an infinite series of optimized omnicolor collectors is "the thermodynamically optimal device for converting solar energy into work."

Petela's [5] blackbody radiation (BR) exergy result is thought to neglect fundamental theoretical issues that are specific to the conversion of TR fluxes. For example, Haught [3] states that "thermodynamic treatments of the radiation field which derive the conversion efficiency from the available work content of the radiant flux neglect the limitations (re-radiation, threshold absorption, etc.) inherent in the conversion process." However, in this thesis it is shown that Petela's BR exergy result does represent the upper limit for the production of work from solar radiation (SR) fluxes approximated as BR. More precisely, SR is NBR, although it is closely approximated by BR, so the result for NBR exergy in chapter 7 precisely represents the upper limit for the work production from SR.

In this thesis Petela's result is shown to represent the upper limit to the conversion of BR fluxes by resolving three main issues as to its significance.

First, exergy is a quantity that depends on the system and its environment, so how can an environment be defined for TR? Uncertainty about the definition of the environment arose because of the unusual nature of TR in the context of exergy analysis and because in Petela's derivation a special environment of strictly BR in a vacuum is specified. Bejan [6] states that "there is no such thing as an "environment" of isotropic blackbody radiation (and pressure), as is assumed most visibly in the availability type derivation". However, in section 5.2 it was shown that the definition of environment in conventional exergy analysis completely suffices for defining TR exergy and the only relevant parameter of the environment is its temperature. It is shown that Petela's specification of a special environment in his derivation only served to isolate TR exergy from other forms of exergy and does not have any repercussions on the definition of the environment for TR exergy calculations.

Second, how is it appropriate to assume that the conversion of BR fluxes can be reversible even though it appears that the conversion of TR fluxes is inherently irreversible? De Vos and Pauwels [4] state that "the conversion of radiation into work cannot be performed ... without entropy creation." It can be readily shown that reversible conversion of an enclosed BR system is theoretically possible. In section 5.3, it is shown that reversible conversion of BR fluxes is likewise theoretically possible. This is true because the exergy flux of BR must be independent on whether it is enclosed in a cavity or incident on a conversion device.

Third, how does the inherent emission of TR affect the maximum work obtainable? Any device that absorbs TR for conversion must also emit TR. In the literature there is a lack of coherence regarding if and how inherent emission effects the upper limit to BR conversion. De Vos and Pauwels [7] state that the "power flow from the solar cell is rightly considered lost." Also Landsberg [8] comments on the effect of inherent emission when he notes that Petela's efficiency is "pulled down below the Carnot efficiency because of the black-body emission from the converter which does not contribute to the useful work output." In chapter 6 inherent emission of TR by the conversion device is indicated to be a fundamental issue that cannot be avoided. It is explained why, in contrast to non-ideal conversion, inherent emission has a beneficial effect on the maximum work output for an ideal device.

Determining the correct maximum ideal work output for TR conversion allows second law efficiencies to be defined and calculated in section 8.2 for common SR conversion processes. Common solar energy conversion devices are inherently irreversible single absorption/re-emission devices where the emitted TR, generally with non-zero exergy, is considered lost. The maximum efficiency analysis of these devices is really a maximum power optimization for particular inherently irreversible conversion processes. The non-ideal behaviour of omnicolor thermal and quantum conversion is discussed in section 8.3, and the effect of concentration on conversion efficiency is covered in section 8.4.

8.2 Second-Law Efficiencies of Common SR Conversion Processes

The resolution of Petela's BR exergy result as the true upper limit to solar-energy conversion allows second-law efficiencies to be evaluated. The second-law efficiency of a particular conversion process is simply the ratio of the maximum work output for that process to the exergy of the available SR accounting for its characteristics (e.g., isotropic or unconcentrated or attenuated by the atmosphere). Table 8-1 lists the second-law efficiencies corresponding to the first-law efficiencies in Table 4-1. Note that in Tables 4-1 and 8-1 the numerical values for the different references used are based on different values of T_S and T_o; Haught uses 6000 K and 300 K, De Vos 5762 K and 288 K, and Bejan 5762 K and 300 K.

The second-law efficiencies in Table 8-1 indicate that the performances of the conversion processes considered are more efficient than indicated by the first-law efficiencies. The second-law efficiencies are the true indicators of efficiency as they are relative to ideal conversion. The first-law efficiencies are unrealistic because they compare the work output to a theoretically unachievable upper limit, an upper limit established by assuming the energy flux of the source radiation is entirely convertible to work.

Table 8-1: Maximum second-law efficiencies (in %) for SR (approximated as BR) conversion

Conversion Process	Unconcentrated, C=1 (Haught [3])	Concentrated, C = 10,000 (Haught [3])	Isotropic Solar, C = 43,600	
			Bejan [11]	De Vos [22]
Single-Stage Thermal	57.9	85.7	91.2	91.5
Single-Cell Quantum	33.1	42.9	------	43.7
Omnicolor Conversion	73.2	90.1	92.5	93.0
Two-Stage Thermal	------	------	96.3	------

The second-law efficiencies in Table 8-1 for single-stage conversion are relatively high, especially for the isotropic case (91.2%). The single-stage efficiency is high because the temperature ratio T_S/T_o is large resulting in a relatively high value for the converter temperature (T_C) and a high value of the Carnot factor for thermal conversion ($1-T_o/T_C$). On the other hand, a high value for the converter temperature (T_C) also causes the energy loss due to emission to be higher and consequently the energy flow through the heat engine to be lower. However, the strong dependence of the BR energy flux on the emission temperature (proportional to T_C^4) reduces the significance of losses due to emission and allows the balance point for the maximum work output to be at a high converter temperature (T_C) and efficiency. Note that BR at half the emission temperature has only one sixteenth the energy flux.

For thermal conversion there is a direct correspondence between high second-law efficiency in Table 8-1 and the maximum temperatures involved in the conversion process. The efficiency of two-stage conversion is the highest (96.3%) followed by omnicolor (92.5%), and single-stage conversion (91.2%) for isotropic

SR fluxes. Correspondingly, the maximum temperatures for two-stage conversion are 1770 K and 3760 K, for omnicolor conversion work is produced from a range of temperatures with a peak near 2450 K and with significant work production at 3300 K, and for single-stage conversion is 2465 K. The operating temperature for single-stage conversion decreases to 1900 K for C = 10,000 and 860 K for unconcentrated BR.

8.3 The Non-Ideal Character of Omnicolor Conversion

The maximum efficiency (or maximum power) analysis of omnicolor conversion has been presented by many researchers as giving the upper limit to solar energy conversion [3,4]. However, from the second-law efficiency in Table 8-1 it is evident that omnicolor conversion is not the optimum conversion process for BR fluxes. For simplicity we will focus on explaining why omnicolor thermal, rather than omnicolor quantum, conversion is not the optimum conversion process for BR fluxes.

The non-ideal behavior of thermal omnicolor conversion is mainly due to irreversibilities in the conversion process because the exergy losses due to emission are very low compared to the exergy flux of the BR source flux. To clearly see the source of irreversibilities and the magnitude of losses due to emission we must first consider in detail the exchange of TR by a typical cell in the set.

A typical cell in the set absorbs a sliver of SR in the frequency range (ν,ν+dν). A typical cell also emits and receives TR from both cells adjacent to it, one at lower frequency and temperature, and the other at higher frequency and temperature (electroluminescence). Figure 8-1 depicts the exchange of TR between two adjacent cells in the set, one cell at T_1 and frequency cutoff ν_{o1}, the other cell at a higher temperature T_2 and cutoff ν_{o2}.

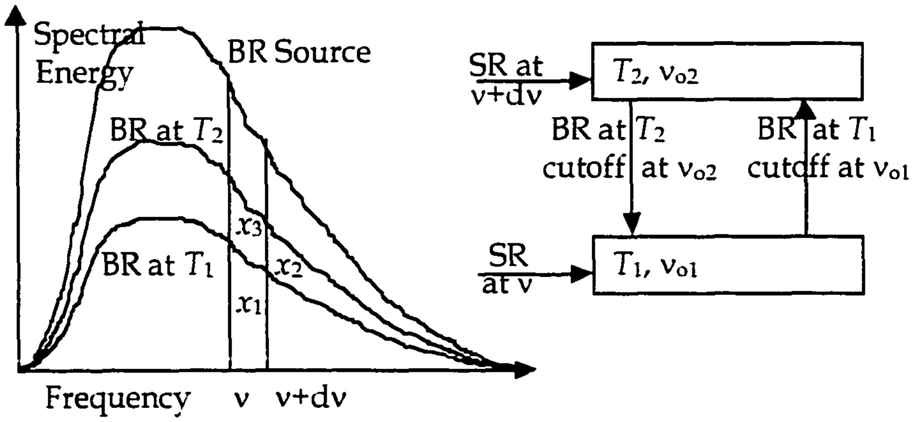

Figure 8-1: Energy spectrums for TR exchange between two adjacent cells in a set for omnicolor thermal conversion.

A portion of the TR emitted by cell 1 at T_1, represented by area x_1 in Figure 8-1, has a frequency lower than the cutoff frequency ν_{o2} and is not absorbed by any cells with $T>T_1$, and is consequently emitted by the stack. As a result, the net emission from the stack is BR with the frequency-dependent temperature $T(\nu)$. Consequently, the threshold behavior of emission from each cell appears as single-frequency emission from the stack. Figure 8-2 depicts the emission spectrum for omnicolor thermal conversion, SR approximated as BR at 5762 K, and a reference BR spectrum at 3800 K. Figure 8-2 shows that the emitted TR is not BR at T_o and thus has non-zero exergy flux but the emitted energy flux is still very low compared to the source flux.

The exchange of TR between adjacent cells in the set also results in heat transfer by TR down the stack, represented by area x_2 in Figure 8-1. This heat transfer results in exergy destruction and is inherent to the omnicolor configuration. However, the irreversibility due to this heat transfer is a minor part of the total irreversibility of the process. Also, note that area x_3 is the product of two differentials and thus has no significance in the limit of an infinite series of cells.

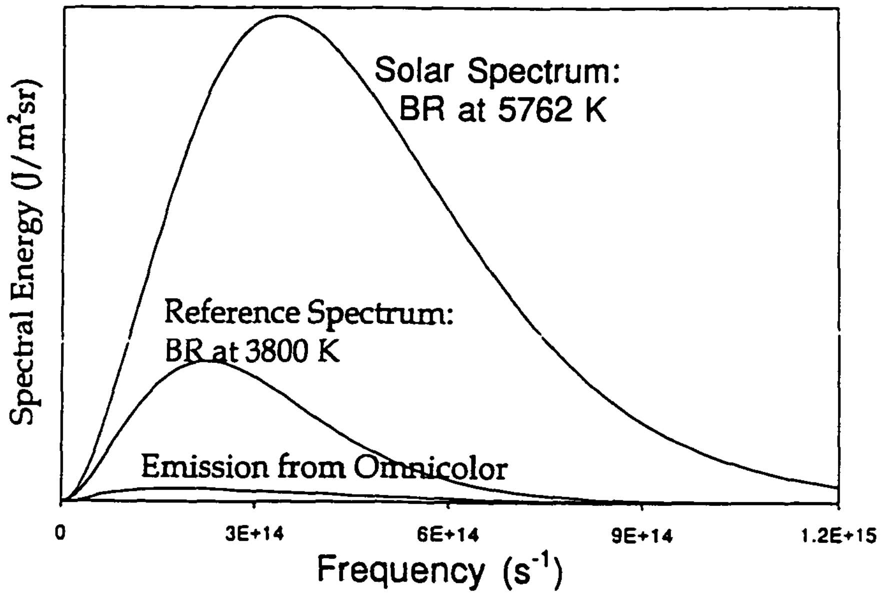

Figure 8-2: Source and emission energy spectrums for omnicolor thermal conversion.

The main source of irreversibility in each cell is due to the absorption of a sliver of SR with a high source temperature accompanied by emission with a relatively low cell temperature $T(\nu)$. Ideal thermal and omnicolor thermal conversion can be qualitatively compared by considering the energy flow through the device as a function of temperature. The net work produced is a product of the energy flow as a function of temperature and the Carnot factor for that temperature.

Figure 8-3 illustrates qualitatively the energy flow (incoming source TR minus emission) as a function of temperature for both processes. From this plot it can be seen that, compared to ideal thermal conversion, the thermal omnicolor process inherently extracts work at much lower temperatures where the Carnot factor for the heat engine is relatively low. For ideal conversion the BR is converted in a continuous manner from T_s to T_0.

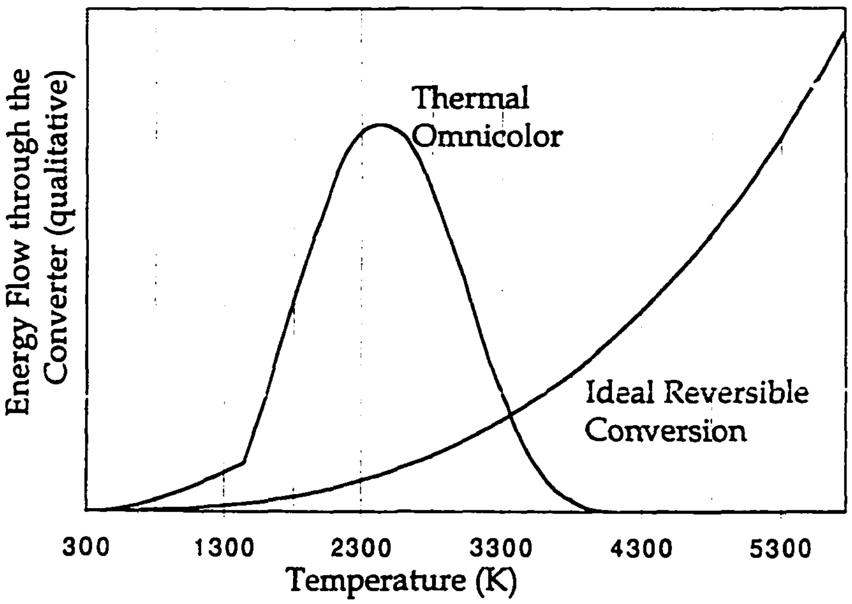

Figure 8-3: Energy flow versus temperature.

The main source, and apparently only source, of non-ideal behavior in each cell for omnicolor quantum conversion is due to the absorption of a sliver of SR accompanied by emission with a relatively low cell temperature T_o. For omnicolor quantum conversion there are no exergy losses because the TR emitted by the stack is BR at T_o. Also, there is no heat transfer along the stack and thus no associated exergy destruction. Thus, in Figure 8-1 the areas x_2 and x_3 do not exist for omnicolor quantum conversion.

8.4 The Effect of Concentration on Conversion Efficiency

Concentration increases the operating temperature and thermal efficiency of thermal solar converters that are used in practice. Also, concentration is of benefit because it reduces the required converter surface area and size for a given solar collection area. The values in Table 8-1 based on Haught's [3] energy efficiency results indicate that the values of second-law efficiency for concentrated SR are substantially higher than those for the unconcentrated case. However, this difference occurs only because Haught considers a specific case of unconcentrated SR conversion.

For Haught's unconcentrated case (typical in practice) emission by the collector occurs over a large solid angle (2π sr) while the incident SR is contained in a very small solid angle. On the other hand, for the concentrated case absorption and emission occur over the same solid angle. Thus, the energy losses due to emission are more significant for the unconcentrated case considered by Haught than for the concentrated case. Concentration is strictly a practical performance improvement measure as it cannot change the spectral distribution of the source TR and cannot increase the maximum theoretical efficiency obtainable from a source flux.

Threshold behavior improves the performance of a single-converter thermal system because it reduces the fraction of energy loss due to emission. However, Haught [3] observes that under full concentration threshold behavior has a marginal benefit. The reason for this phenomenon is that under full concentration absorption and emission are over the same solid angle and thus losses due to emission are less significant and consequently the benefit of threshold behavior becomes marginal.

Chapter 9 On the Entropy of TR in Engineering Thermodynamics

9.1 Motivation for Research

Many thermodynamic texts imply that the entropy flux of 'heat' transfer is the ratio of the heat flux to the local temperature (q/T) with no restriction for TR (e.g. Moran and Shapiro [1, p. 256 and 266]; Reynolds and Perkins [29, p. 223]; McGovern [30, p. 177]). It is well known in the fields of physics and solar engineering that the entropy flux for TR emission is not calculated in the same way as for heat conduction. For BR emission a 4/3 factor is present and it was recently shown [2] that the entropy flux of NBR emission is even farther removed from q/T. This clarification is important because incorrectly calculating TR entropy transfer can lead to serious errors in the calculated value for the irreversibility of energy conversion devices.

However, some of the fundamental equations that are used in thermodynamics express the entropy flux of heat transfer as q/T. Thus, it is important to determine whether these equations are applicable when TR is involved. In section 9.2 our purpose is to investigate whether the Clausius equality, and expressions extended from it for irreversible processes, are applicable when TR is involved.

Also, the occurrence of the 4/3 coefficient for BR entropy is evident from theoretical derivations yet it has not been explained physically. The 4/3 coefficient for BR entropy has been derived by two different methods but the source of the 4/3 coefficient is not clearly evident. In section 9.3 we present an alternative derivation that shows that the 4/3 coefficient follows directly from the observable relation between BR energy and emission temperature (i.e., energy is proportional to T^4). This is done without using Maxwell's radiation pressure or Planck's spectral entropy radiance expression.

9.2 Applicability of the Clausius Statements for Reversible and Irreversible Processes when TR is Involved

Some of the fundamental equations that are used in thermodynamics express the entropy flux as the heat flux divided by the local temperature. However, as we have seen this relation does not generally hold for TR transfer. In this section we consider the implications of this observation for the Clausius equality and expressions derived from it for irreversible processes.

The Clausius inequality for a cycle

$$\oint \frac{dQ}{T} \leq 0 \tag{9.1}$$

is a consequence of the second law of thermodynamics. In (9.1) dQ represents an infinitesimal heat transfer to the system at the boundary where the temperature is T (the temperature may vary on the boundary). The integration is carried out over a complete cycle. Physically, the Clausius inequality indicates that the net transfer of entropy out of the system is positive for an irreversible cycle and zero for a reversible cycle. If instead we look at a portion of the cycle, say between equilibrium states 1 and 2, then this inequality can be re-stated as

$$\Delta S_{12} \geq \int_1^2 \frac{dQ}{T} \tag{9.2}$$

The change in entropy of a closed system between two equilibrium states is greater than or equal to what can be accounted for due to entropy transfer by heat flow into the system during the process. This statement implies that entropy production during the process must be positive, or zero in the case where the process is reversible:

$$\Pi = \Delta S_{12} - \int_1^2 \frac{dQ}{T} \geq 0 \tag{9.3}$$

In all these statements the entropy transfer is expressed as the heat transfer divided by the local temperature. To determine the applicability of these equations when TR is involved consider a system consisting of a solid BB sphere with effectively uniform temperature due to a sufficiently high thermal conductivity (see Figure 9-1). The solid sphere is contained in a vacuum so the only form of heat transfer is by TR.

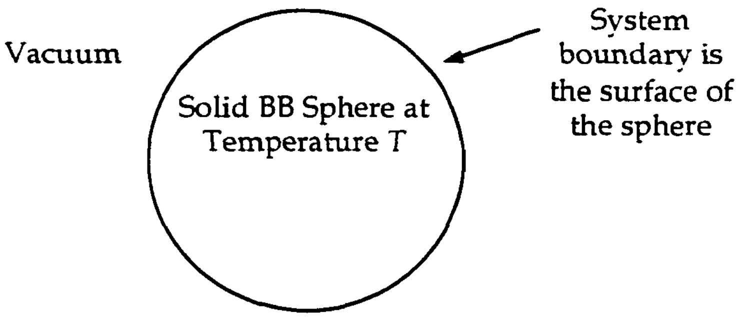

Figure 9-1: Solid BB sphere system.

First, consider a quasi-static reversible energy transfer between the system and a spherical enclosure with blackbody characteristics. Note that the shape of the enclosure is arbitrary. For reversible BR transfer, the temperature difference between the system and the enclosure must be infinitesimal. The *net* heat transfer rate is

$$\dot{Q}_{net} = 4\pi R^2\sigma\left\{(T+\Delta T)^4 - (T)^4\right\} \tag{9.4}$$

where R is the radius of the sphere. For an infinitesimal temperature difference ΔT becomes a differential dT and terms of higher order can be neglected:

$$\dot{Q}_{net} = 4\pi R^2\sigma\left\{4T^3 dT\right\} \tag{9.5}$$

Similarly, using (3.3) the *net* entropy transfer rate at the system boundary is

$$\dot{S}_{net} = 4\pi R^2\ \tfrac{4\sigma}{3}\left\{(T+dT)^3 - (T)^3\right\} = 4\pi R^2\ \tfrac{4\sigma}{3}\left\{3T^2 dT\right\} \tag{9.6}$$

The entropy transfer rate given by (9.6) is equal to the energy transfer expressed in (9.5) divided by the temperature T. Thus, the Clausius expression for reversible processes is valid when TR is involved. This occurs because for reversible energy transfer there is no entropy production so the entropy transfer by heat conduction (q/T) in the solid is equal to the net entropy transfer by the TR.

Now consider irreversible TR transfer between the system and its enclosure when the temperature difference is not infinitesimal. The net energy transfer rate to the system at the system boundary is

$$\dot{Q}_{net} = 4\pi R^2\sigma\left\{T_E^4 - T^4\right\} \tag{9.7}$$

where T_E is the temperature of the enclosure. Similarly, the net entropy transfer rate at the system boundary is

$$\dot{S}_{net} = 4\pi R^2\frac{4\sigma}{3}\left\{T_E^3 - T^3\right\} \tag{9.8}$$

The net energy transfer rate in (9.7) divided by the temperature T is

$$\frac{\dot{Q}_{net}}{T} = 4\pi R^2\sigma\left\{\frac{T_E^4}{T} - T^3\right\} \tag{9.9}$$

The entropy fluxes given by equations (9.8) and (9.9) are clearly not equal for $T \neq T_E$. Beyond a certain distance (or depth) within the solid sphere heat transfer is strictly by conduction and the entropy transfer is given by equation (9.9). The thin surface layer of the solid where TR interaction takes place is referred to here as the interaction region. Thus, equation (9.9) represents the entropy flux at the inner boundary of the interaction region[1] and equation (9.8) represents the entropy flux at the surface (system boundary).

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[1] Strictly speaking the temperature in the interaction region is not uniform. So it may be argued that the emission temperature and the temperature at the inner boundary of the interaction region are not strictly equal. However, the temperature variation is very small because (1) the interaction region is usually very thin, e.g. on the order of a few micrometers for metals, and (2) the temperature gradient decreases to zero at the surface of the solid because heat conduction decreases to zero at the surface. Furthermore, in a theoretical sense the temperature difference can be made arbitrarily small by specifying a sufficiently large thermal conductivity.

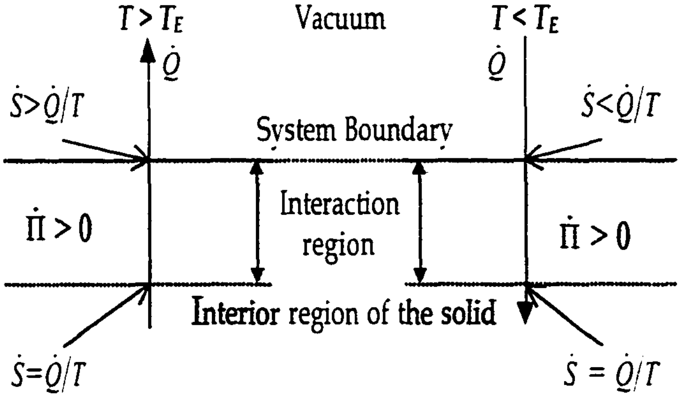

Figure 9-2: Net TR transfer for both hot and cold cases.

Using (9.8) and (9.9) it can be shown that entropy is produced ($\dot{\Pi}$) in the interaction region whether the system is hot or cold relative to its surroundings. Figure 9-2 depicts both these cases but note that $\dot{S}$ and $\dot{Q}$ depicted in the figure are the magnitude of the net flows in equations (9.8) and (9.9), respectively.

Thus, in (9.2) $đQ/T$ represents the entropy transfer at the interaction region boundary rather than the system boundary. Mathematically (9.2) is valid but from a thermodynamic perspective it is insufficient. In this context (9.2) states that the entropy change must be greater than the entropy transfer rate into the system at the interaction region boundary. It would be more precise if (9.2) stated that the entropy change must be greater than the entropy transfer rate into the system at the system boundary. To make this statement however, the entropy transfer cannot be specified as $đQ/T$.

However, careful examination of (9.3) reveals that this equation is incorrect in a thermodynamic sense. When this equation is applied to our illustration the entropy production rate calculated is only due to heat conduction within the solid excluding the interaction region. The total entropy production includes the entropy production in the interaction region, which can be a large fraction of the total. For (9.3) to give the total entropy production rate as expected, the entropy transfer rate at the system boundary must be evaluated correctly. Thus, it must be either specified that the heat transfer does not include TR exchange, or the entropy transfer must not be given as $đQ/T$ in (9.2) and (9.3).

9.3 Alternative Straightforward Derivation of the 4/3 Coefficient for BR Entropy without Planck's Formulas or Maxwell's TR Pressure

The 4/3 coefficient that arises from theoretical derivations of BR entropy has not been explained physically. The BR entropy expression (equation (3.3)) has been derived by integrating Planck's spectral entropy radiance expression (equation (3.2)) after substitution of equation (3.1). The BR entropy has also been derived for an equilibrium BR system using Maxwell's radiation pressure and a differential form of the first law (see, for example, Bejan's advanced thermodynamics text [11] p. 448). However, in these derivations it is difficult to track the source of the 4/3 factor. In this thesis the physical reason for the 4/3 factor is not explained but an alternative approach for arriving at the BR entropy expression is presented that may prove useful in obtaining a physical understanding of the 4/3 coefficient based on an understanding of the T^4 dependence for BR energy.

The relationship between BR energy and emission temperature, i.e. energy is proportional to T^4, is well known, accepted, and directly measurable. Note that the T^4 relationship can be observed experimentally and described by an empirical relation but the analytical proof requires Planck's spectral energy radiance formula (3.1). In the present derivation we see that the 4/3 coefficient directly follows from the T^4 relationship. This approach involves considering the equilibrium condition between a BR system and its enclosure without using Maxwell's radiation pressure ($P = u/3$) or Planck's energy (3.1) or entropy (3.2) explicitly, although they are both implied by the empirical relation used herein.

Consider an evacuated cavity inside a solid that is isolated from its surroundings. At equilibrium the cavity will contain isotropic BR. The combined system consists of the TR system (denoted by TR) and the material system (denoted by m). The fundamental equations for the two systems are $S^{(m)} = S^{(m)}(U^{(m)}, V^{(m)})$ and $S^{(TR)} = S^{(TR)}(U^{(TR)}, V^{(TR)})$, respectively. The entropy of the combined system is $S = S^{(TR)} + S^{(m)}$.

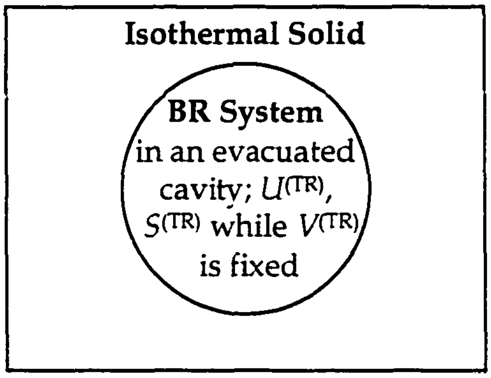

Figure 9-3: A BR system contained in an evacuated cavity inside an isothermal solid.

If $U^{(TR)}$ and $U^{(m)}$ are changed by a virtual energy transfer the entropy change is:

$$dS = \left.\frac{\partial S^{(TR)}}{\partial U^{(TR)}}\right|_{V^{(TR)}} dU^{(TR)} + \left.\frac{\partial S^{(m)}}{\partial U^{(m)}}\right|_{V^{(m)}} dU^{(m)} \tag{9.10}$$

By conservation of energy $dU^{(TR)} = -dU^{(m)}$. The condition of equilibrium demands that dS vanish for arbitrary values of $dU^{(TR)}$, i.e. that entropy has a maximum at equilibrium. Consequently, for a TR system in equilibrium with its material enclosure the partial derivatives of entropy with respect to energy must be equal:

$$\left.\frac{\partial S^{(TR)}}{\partial U^{(TR)}}\right|_{V^{(TR)}} = \left.\frac{\partial S^{(m)}}{\partial U^{(m)}}\right|_{V^{(m)}} \tag{9.11}$$

If this equation were not valid energy would spontaneously transfer between the two systems, thereby increasing the combined entropy of the two systems. For the material system the volume and mole number are fixed and the partial derivative is simply the inverse of the temperature of the isothermal material enclosure ($1/T_m$). For the TR system the volume is fixed so the entropy is a function of the energy only, i.e. $S = S(U)$, and thus the partial derivative becomes a total derivative and equation (9.11) becomes:

$$\frac{dS^{(TR)}}{dU^{(TR)}} = \frac{1}{T_m} \tag{9.12}$$

Note that equation (9.12) can be expressed as $dU = TdS$, and represents the differential form of the first law when volume is fixed, provided we define radiation temperature as the partial derivative of the entropy with respect to the entropy.

It can be experimentally verified that the entropy flux of BR is $H = \sigma T_m^4$ (Stefan-Boltzmann law). The irradiance and specific internal energy of the BR system are geometrically related by $H = Uc/4V$ where c is the speed of light (see, for example, Jakob [27] p. 29). Thus, the internal energy of the BR system is $U^{(TR)} = a\,T_m^4 V$, where $a = 4\sigma/c$. By eliminating temperature and dropping the superscript (TR), and the subscript (m), we have:

$$\frac{dS}{dU} = (aV)^{1/4} U^{-1/4} \tag{9.13}$$

Upon integrating and setting the integration constant to zero, because the entropy of the radiation must be zero when there is no radiation, we have:

$$S = \frac{4}{3}(aV)^{1/4} U^{3/4} = \frac{4}{3} a V T^3 \tag{9.14}$$

Therefore, the 4/3 factor of the entropy expression can be seen as a direct result of the fourth degree form (T^4) of the energy expression. This result has been shown by simply considering the equilibrium condition between a BR system and its enclosure and relying on the empirical relation involving T^4 for BR energy.

Chapter 10 Planetary Entropy Production and its Relevance in Atmospheric Modeling

10.1 Motivation for Research

Predicting the global effects of rising greenhouse gas levels in the atmosphere is a primary motivating factor for modeling the atmosphere. It is expected that rising carbon dioxide levels will not only cause global warming, and consequently rising sea levels, but may also cause sudden changes in climate due to the climate's inherent meta-stability. Such concerns have resulted in efforts to model the atmosphere to predict the effects of higher levels of carbon dioxide. The interaction of many contributing phenomena, however, makes modeling of the atmosphere a difficult task. For an overview of this subject see, for example, Peixoto and Oort [31].

Conventional general circulation models incorporate the principles of energy, momentum (linear and angular), and mass conservation. To avoid the complexity encountered with these models some researchers have tried to identify an extremum principle that can be used to predict steady states without modeling the large number of processes that occur in the atmosphere (O'brien and Stephens [32, p. 1773]). Research has focused on the minimum entropy production principle of Prigogine [33] and the maximum dissipation principles of Paltridge [34] and Zeigler [35].

Stephens and O'brien state that the fundamental question regarding the entropy production rate of Earth's climate is whether or not it is at a maximum or minimum [36, p. 147]. Stephens and O'brien's perspective is that the observed entropy production rate of Earth supports the maximum dissipation viewpoint. They conclude that "the observed rate of entropy production is close to the upper bound for a planet with the albedo of Earth ... it is not possible to prove that the planet is in a state of maximum dissipation, but we have accumulated evidence that suggests that the conjecture may be true" [32, p. 1791].

Also, researchers have presented simple blackbody (BB) type planetary models to theoretically estimate planetary entropy production rates. The analysis of the simple radiative models of the Earth system provides insight into the thermodynamic behavior of the Earth system even though it is a complex system. This is because radiative processes play a major role in the thermodynamics of the Earth system. From a thermodynamic perspective thermal radiation (TR) exchange, incoming sunlight and outgoing TR, is the only significant form of energy transfer between the Earth and the Universe. Further, processes such as absorption and emission dominate planetary entropy production, and the non-uniform absorption of SR on the Earth causes circulation of the atmosphere and oceans.

In the research of this chapter the objectives are:

1) to present an improved, yet simple, graybody planetary model to better the understanding of the radiative behavior of the Earth system,

2) to examine Stephens and O'brien's conclusion that the observed entropy production rate of Earth supports the maximum dissipation viewpoint, and

3) to determine the significance of Prigogine's minimum entropy production principle as a governing principle in atmospheric modeling.

10.2 Simple Graybody Planetary Model

Researchers have analyzed simple blackbody planetary models to investigate the radiative behaviour of the Earth system and to estimate planetary temperature and entropy production rates (for example see Aoki [38], Stephens and O'brien [36], and Weiss [39]). It is more accurate to model the Earth system as a graybody because absorption of sunlight and emission of TR are substantially less than that of a blackbody. In this thesis we present a simple graybody planetary model that more closely models the radiative behaviour of the Earth system and results in a more accurate expressions for planetary entropy production rates and mean temperatures.

In this analysis the Earth system is represented by an isothermal, solid sphere with uniform properties. The analysis is at steady state and the 'long wave' emissivity of the sphere is taken as one minus the 'short wave' albedo of Earth ($\varepsilon_{LW} = 1 - a$), where the albedo a is an overall measure of the reflectivity of the planet. In actuality this relation only holds approximately; for Earth the long wave emissivity ε_{LW} is 0.61 while the short wave albedo a is 0.30. The purpose for using this approximation will be discussed in section 10.2.2.

The effective planetary temperature is determined by specifying that the energy inflow (absorbed) and outflow (emitted) of the planet are equal at steady state. Otherwise, the planet would be heating up if there were a continual net influx of energy or cooling down if there were a net outflux. The energy flow absorbed by the planet is

$$\dot{E}_{Abs} = (1 - a)\dot{E}_{Inc} \tag{10.1}$$

and the energy flow emitted by the planet is

$$\dot{E}_{Emi} = 4\pi R^2 \varepsilon_{LW} \sigma T_P^4 = 4\pi R^2 (1 - a)\sigma T_P^4 \tag{10.2}$$

where T_P is the effective temperature of the planet. To determine this temperature we first need to calculate the incident energy flow rate in Eq. (10.1). The incident energy flow rate on a planet with cross-sectional area πR^2 is

$$\dot{E}_{Inc} = \pi R^2 H_{Inc} = \pi R^2 \Omega K_{Inc} \tag{3}$$

The influx of sunlight to the Earth is contained in a small solid angle as shown in Figure 10-1. Sunlight is uniformly incident on the Earth so random positions are chosen to illustrate the influx of sunlight within a small solid angle. The solid angle of sunlight incident on a planet is equal to 4π times the ratio of the cross-sectional area of the planet to the surface area of the sphere with radius equal to the mean orbital radius of the planet

$$\Omega \approx 4\pi\left(\frac{\pi R_S^2}{4\pi r^2}\right) = \pi\left(\frac{R_S}{r}\right)^2 \tag{10.4}$$

where R_S is the radius of the Sun, and r is the distance from the center of the Sun to the planet and is approximated as constant in this analysis.

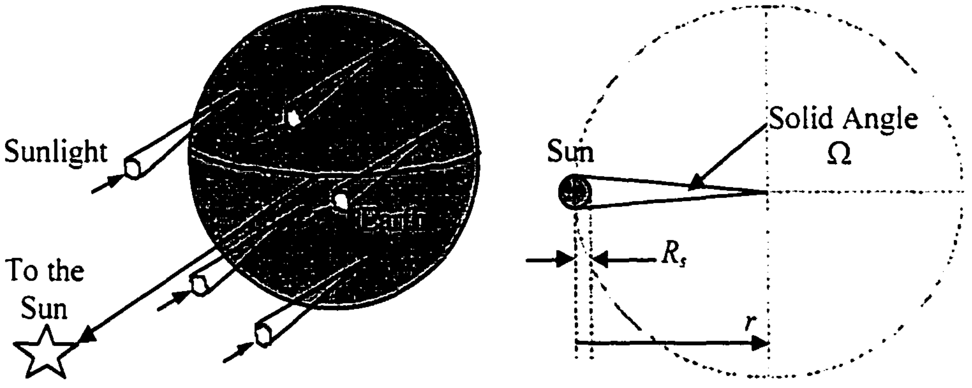

Figure 10-1: SR incident on Earth.

The next step is to determine the energy radiance K of solar radiation contained in the solid angle Ω. From conservation of energy, the flow rate of energy at any distance from the Sun is equal to the energy flow rate at the surface of the Sun:

$$4\pi R_S^2 H_{Sf} = 4\pi r^2 H \tag{10.5}$$

where the energy irradiances H and H_{Sf} are the energy flux per unit area (irradiance) at distance r from the Sun and at the surface of the Sun, respectively. By approximating emission from the Sun as blackbody radiation (BR) we have

$$H_{Sf} = \pi K_{Sf} = \sigma T_S^4 \tag{10.6}$$

where T_S is the effective temperature of the Sun based on the BR approximation, and K_{Sf} is the energy radiance at the surface of the Sun. Thus using Eq. (10.5) and Eq. (10.6), the energy irradiance H at distance r from the Sun is given by

$$H = \left(\frac{R_S}{r}\right)^2 \sigma T_S^4 \tag{10.7}$$

The energy irradiance *H* is equal to the energy radiance *K*, times the solid angle given by Eq. (10.4) so we have

$$K = \frac{H}{\Omega} = \frac{\sigma}{\pi} T_S^4 \tag{10.8}$$

Note that the energy radiance *K* at any distance from the Sun is the same as at the surface of the Sun K_{Sf}. The entropy radiance *L*, and the energy and entropy spectrums, are also invariant with the distance from the Sun. However, the energy irradiance *H*, equal to $K\Omega$, decreases as *r* increases because the solid angle of the sunlight given by Eq. (10.4) decreases.

After substituting for the incident energy irradiance from Eq. (10.7) the incident energy flow rate on Earth given by Eq. (10.3) becomes

$$\dot{E}_{Inc} = \pi R^2 H_{Inc} = \pi R^2 \sigma T_S^4 \left(\frac{R_S}{r}\right)^2 \tag{10.9}$$

By equating Eq. (10.1) and Eq. (10.2), and using Eq. (10.9), the effective planetary temperature can be expressed as

$$T_p = \left[\frac{1-a}{\varepsilon_{LW}}\right]^{\frac{1}{4}} \left[\frac{R_S}{2r}\right]^{\frac{1}{2}} T_S = \left[\frac{R_S}{2r}\right]^{\frac{1}{2}} T_S \tag{10.10}$$

taking $\varepsilon_{LW}=1-a$ (the reason for this approximation will be discussed at the end of section 10.2.2). Surprisingly, the graybody planetary temperature only depends on the mean planetary orbital radius and not the planetary albedo. A blackbody planet absorbs all incident SR but does not have a higher temperature than a graybody planet because the emitted energy is correspondingly higher as well.

The entropy production rate of the planet is simply the difference between the entropy of incoming and outgoing TR. The incoming TR is incident SR and the outgoing TR is a combination of reflected SR and TR emitted from the planet. Assuming that the reflected and emitted energy spectrums do not overlap significantly the reflected and emitted entropy can be calculated separately [37]. In this case we have

$$\dot{\Pi} = \dot{S}_{Emi} + \dot{S}_{\mathrm{Re}f} - \dot{S}_{Inc} \tag{10.11}$$

The inaccuracies in Aoki's [38] and Weiss' [39] analysis are as follows:

1) Incorrectly calculated the entropy production rate as the difference between the absorbed and emitted entropy flow rates. This is incorrect as the absorbed entropy flow rate is not equal to the difference between the reflected and incident entropy flow rates.
2) Incorrectly calculated the absorbed entropy flow rate as a linear fraction (1- a) of the incident SR entropy. This is incorrect because the entropy of GR with emissivity of (1- a) is not equal to (1- a) times the entropy of BR with the same material emission temperature.
3) As noted in Aoki's paper, neglected the entropy production rate due to diffuse reflection of incident SR over a large solid angle.
4) Calculated the emitted and reflected entropy flow rates independently without specifying that this approximation was made.

In the current analysis we first calculate the incident entropy flow rate followed by the reflected and emitted contributions to the entropy production rate. The incident entropy flow rates on a planet with cross-sectional area πR^2 is

$$\dot{S}_{Inc} = \pi R^2 \Omega L_{Inc} = \pi R^2 \tfrac{4}{3} \sigma T_S^3 \left(\frac{R_S}{r}\right)^2 \tag{10.12}$$

The reflected *energy* flow rate from the planet is simply the albedo times the incident energy flow rate in Eq. (10.9). However, the reflected *entropy* is not as easily calculated because it is not linearly related to the energy. In addition, the reflected solar radiation can be approximated as GR but it is diluted by diffuse reflection so its emissivity is less than the albedo of the planet. This is because the incoming SR is contained in a small solid angle whereas it is reflected into a large solid angle. In this analysis we approximate the reflected solid angle as 2π, a hemisphere of directions, and approximate the reflected SR as isotropic. That is, we approximate the reflected SR as uniformly distributed over the solid angle of

2π. For isotropic radiation the irradiance is equal to π times the radiance so for the reflected TR we have $H_{Ref} = \pi K_{Ref}$.

The incident SR is distributed over a small angle perpendicular to the cross-section of the planet, as depicted in Figure 10-2, so $H_{Inc} = \Omega K_{Inc}$. A fraction of the incident SR is reflected so by definition of the albedo we have

$$H_{Ref} = aH_{Inc} = a\Omega K_{Inc} \tag{10.13}$$

and thus Eq. (10.4) for the reflected energy radiance becomes

$$K_{Ref} = \frac{H_{Ref}}{\pi} = \frac{a\Omega}{\pi} K_{Inc} = a\left(\frac{R_S}{r}\right)^2 K_{Inc} \tag{10.14}$$

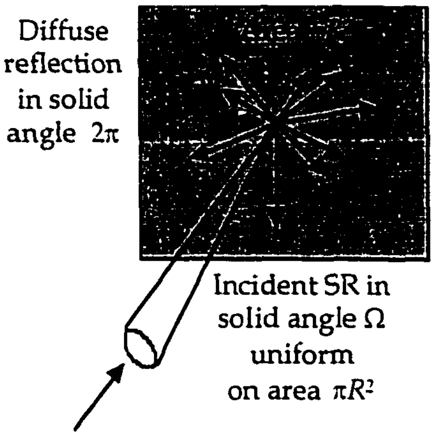

Figure 10-2: An illustration of diffusely reflected solar radiation.

The incident SR is approximately BR emitted at temperature T_S so the reflected SR is GR with emission temperature T_S and an emissivity

$$\varepsilon_{Ref} = a\left(\frac{R_S}{r}\right)^2 \tag{10.15}$$

The entropy-to-energy ratio of GR is higher than that of BR with the same material emission temperature [37], i.e.

$$\frac{L_{GR}}{K_{GR}} = I(\varepsilon)\frac{L_{BR}}{K_{BR}} > \frac{L_{BR}}{K_{BR}} \tag{10.16}$$

For the entropy of the emitted and reflected entropy we use the approximations from Table 3-1

$$I_1(\varepsilon) = 1-\tfrac{45}{4\pi^4}(2.292-0.150\varepsilon)\ln\varepsilon \qquad (10.17)$$

which is within 0.03% for $\varepsilon > 0.2$ and

$$I_2(\varepsilon) = 1-\tfrac{45}{4\pi^4}(2.336-0.260\varepsilon)\ln\varepsilon \qquad (10.18)$$

which is within 0.33% for $0.005< \varepsilon<0.2$. For the reflected TR we use $I_2(\varepsilon)$ to obtain the following:

$$\frac{L_{Ref}}{K_{Ref}} = I_2\left(\varepsilon_{Ref}\right)\frac{L_{Inc}}{K_{Inc}} > \frac{L_{Inc}}{K_{Inc}} \qquad (10.19)$$

The emissivity given by Eq. (10.15) is outside the range indicated for an approximation within 0.33% using Eq. (10.18). However, when applied to the reflected SR for planets of our solar system Eq. (10.18) is within 2% of the numeric value. Keep in mind that the reflected entropy is a relatively small contributor to the total entropy production rate of the planet.

The reflected entropy irradiance is then

$$J_{Ref} = \pi L_{Ref} = \pi I_2\left(\varepsilon_{Ref}\right)\frac{K_{Ref}}{K_{Inc}}L_{Inc} = aI_2\left(\varepsilon_{Ref}\right)J_{Inc} \qquad (10.20)$$

and the reflected entropy flow rate is

$$\dot{S}_{Ref} = \pi R^2 J_{Ref} = aI_2\left(\frac{aR_S^2}{r^2}\right)\dot{S}_{Inc} \qquad (10.21)$$

Now the entropy flow of GR emitted from the planet is

$$\dot{S}_{Emi} = 4\pi R^2(1-a)I(1-a)\frac{4}{3}\sigma T_P^3 \qquad (10.22)$$

and using Eq. (10.10) this becomes

$$\dot{S}_{Emi} = 4\pi R^2(1-a)I(1-a)\left[\frac{R_S}{2r}\right]^{\frac{3}{2}}\frac{4}{3}\sigma T_S^3 \qquad (10.23)$$

The entropy production rate of the planet is the difference between the entropy flow rates of the incoming and outgoing TR. Thus, using Eq. (10.12), Eq. (10.21) and Eq. (10.23) the planetary entropy production rate may be approximated as

$$\dot{\Pi} = \pi R^2\left[\frac{R_S}{r}\right]^{\frac{3}{2}}\left\{\sqrt{2}(1-a)I(1-a) - \left[1 - aI_2(\frac{aR_S^2}{r^2})\right]\left(\frac{R_S}{r}\right)^{\frac{1}{2}}\right\}\frac{4}{3}\sigma T_S^3 \qquad (10.24)$$

By substituting data for the Earth (a = 0.30, R = 6.37x10^6 m and r = 1.486x10^{11} m) and the Sun (R_S = 6.923x10^8 m and T_S = 5760 K) the planetary entropy production rate of the Earth is estimated as

$$\dot{\Pi}_{Earth} = 6.44\text{x}10^{14}\ \text{W/K} = 644\ \text{TW/K} \qquad (10.25)$$

10.2.1 Discussion of planetary model results

The planetary entropy production rate for the Earth calculated using the graybody model of 644 TW/K is within 5.3% of Stephens and O'brien's [36] calculation based on satellite energy measurements of 680 TW/K. This is reasonable agreement considering the uncertainty in Stephens and O'brien's calculation. However, one would expect that the planetary entropy production rate of the actual Earth would be lower than the graybody model with the same albedo. This is because the greenhouse effect will tend to increase the mean planetary temperature. We were able to reproduce Aoki's [38] result for the planetary entropy production rate which may be expressed as:

$$\dot{\Pi} = \pi R^2\left[\frac{R_S}{r}\right]^{\frac{3}{2}}\left\{\sqrt{2}(1-a)^{3/4} - [1-a]\left(\frac{R_S}{r}\right)^{\frac{1}{2}}\right\}\frac{4}{3}\sigma T_S^3 \qquad (10.26)$$

The planetary entropy production rate for Earth using the Aoki's approach given by Eq. (10.26) is 606 TW/K. Weiss [39] incorrectly calculates the entropy of the GR emitted by the planet and consequently his result is of minor significance because the emitted entropy flow rate dominates the entropy production rate calculation. Weiss calculates the entropy of GR as equal to the emissivity times the entropy flux of BR. For an emissivity of 0.7 used for the Earth this results in a 9% error in the entropy flux calculation (for lower emissivities the error is much greater; for example, the error is 61% for an emissivity of 0.1).

To explain the difference between the graybody approach and Aoki's approach it is convenient to look at the results for all the planets in our solar system. In Table 10-1 planetary temperatures and entropy production rates are presented for Aoki's approach and the graybody model.

Table 10-1: Mean planetary temperature and entropy production rates.

Planet	Albedo a	Planetary Temperature, T_P (K)			Entropy Production Rate, $\dot{\Pi}_{Planet}$ (TW/K)	
		Measured	GB Model	Aoki's Approach	GB Model	Aoki's Approach
Mercury	0.058	440	445	439	448	441
Venus*	0.77	733	326	226	519	385
Earth	0.30	288	278	254	644	606
Mars	0.20	220	224	212	104	101
Jupiter	0.42	124	121	106	5960	5680
Saturn	0.76	95	90	63	926	835
Uranus	0.93	59	63	33	26.7	21.8
Neptune	0.84	59	51	32	20.4	18.9
Pluto	0.14	50	44	42	0.164	0.163

* The actual temperature of Venus is largely due to the greenhouse effect.

Aoki's planetary temperatures are substantially different from those of the graybody model. In Aoki's model the entropy of emitted NBR from the planets is approximated as that of BR with the same energy, and the effective temperature is taken as that of a blackbody planet emitting the same energy flow rate. However, for the same energy flow rate a blackbody must be at a lower emission temperature. Thus, in Aoki's blackbody model all planetary temperatures are underestimated. Note that Weiss' [39] calculation of planetary temperature is the same as Aoki's [38].

Aoki's planetary entropy production rates are relatively close to those of the graybody model. There are at least three sources of inaccuracy in Aoki's calculation but they have a canceling effect on one another. First, Aoki calculates the emitted entropy as that of BR. The inaccuracy introduced by this simplification is usually within about 1% but it becomes more significant when the albedo of the planet is above 0.5, as is the case for the planets Venus, Saturn, Uranus, and Neptune. Second, Aoki neglects the entropy production due to diffuse reflection. The inaccuracy introduced by this omission becomes more significant the higher the amount of SR that is reflected, that is the higher the albedo as with the first source of error. Third, Aoki inappropriately calculates the entropy of absorbed SR. However, the entropy of sunlight is relatively low compared to entropy of TR emitted from a planet, except when the planet is very close to the Sun. Note that the first source of error mentioned causes an overestimation of the entropy production rate while the second and third sources cause the opposite effect.

Also, we find that Aoki's conclusions regarding the criteria for the existence of organized structures on a planet are unjustified and misleading. Aoki concludes that the net outflow of entropy from the Earth is the "basis from the entropy point of view for the existence of organized structures on the Earth". This is an incorrect conclusion because any planet that is at steady state will have a net outflow of entropy due to entropy production on the planet regardless of the existence of 'organized structures'. Every non-equilibrium process such as the absorption/emission of TR from inanimate matter produces entropy. There must be a net outflow of entropy or it would continually accumulate on the planet (an unsteady condition). Apart from other processes the net outflow of entropy from a real planet is an inherent consequence of TR exchange between the planet and its surroundings: a fraction of the incident low entropy SR is absorbed and high entropy TR is emitted by the planet. Even diffuse reflection of sunlight by a totally reflective (theoretical) planet would produce entropy.

Aoki also concludes that a planet with 'organized structures' must have an entropy production rate (per unit surface area) in the same order of magnitude as that of Earth. To us, this conclusion is unsubstantiated in his study. Furthermore, planetary entropy production rate is not independent of the planetary temperature and the energy flow rate. These parameters can all be expressed as a function of the planetary albedo a, the radius of the planet R, and the distance from the sun r. If the planet is close to the sun and/or has a low reflectivity it will be hot, and have high energy and entropy flow rates. If the planet is far from the Sun and/or has a high reflectivity it will be cold and have low energy and entropy flow rates. It is the author's viewpoint that planetary temperature is the most logical choice of these dependent parameters for qualifying planetary conditions in respect of suitability for having 'organized structures'.

10.2.2 Relevance of the graybody radiative model to the thermodynamics of the Earth

Simple radiative models of the planet are beneficial in understanding the behaviour of the Earth system because radiative processes play a major role in the thermodynamics of the Earth system. The present graybody model provides more accurate expressions for planetary entropy production rate and mean temperature than the BB models. The estimated entropy production rate for Earth emphasizes that planetary entropy production is dominated by radiative processes. A small part of the total entropy production rate of Earth is due to circulation. The high entropy production rate due to absorption/re-emission results because SR is emitted from a high temperature source near 6000 K while the material on Earth is near 300 K.

It is evident that approximating the emitted entropy as that of BR with the same energy in Aoki's approach is accurate. However, it is simply a numerical simplification. The corresponding BB temperature is not physically realistic. This conclusion is important when considering Stephens and O'brien's support of a maximum dissipation, as discussed in section 11.3.

The present model is also beneficial because it illustrates that surprisingly the mean planetary temperature has a tendency to be independent of the planet's albedo. This is not strictly the case because the thermal emissivity (ε_{LW}) of the Earth is not strictly equal to 1 minus the shortwave albedo (a). For the Earth this difference (ε_{LW} is 0.61 while $1- a =0.70$) is mainly due to the 'greenhouse effect', the difference between longwave and shortwave absorption and emission behavior in the atmosphere. The greenhouse effect is relatively mild on Earth as can be seen by the closeness of the mean planetary temperature predicted by the model 278 K compared to the actual value near 288 K. However, we were not indicating that $\varepsilon_{LW}\neq 1- a$ should be ignored but that insight can be gained into the behavior of the Earth system by omitting this fact in the present analysis.

This work could be easily extended to include the fact that $\varepsilon_{LW} \neq 1- a$. This would result in improved estimates of mean planetary temperature and global entropy production rates - for the Earth we would expect a 3% increase for the planetary entropy production rate. This estimate is based on the comparison to the entropy flux of GR with a slightly lower emissivity ($\varepsilon_{LW}<1- a$) and a higher emission temperature. Also, this would show that planetary temperature is affected by a difference between ε_{LW} and $1- a$: for a fixed the calculated temperature will increase as emissivity ε_{LW} decreases. However, the graybody model as it is now provides insight that would be somewhat obscured by only considering the model that incorporates the fact that $\varepsilon_{LW} \neq 1- a$ right from the start. Using the GB model results we can conclude that the Earth's mean temperature has a tendency of being independent of planetary albedo but that it is dependent on the greenhouse effect.

10.2.3 Exergy analysis of the earth and the biosphere

Living systems require an exergy flow, a relatively low entropy energy source, to survive. Almost exclusively sunlight provides the exergy flow for the biomass. Living systems divert part of the incoming exergy flux of sunlight. However, the final destination of the solar energy flow is heat radiation from material on Earth. This is true whether the SR is utilized by living systems or whether it is simply absorbed by material and re-emitted. Consequently, there is no obvious relation between the magnitude of the entropy production rate of the planet to the existence of living systems on the planet.

Over a sufficiently large enough period of time the exergy storage in biomass can be approximated as invariant. For every plant or animal that dies a new one is growing. Also, the incoming flow rate of exergy with sunlight and the outgoing exergy flow rate with TR may also be regarded as invariant. Thus, the exergy balance calculation for the Earth may be approximated as steady state.

The SR energy flow rate incident on Earth from Equation (10.9) is 173,000 TW and the estimated entropy production rate from Equation (10.25) is 644 TW/K. The incoming exergy flow rate of the SR can be estimated using Equation (5.3) and the irreversibility of the planet using Equation (2.1). The exergy flow rate of the SR and the exergy destruction rate of the planet are strongly dependent on the environmental temperature chosen. For the outer space environment $T_o \approx 3$K so the irreversibility rate is 1932 TW which is only 0.27% of the corresponding exergy flow rate of the incoming SR. However, for the terrestrial environment T_o=288K the outgoing TR has approximately zero exergy flux because it has the same emission temperature, so all the incoming exergy flux (approximately 0.933*173,000 TW = 162,000 TW) with SR is destroyed.

10.3 Stephens and O'brien's Support of a Maximum Dissipation Conjecture

Stephens and O'brien [36] estimated the total entropy production rate of Earth based on satellite TR energy measurements. These measurements were carried out in the Earth Radiation Budget Experiment (ERBE) by satellites orbiting at the top of the atmosphere (TOA). Barkstrom and Smith [40] presents an overview of the ERBE experiment. Stephens and O'brien found that the monthly entropy production rate of Earth is approximately constant at $6.8\text{x}10^{14}$ W/K with an annual cycle variation of 1 to 2%.

Stephens and O'brien conclude that their calculation of the total entropy production rate of Earth $\dot{\Pi}_{Earth}$ appears to support the maximum dissipation viewpoint for atmospheric circulation. They state "we present an analysis that suggests the Earth is near its maximum entropy production *for a given observed albedo* of the planet. This arises from the fact that the long-wave entropy flux to space is very closely approximated by the *equivalent blackbody entropy flux.*" [36, p.147]. Note that the emitted entropy flow rate dominates $\dot{\Pi}_{Earth}$ because the entropy of SR is relatively low.

Stephens and O'brien's conclusion is based on the fact that the entropy of the TR emitted from Earth can be accurately approximated by the entropy of *BR with the same energy flux,* which they term the *equivalent* BR entropy flux. So, their conclusion is based on their understanding of the 'equivalent' blackbody entropy flux. BR is associated with maximum entropy. It appears that Stephens and O'brien reason that the emitted entropy is near that of the 'equivalent' BR entropy, and BR is associated with maximum entropy, therefore $\dot{\Pi}_{Earth}$ is near its maximum in support of the maximum dissipation viewpoint. However, from thermodynamic arguments we feel that this conclusion is not justified.

First, the comparison of the entropy of NBR to that of BR with the same energy level is the comparison of the current state of the Earth system to a state where the planetary albedo and thus the absorbed energy flow rate are the same but the global emissivity and temperature are very different. This approximation simplifies the calculation but the 'equivalent' BR material emission temperature is much lower. For example, the 'equivalent' BR emission temperature[1] for GR is given by $T_{BR}^4 = \varepsilon T_{GR}^4$. For example, with ε=0.5 the emission temperature of the BR is about $T_{BR} \approx 0.84 T_{GR}$. So the 'equivalent' BB state has the same albedo and similar planetary entropy production rate but has a very different longwave emissivity and temperature from the current value. In approximating the outgoing entropy as that of BR with the same energy is accurate over a large range of emissivities [2] and therefore over a large range of different states of the Earth system. For example, the approximation is within 1% for GR with emissivity $0.5<\varepsilon<1.0$, and within 5% for $0.2<\varepsilon<1.0$ (see Figure 3-1).

Secondly, to substantiate the use of an extremum principle the actual state is compared to the extremal state of the modeled system. At the outset one might expect that the maximum entropy production rate[2] would occur for a = 0 (BB character) because the energy flow rate is at a maximum. For example, the entropy production rate for the simple graybody model in section 10.2 increases to 788 TW/K from 644 TW/K for an albedo of unity[3]. However, due to the actual radiative character of material that occurs on Earth and feedback effects such as

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[1] Note that if a = fixed then the energy flow rate into and out of the Earth system is fixed, but if the emissivity is allowed to decrease from its current value then the mean global temperature must increase to keep the same outgoing energy flow rate. The increase in temperature associated with a decrease in emissivity is in agreement with the greenhouse effect where the emissivity of the system is less than the absorptivity (1-a) hindering the emission of outgoing radiation and thereby increasing the temperature of the system. If on the other hand the emissivity where much greater than the absorptivity then the mean global temperature would be lower, the reverse of the greenhouse effect. This observation is important when considering the relevance of the simple graybody radiative model in section 10.2.2.

[2] This would occur when the emissivity was equal to unity because as the emissivity decreases the temperature increases and the entropy production rate decreases.

[3] Note that the entropy production rate quoted in the last paragraph for an absorptivity (1 - a) of 70%, that is 644 TW/K, is substantially higher than 70% of the value for an absorptivity of 100%, 788 TW/K. This is due to the fact that BR has the minimum ratio of entropy-to-energy for all TR with the same material emission temperature (see section 3.2 and Figure 3-2).

the ice-feedback effect, plant-feedback effect, and the cloud feedback effect the state of maximum entropy production rate cannot be easily determined. For example, if the planet gets too hot plants will die and ice will melt in the northern regions thereby affecting the albedo of the planet. Thus, to find an extremal state factors like planetary albedo must be allowed to vary.

Thus, although the approximation that Stephens and O'brien used to simplify the entropy calculation is accurate, it does not seem relevant in supporting a governing principle for atmospheric circulation. Stephens and O'brien state in a later article, regarding maximum dissipation, that "the rate is close to the maximum possible for a planet with the albedo of Earth" and that the "relation to Paltridge's definition is unclear" [32, p. 1773]. It is the authors viewpoint that Stephens and O'brien's calculation of the entropy production rate of Earth does not support the maximum dissipation conjecture.

One would expect that if the *planet* is in a state of maximum dissipation then the process of *atmospheric circulation* is in a state of maximum dissipation because circulation and radiative behaviour of the planet are coupled. Based on the results of this section, it would seem advantageous to consider a graybody type solid sphere model with radiative character and temperature as a function of position, with cloud, plant and ice feedback effects. The actual state of Earth system could be compared to the extremum state (maximum entropy production state) of the model. The results of this comparison would likely bring further improvements to the model and then the effect of CO_2 change could be considered.

10.4 Prigogine's Minimum Entropy Production Principle

The maximum entropy production principles of Paltridge[4] [34] and Ziegler [35] appear to be in direct opposition to Prigogine's minimum entropy production principle. It was our purpose in the present work to determine whether Prigogine's principle is relevant in atmospheric modeling. In Prigogine's analysis restrictions are applied to the character of the force-flux relationships that are quite severe[5]. These limitations are well known in thermodynamics.

Some researchers have considered whether Prigogine's four restrictions are sufficient for differentiating between systems where the minimum entropy production principle applies and when it does not. For example, see Pelkowski [41] who considers Prigogine's principle for continuous systems applied to a system consisting of a radiating graybody layer between two blackbody plates near equilibrium. The present analysis questions the general significance of Prigogine's result as a governing principle for any system. This is done by analyzing Prigogine's approach and conclusions for the example system that he used in his analysis.

Prigogine's approach was to extend the second law to non-equilibrium processes in order to develop an entropy production rate expression (see Prigogine [33], pp. 18-21 for closed systems and pp. 28-29 for open systems). From the entropy production expression generalized forces and fluxes were identified. Then Prigogine stated that a stationary (steady) state "may be characterized by an

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[4] Note that in Paltridge's approach linear phenomenological coefficients are not necessary as the are in Prigogine's and Ziegler's approaches. Also, Paltridges principle applies to comparing the entropy production rates of all possible stationary states.

[5] In Prigogine's illustration the following conditions applied:

1) The force-flux relationships are linearly coupled.
2) The phenomenological coefficients are constants (L_{ij} = constant).
3) Onsager's Reciprocity applies ($L_{ij} = L_{ji}$). Note that this does not cause any additional loss of generality with regard to entropy production because the antisymmetric part of L_{ij}, if it were to exist, would not contribute to the entropy production rate $L_{ij}X_iX_j$ because X_iX_j is symmetric. In Prigogine's example Onsager's reciprocity means that $L_{21} = L_{12}$.
4) Time independent boundary conditions.

extremum principle which states that in the stationary state, the entropy production has its minimum value compatible with some auxiliary conditions to be specified in each case" [33, p. 75].

To determine the significance of this observation, consider the illustrative example that Prigogine presents in his analysis. The system is composed of two vessels, I and II, containing the same gas, which communicate by means of a small hole, capillary, membrane, or porous wall. An external thermodynamic force, a temperature difference, is applied and maintained across the system. When this external driving force is applied and maintained (stationary) the system will eventually reach steady state (stationary state) where the fluxes, the internal forces, the entropy production rate, and all other quantities are no longer a function of time.

Now, the specific entropy production rate $\dot{\pi}$ for the two-flux system that Prigogine considers is

$$\dot{\pi} = \sum_{i=1}^{N} J_i X_i = J_m X_m + J_{th} X_{th} \tag{10.27}$$

where X is a thermodynamic force, J is a flux, and the subscripts 'm' and 'th' denote respectively 'mass' and 'thermal'. When the force-flux relationships are linear,

$$\begin{aligned} J_{th} &= L_{11} X_{th} + L_{12} X_m \\ J_m &= L_{12} X_{th} + L_{22} X_m \end{aligned} \tag{10.28}$$

The entropy production rate is simply

$$\dot{\pi} = J_{th} X_{th} + J_m X_m = L_{11} X_{th}^2 + 2 L_{12} X_{th} X_m + L_{22} X_m^2 \tag{10.29}$$

Using partial differentiation Prigogine considers the extremum of the entropy production rate $\dot{\pi}$, with respect to one force (X_m), independent of the other force (X_{th}). The result is that $\dot{\pi}$ has an extremum (minimum) when the flux of mass flow J_m, corresponding to the force X_m, is zero. In this case the term $J_m X_m$ drops out of the entropy production expression, and the remaining term $J_{th}X_{th}$ is reduced due to coupling as follows:

$$\dot{\pi} = J_{th}X_{th} = \left[\left(L_{11} - \tfrac{L_{12}^2}{L_{22}}\right)X_{th}\right]X_{th} = \left(L_{11} - \tfrac{L_{12}^2}{L_{22}}\right)X_{th}^2 \leq L_{11}X_{th}^2 \qquad (10.30)$$

Note that coupling in the force-flux relationships leads to a lower value of $\dot{\pi}$ at the stationary state than if coupling were not present ($L_{12}=L_{21}=0$). Coupling causes the system to increase its 'thermal resistance' to the applied external thermodynamic force X_{th} by re-distribution of mass; the hot side becomes less dense while the density of the cold side increases.

In the particular example under consideration the combined system is closed to mass flow so at the stationary state the mass flux J_m must be zero. Prigogine concludes that he derived the stationary condition $J_m = 0$ as the condition that the entropy production is a minimum for a given value of X_{th}. However, the exercise of obtaining an extremum with respect to one of the forces does not determine a stationary state. A 'parallel' extremum is obtained, $J_{th} = 0$, for the entropy production rate with respect to the force X_{th}. By extending this exercise we see that it would lead to an absolute minimum for $\dot{\pi}$, namely zero, when all the fluxes are zero - the equilibrium condition. In a qualitative way we see that $\dot{\pi}$ is a minimum with respect to a certain force when the corresponding flux has ceased.

Prigogine's choice of which force to find an extremum of $\dot{\pi}$ with respect to was based on knowledge of the constraints on the system. However, knowledge of the constraints allows us to determine which fluxes are zero at the stationary state without considering the variation of the entropy production rate. The force-flux relationships can be simplified by specifying which fluxes are zero, and the stationary entropy production rate can be determined.

To speak of the variation of the entropy production rate as a governing principle when the system is away from equilibrium appears to be misleading. Prigogine's analysis requires a knowledge of the force-flux relationships but the instantaneous response of the system to external thermodynamic forces, under certain constraints, is completely governed by the force-flux relationships. Prigogine's observation regarding the variation of the entropy production rate as the stationary state is approached quantitatively shows that the entropy production rate decreases with respect to a certain force as the corresponding flux decreases to zero. However, it does not explain in what manner or how fast the system changes.

One might expect that even for arbitrary phenomenological coefficients, that are not necessarily linear, the entropy production rate would decrease as the stationary state was approached. This makes sense because the stationary state appears to be a more 'relaxed' state than the transient state of the system during the approach to the stationary state. The stationary state may be considered a more relaxed state because a balance has been reached between the tendency to reach equilibrium and the thermodynamic forces that are applied that prevent equilibrium from being established. However, this is not the case. In section 10.4.1 it is shown that the entropy production rate for one-dimensional heat conduction only decreases as the stationary state is approached if the phenomenological coefficient, the ratio of thermal conductivity to temperature squared (k/T^2), is a constant. Note that this specification of material properties ($k \propto T^2$) is not representative of common engineering materials.

10.4.1 Prigogine's result applied to one-dimensional heat conduction in a plate

As a simple illustration of Prigogine's analysis consider one dimensional heat conduction through a slab according to Fourier's Law. The slab is made of solid isotropic and uniform material with thermal conductivity k. The temperature at the boundaries of the slab are maintained at T_H for $x = 0$ and T_o for $x = l$. Figure 10-3 depicts an arbitrary temperature distribution $T(x)$.

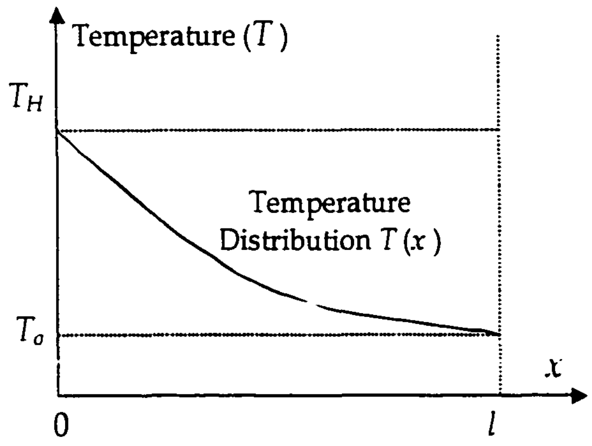

Figure 10-3: One-dimensional heat conduction in a solid.

The heat flux q is related to the thermal force according to Fourier's law:

$$q = -k\,\mathbf{grad}T \qquad \text{OR} \qquad q = +kT^2\mathbf{grad}(1/T) \tag{10.31}$$

The local entropy production rate $\dot{\sigma}$ is

$$\dot{\sigma} = q\cdot\mathbf{grad}(1/T) = +k/T^2[\mathbf{grad}T\cdot\mathbf{grad}T] = +kT^2[\mathbf{grad}(1/T)\cdot\mathbf{grad}(1/T)] \geq 0 \tag{10.32}$$

and in one dimension we have

$$\dot{\sigma} = +k/T^2\left(\frac{dT}{dx}\right)^2 = +kT^2\left(\frac{d}{dx}\left(\frac{1}{T}\right)\right)^2 \tag{10.33}$$

Variational calculus can be utilized to determine whether or not the steady state temperature distribution $T(x)$ is such that $\dot{\sigma}$ is a minimum. Using the first form of Eq. (10.33), the total entropy production rate in the slab per unit surface area is

$$I = \int_0^l \frac{k}{T^2}\left(\frac{dT}{dx}\right)^2 dx \tag{10.34}$$

The solution to the Euler equation

$$\frac{d}{dx}\left(\frac{\partial f}{\partial T'}\right) - \frac{\partial f}{\partial T} = 0 \tag{10.35}$$

gives the temperature distribution such that the integral I is a minimum where

$$T' = \frac{dT}{dx} \qquad f = k\frac{(T')^2}{T^2} \tag{10.36}$$

In general the temperature distribution $T(x)$ that satisfies (10.35), and thus gives the minimum value of $\dot{\sigma}$, is not the temperature distribution at steady state. For example, if the thermal conductivity k is constant then $T(x)$ will be linear according to Fourier's law (10.31), but the distribution $T(x)$ that satisfies Eq. (10.35) is not linear. And if k/T^2 is specified as constant then the temperature $T(x)$ obtained by using Fourier's law (10.31) will not be linear but the distribution $T(x)$ that satisfies (10.35) is linear.

The entropy production rate at the steady state is a minimum only when it is specified that kT^2 is a constant (phenomenological coefficient is a constant), as is done by DeGroot and Mazur [42, p. 46]. In this case the problem is easier to solve if Eq. (10.34) is re-stated as

$$I = \int_0^l kT^2 \left(\frac{d(1/T)}{dx} \right)^2 dx \tag{10.37}$$

It is straightforward to show that when kT^2 is not a constant $\dot{\sigma}$ may increase or decrease as the stationary value is approached depending on the initial conditions. In fact, when a temperature is suddenly applied and maintained to a slab of solid, that was initially in steady state, $\dot{\sigma}$ may pass through its minimum value as the new stationary state is approached.

10.5 Irreversible Thermodynamics of the Atmosphere

The fundamental equations used in fluid dynamics incorporate the force-flux approach of thermodynamics for mass and heat flow, and could incorporate the source-sink nature of TR emission and absorption. However, a common outcome of atmospheric modeling is that numerous stationary states are predicted that satisfy the given constraints and external fluxes on this complex system.

Also, Stephens and O'brien conclude that Zeigler's theorem appears to provide no new information because it is simply a consequence of assumptions already implicit in the Navier-Stokes equation [36, p. 1789]. Zeigler states that the maximum dissipation principle applies only when the force-flux relationships are coupled [35, p. 272]. However, the Navier-Stokes energy equation does not contain any coupling so it appears from a preliminary viewpoint that Zeigler's theorem does not apply to a Navier-Stokes fluid.

However, Paltridge's maximum dissipation theorem could allow the correct stationary state to be determined as the one that has the maximum entropy production rate for all stationary states that satisfy the constraints. One difficulty is that the entropy production rate due to the circulation of the atmosphere and ocean is unknown. This is because it is such a small fraction of the total entropy production rate of Earth and it is difficult to isolate it from entropy production due to radiation absorption and emission.

One would expect that if the *planet* is in a state of maximum dissipation then the process of *atmospheric circulation* is in a state of maximum dissipation because circulation and radiative behaviour of the planet are strongly coupled. In this regard a simple radiative model could be used to determine if the total Earth system is in a state of maximum dissipation. The radiative model would be more advanced than the one considered in section 10.2. The model could allow the incident SR and the temperature on the sphere to be non-uniform, with plant and ice feedback effects. The actual state of Earth system could be compared to the extremum state (maximum entropy production state) of the radiative model. The radiative model would also be beneficial a preliminary impression for the effect of higher CO_2 levels on the temperature distribution and the radiative character of the Earth system.

Chapter 11 Summary

11.1 Conclusions and Encapsulation of New Results

The research results presented in this thesis enhance the understanding, formulation, and accuracy of exergy analysis applied to any energy systems where TR heat transfer is significant. This research shows that Petela's result, considered by many researchers to be irrelevant to the conversion of TR fluxes, represents the exergy flux of BR and the upper limit to the conversion efficiency of SR approximated as BR. This is done by resolving a number of fundamental issues including inherent irreversibility, definition of the environment, inherent emission, and the effects of threshold behaviour and concentration. Also, a new expression based on inherent irreversibility is presented for the exergy flux of TR with an arbitrary spectrum.

The general entropy and exergy balance equations for thermodynamic systems are re-stated so that they correctly apply to TR heat transfer. Second-law (exergetic) efficiencies of common solar energy conversion processes such as single cell photovoltaics are presented. The non-ideal character of omnicolor conversion, the widely held ideal conversion process for SR, is explained in terms of exergy destruction and exergy losses. Also, an ideal (reversible) infinite stage thermal conversion process for BR fluxes is presented along with two-stage thermal conversion as a practical alternative.

The following is a summary of new results for each chapter.

Chapter 5: Exergy of Blackbody Radiation (BR)

1. In his determination of BR exergy Petela used an environment of strictly BR at T_o in a vacuum. However, this 'pseudo' environment of strictly BR at T_o in a vacuum is acceptable because it only serves to isolate TR exergy from other forms of exergy such as mechanical and chemical exergy. The use of the 'pseudo' environment in Petela's analysis places no restriction on the generality of his result.

2. The conventional definition of the environment in exergy analysis completely suffices for TR exergy analysis and the only relevant parameter is the temperature T_0. The physical reason for this result is discussed in section 5.2 using a comparison to the operation of the ideal Carnot heat engine.

3. Petela's parallel-plate approach offers no insight into the question of inherent irreversibility for BR conversion. No insight can be gained because the use of the Guoy-Stodola theorem in this approach assumes that no part of the entropy production is theoretically inherent.

4. Reversible conversion of an enclosed BR system is possible because equilibrium can exist between a BR system and matter (such as its enclosure).

5. The exergy flux of BR is simply related to the exergy of an enclosed isotropic BR system. The exergy flux of BR must be independent of whether it is inside an enclosed BR system or whether it is incident on a conversion device. Thus, in contrast to the viewpoint held by Bejan [11] and Jeter [26], Petela's BR exergy result applies to the conversion of BR fluxes.

6. An infinite-stage thermal device with infinitesimal temperature differences between each stage is theoretically reversible and thus provides a work output equal to the exergy flux of BR. The black-box re-direction of BR fluxes between each stage poses a practical difficulty but is theoretically acceptable because simply re-orientating the BR does not necessarily change its energy or entropy.

7. From a statistical thermodynamics perspective the physical reason why irreversibility occurs is due to energy transfer between groups of statistical particles that are not in mutual equilibrium, for example energy transfer across a finite temperature difference between electrons and phonons.

8. In section 5.4 general entropy and exergy balance equations for a control volume corrected for TR transfer are presented.

Chapter 6: The Effect of Inherent Emission on TR Conversion

1. Inherent emission is a fundamental issue that cannot be ignored when determining the maximum work obtainable from TR conversion (sections 6.1 & 6.2). Petela's parallel-plate approach gives the impression that there is no inherent emission term because these terms cancel out in this approach.

2. It is logical to expect that inherent emission would always reduce the work output of a conversion device. However, in contrast to non-ideal conversion, inherent emission has a beneficial effect on the work output for

ideal conversion. The entropy of the source radiation leaves the conversion device by two paths: heat conduction at T_o and by BR at T_o. Inherent emission results in an additive term because emission of BR at T_o is a better means of rejecting entropy to the environment than heat conduction at T_o (see Figure 6-2). That is, BR at T_o carries a higher ratio of entropy to energy than heat conduction at T_o.

Chapter 7: Inherent Irreversibility and Non-Blackbody Radiation (NBR) Exergy

1. Petela's approach can be extended to consider NBR fluxes and is equivalent to Karlsson's approach. These approaches are based on the Guoy-Stodola theorem, assume that reversible conversion of NBR is possible, and specify the absorption of source TR by a blackbody surface at T_o. The difference in these approaches is that Karlsson's eliminates the need to consider TR reflections (there is no non-blackbody surface).

2. Karlsson's presentation of his result for NBR exergy requires that the exergy flux of NBR is zero at each frequency (on a spectral basis).

3. Analogous to BR exergy, the exergy flux of NBR can be determined by considering the internal exergy of an enclosed NBR system (equation 7.9).

4. The production of work from NBR appears to be inherently irreversible. This is because NBR must interact with matter to produce work but the interaction of NBR with matter, including its own emitting material, appears to be an inherently irreversible (entropy producing) process. Consequently the exergy radiance of NBR given by equation (7.13) is the maximum work not the reversible work:

   $$N = K - T_0\left\{\tfrac{4}{3}\left(\tfrac{\sigma}{\pi}\right)^{1/4} K^{3/4}\right\} + \tfrac{\sigma}{3\pi} T_0^4 \qquad (7.13)$$

   and for GR

   $$N = \tfrac{\sigma}{\pi} T^4\left\{\varepsilon - \tfrac{4}{3}\varepsilon^{3/4} x + \tfrac{1}{3} x^4\right\} \qquad (7.14)$$

   The present result (7.14) reduces to Petela's result for BR when $\varepsilon=1$. Figure 7-4 illustrates the energy and entropy flows required for an ideal NBR conversion device.

5. In the case that NBR conversion is inherently irreversible, the exergy radiance N does not depend on the entropy radiance L and consequently depends on the area (K) under the K_ν spectrum but is independent of its spectral shape. The exergy-to-energy ratio (N/K) is the same for NBR and BR with the same energy, rather than BR having a minimum ratio for all TR with the same energy.

6. The only possibility for the reversible conversion of a NBR system, and the possibility of equilibrium existing between matter and a NBR system, requires that material could at least theoretically exist that absorbs and emits radiation only within an infinitesimal frequency range. However, evidence has been presented that suggests that single-frequency behaviour is not physically possible. Quantum systems exhibit threshold absorption and emission behaviour including omnicolor quantum conversion. Likewise, for thermal conversion emission cannot be confined to a single frequency and single-frequency absorption in a thermal device would not be reversible.

7. In the case that NBR conversion is inherently irreversible, Petela's and Karlsson's approaches give an upper limit to the work output that is not even theoretically obtainable. Part of the entropy production rate calculated in these approaches, based on the non-equilibrium NBR entropy, cannot even theoretically be avoided. This would imply that the Guoy-Stodola theorem is either violated or not applicable to NBR conversion. The most likely possibility is that the Guoy-Stodola theorem is not applicable because of the non-equilibrium nature of NBR entropy. Likewise, exergy cannot be determined based on non-equilibrium NBR entropy. In contrast, the entropy of BR with the same energy used in the present result is an equilibrium entropy.

8. The percent difference between the present result and Karlsson's result for NBR exergy radiance is presented in section 7.5.

Chapter 8: Significance of TR Exergy in Solar Energy Conversion

1. Petela's BR exergy result represents the upper limit for the production of work from solar radiation (SR) fluxes approximated as BR. This conclusion contrasts the common viewpoint, held by De Vos and Pauwels [4] and Haught [3], that omnicolor conversion is the ideal process for SR conversion.

2. Second-law efficiencies for common solar energy conversion processes are presented in section 8.2, Table 8-1. Second-law efficiencies are true indicators of performance and the values presented for common SR conversion processes show that their performance is better than indicated by the first-law energy efficiencies in Table 4-1. The first-law efficiencies compare the performance to an upper limit that is not even theoretically achievable.

3. For omnicolor thermal conversion the exergy losses are low so the majority of the non-ideal behaviour is due to the two sources of irreversibilities in the process (section 8.3). Heat transfer down the stack by TR is a minor source of irreversibility. The main source of irreversibility in each cell is

due to the absorption of a sliver of SR accompanied by the emission at a relatively low cell temperature.

4. For omnicolor quantum conversion the only source of irreversibility is due to the absorption of a sliver of SR accompanied by emission with a low cell temperature (T_0). For omnicolor quantum conversion there are no exergy losses because emission from the stack is BR at T_0 and there is no heat transfer along the stack by TR and thus no associated exergy destruction.

5. Concentration cannot affect the maximum work obtainable from thermal radiation conversion. However, concentration results in practical benefits in performance because devices used in practice commonly receive SR over a small solid angle and emit TR over a large solid angle (2π).

6. For thermal conversion there is a direct correspondence between high second-law efficiency and the maximum temperatures involved in the conversion process. The consequent material requirements have a direct bearing on the practical viability of any particular conversion process.

7. Omnicolor thermal conversion provides a slight increase in efficiency over single-stage conversion but does not appear to be a practical option because of the impact of higher operating temperatures on material property requirements and because of the difficulty involved in producing work over a range of source temperatures. Two-stage thermal conversion offers a greater efficiency improvement than omnicolor thermal conversion and requires work production at only two sources temperatures. However, two-stage thermal conversion involves the highest operating temperatures and requires selective re-direction of the BR fluxes between stages.

8. In contrast to thermal conversion, omnicolor quantum conversion offers substantial improvements over single-cell quantum system for all levels of concentration. It is yet to be determined if reversible quantum conversion of BR fluxes is theoretically possible although it appears that it may not be possible because of the inherent threshold behavior of quantum conversion. If this is the case then omnicolor quantum conversion is the optimal quantum conversion method, although it is irreversible, and then ideal reversible conversion of BR fluxes is only theoretically possible by thermal methods.

Chapter 9: On the Entropy of Thermal Radiation in Engineering Thermodynamics

1. The Clausius equality for reversible processes is applicable when TR is involved but expressions derived from it for irreversible processes are not applicable. These expressions should either be modified or it should be stated that they do not apply when there is significant heat transfer by TR.

2. The derivation of the 4/3 coefficient for BR entropy presented here shows in a concise and clear way that the 4/3 coefficient directly follows from the experimentally observable relationship between BR energy and emission temperature: energy $\propto T^4$. This derivation is done without involving Maxwell's radiation pressure or Planck's relationships. It is thought that this alternative derivation or perspective may prove useful in understanding the physical reason for the occurrence of the 4/3 factor for BR entropy.

Chapter 10: Planetary Entropy Production and its Relevance in Atmospheric Modeling

1. The present graybody model provides more accurate expressions for planetary entropy production rate and mean temperature than blackbody type models. The entropy production rate for this model is 644 TW/K and is within 5% of Stephens and O'brien's value based on satellite energy measurements, 680 TW/K. The estimated mean planetary temperatures are very close to the experimental values for planets in our solar system. For Earth the estimated value is 278 K compared to the accepted value of 288 K. The high value of the estimated entropy production rate for Earth emphasizes that planetary entropy production is dominated by radiative processes. A small part of the total entropy production rate of Earth is due to circulation. The high entropy production rate due to absorption/re-emission results because SR is emitted from a high temperature source near 6000 K while material on Earth is near 300 K.

2. The present model is also beneficial because it illustrates that surprisingly the mean planetary temperature has a tendency to be independent of the planet's albedo. This is not strictly the case because the thermal emissivity (ε_{LW}) of the Earth is not strictly equal to 1 minus the shortwave albedo (a). For the Earth this difference (ε_{LW} is 0.61 while 1- a is 0.70) is mainly due to the 'greenhouse effect', that is a difference between longwave and shortwave absorption and emission behavior in the atmosphere. We can conclude that the Earth's mean temperature has a tendency of being independent of planetary albedo while being dependent on effects like the greenhouse effect.

3. Prigogine's minimum entropy production principle does not appear to be applicable as a governing principle for atmospheric circulation and, in general, it may have little significance. Prigogine's principle depends on a set of restrictive conditions that are commonly not satisfied. More importantly though, Prigogine's approach requires prior knowledge of the force-flux relationships while the response of the system to external forces, under certain constraints, is completely determined by the force-flux relationships. The steady state condition of the system is completely determined without considering the variation of the entropy production rate with respect to any of the forces. Finding the extremum only serves to emphasize that the entropy production rate is a minimum with respect to any force when the corresponding flux has ceased.

4. Stephens and Obrien have calculated the total entropy production rate of Earth from satellite energy measurements and have suggested that its value supports the maximum dissipation viewpoint. In this thesis we show that Stephens and Obrien's conclusion is not justified for a number of reasons. For example, there is no reason given for considering the case where planetary albedo (a) is fixed, and even with the albedo fixed the approximation used by Stephens and O'brien is accurate for a large range of thermal emissivities (within 1% of the actual value for $\varepsilon_{LW} > 0.5$) and thus a large range of possible states of the system.

11.2 Recommendations

The following are some recommendations for future work:

1. Apply the exergy results of this thesis to the exergy analysis of engineering systems where TR transfer is significant.

2. Calculate the exergy of SR based on its NBR character at (1) the top of the atmosphere, (2) at ground level under clear sky conditions, and (3) at ground level under typical cloud cover conditions.

3. Compare the practical performance of various thermal, quantum, and hybrid quantum-thermal conversion processes.

4. Provide a complete explanation of the non-ideal behaviour of omnicolor quantum conversion and resolve the question of whether reversible quantum conversion is theoretically possible. Investigate thermal processes that allow the reversible conversion of BR fluxes.

5. Resolve the question of the correct expression for NBR exergy. Determine with certainty whether single-frequency quantum or thermal systems are theoretically permissible. A statistical viewpoint of exergy based on a non-equilibrium NBR entropy may be useful.

6. Provide a physical explanation for the occurrence of the 4/3 coefficient for BR entropy.

7. Create a graybody type radiative model of the Earth with radiative character and temperature that can vary as a function of position, with cloud, plant and ice feedback effects. The actual state of the Earth system could be compared to the extrenum state of this model to provide insight into the question of whether the Earth system is in a state of maximum dissipation. The model could also be used to see the effect of increased greenhouse gases (altering radiative behaviour) on planetary conditions.

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