MEASUREMENT OF THE TOTAL HEMISPHERICAL
EMITTANCE OF COPPER AND OF
SPECTRALLY SELECTIVE SURFACES

by

Robert Smalley

Master of Science Thesis
Cornell Material Science Center
GL-77-5-03-1456

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

✓
Ms Thesis
May 1978

Research Group:
Prof. A. J. Sievers
LASSP

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ACKNOWLEDGEMENTS

The author wishes to express his thanks to Professor A. J. Sievers, whose guidance and encouragement made this thesis possible. He would also like to thank the members of the far-infrared group, especially Yves Chaval, Eric Schiff and W. E. Moerner, for answering his many questions and offering valuable suggestions.

L. Wojick deserves a special word of thanks for helping on some of the measurements and data analysis. The author would like to acknowledge the technical assistance of J. Hart of the Technical Operations Lab, and G. Schmidt of the crystal growing facility.

The author also wishes to acknowledge the financial support provided by the Department of Energy, through Contract No. EG-77-S-0301456 and additional support from the NSF through Cornell Materials Science Center, Contract No. 7681083.

TABLE OF CONTENTS

<u>CHAPTER</u>	<u>PAGE</u>
I. INTRODUCTION.	1
A. Background.	2
II. NOMENCLATURE.	6
A. Basic Radiative Processes	6
B. Black Body Radiation.	7
C. Geometric and Frequency Dependence.	8
D. Kirchhoff's Law	10
III. THEORY.	12
A. IR Properties of Copper	12
1. Drude Free Electron Model	12
2. Fresnel Equations	14
3. Surface Impedance	17
4. Absorptivity and Emissivity	18
B. Total Normal Emissivity	19
C. Total Hemispherical Emissivity.	24
IV. APPARATUS AND PROCEDURE	30
A. The Emittance Calorimeter	32
B. The Instrumentation	34
C. Sample Preparation.	36
D. Sample Mounting	38
E. Operation and Data Collection	40

	<u>PAGE</u>
V. DATA ANALYSIS AND CONCLUSIONS	45
A. Data Analysis and Error Estimates	45
1. Non-radiative Terms $\dot{Q}_C$ and $\dot{Q}_g$	45
2. Radiation Term $\dot{Q}_r$	46
B. Estimation OF Errors.	47
C. Experimental Results and Conclusions.	48
1. Copper.	48
2. Solar Selective Thin Films on Cu.	50
3. Solar Selective Thin Films on Metal Films on Quartz	52
APPENDIX A - CALCULATION OF TOTAL HEMISPHERICAL EMISSIVITY OF COPPER FROM THEORY.	55
APPENDIX B - CALCULATION OF EXPERIMENTAL RESULTS AND ERRORS.	58
REFERENCES	63

LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
1.	Data for calculation of total hemispherical emissivity of copper from theory.	57
2.	Experimental data for total hemispherical emittance of copper.	58
3.	Experimental data for Pt/Al ₂ O ₃ , Ni/Al ₂ O ₃ and Al ₂ O ₃ on copper.	60
4.	Experimental data for Pt/Al ₂ O ₃ on Pt on Quartz.	62

LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE</u>
1.	Total hemispherical emittance of copper. Theory of Davisson and Weeks and experimental data of Ramanathan, et. al.	5
2.	Diagram of parallel and perpendicular polarization for reflected radiation. . . .	15
3.	Normal spectral emissivity for copper from Drude theory and extreme relaxation region limit approximation.	21
4.	Normal spectral emissivity for copper from Drude theory and Hagen Rubens approximation.	23
5.	Geometry of emitted radiation.	24
6.	Angular dependence of integrand for total hemispherical emissivity of copper.	27
7.	Theoretical results for total hemispherical emissivity of copper.	29
8.	Schematic of emittance calorimeter.	33
9.	Schematic of instrumentation.	35
10.	Schematic of evaporation equipment for producing thin film.	39
11.	Sample mounting.	41
12.	Data collection.	44
13.	Experimental results for the total hemispherical emittance of copper.	49
14.	Experimental results for total hemispherical emittance of Ni/Al ₂ O ₃ , PT/Al ₂ O ₃ , and Al ₂ O ₃ on copper.	51

PAGE

15. Experimental results for total
hemispherical emittance of Pt/Al₂O₃
on Pt on Quartz. 54

ABSTRACT

The transient calorimetric technique is used to measure the temperature dependence of the total hemispherical emittance of polished copper, solar selective thin films on copper and a solar selective thin film on a metal film on quartz. Our experimental results on copper do not agree with the predictions of the Davisson and Weeks theory. A new theory of the emissivity of metals based on the Drude Free Electron model is developed and compared with the experimental data on copper. With no adjustable parameters, good agreement between this theory and experiment is obtained.

CHAPTER I

INTRODUCTION

All matter is continuously exchanging energy with its environment by absorbing incident radiation from its surroundings and emitting thermal radiant energy to its surroundings. In this work the thermal radiative property called emittance is measured for three classes of materials. The first of these classes is that of good conductors for which the Drude Free Electron model is valid. A simple theoretical model for the emittance can be constructed. Copper is an example of such a material and its emittance is measured and compared with the theory. The second class is that of solar selective thin film coatings on a substrate which is a good conductor. In this class of materials a simple theory is not available so the experimental results are presented without a theoretical discussion for $\text{Ni/Al}_2\text{O}_3$ on copper, $\text{Pt/Al}_2\text{O}_3$ on copper and Al_2O_3 on copper. The final class is that of solar selective thin films over thin metal films on a dielectric substrate. Here again there is no simple theory so the data is presented for $\text{Pt/Al}_2\text{O}_3$ on Pt on Quartz without a theoretical discussion.

-2-

A) BACKGROUND

The problem of the interaction of radiation with matter has been of interest to physicists for a number of years, the first work being done around the turn of the century by Planck,¹ Hagen and Rubens,² and Foote³. More recently the problem has become important in the engineering of spacecraft and solar energy converters, where it is desirable to tailor the thermal radiative properties of an object to accomplish specific tasks.

The terms, emittance and absorptance, are defined as the ratio of the flux emitted or absorbed by a body to some reference flux. Emittance is the ratio of the flux emitted per unit area by a body to the flux emitted per unit area of a perfect radiator, known as a black body. Absorptance is the ratio of the flux per unit area absorbed by a body to the total flux per unit area incident upon the body. These properties are functions of the temperature of the body, the frequency of the radiation, the relative direction between the normal to the surface of the body and the radiation propagation vector, and the surface condition of the body. The dependence upon the surface condition of the body makes it necessary to distinguish between properties of the material and properties of the real specimens measured in the laboratory. The suffix, "ance", on a property will

-3-

signify that it refers to a property of a specimen, such as the emittance of a copper specimen. The suffix, "ivity", on a property will specify that it refers to a property of the material, such as the emissivity of copper. For a specimen which is opaque and has optically smooth, clean surfaces, the emittance is numerically equal to the emissivity.

For metals, which are good electrical and thermal conductors, the Drude Free Electron model combined with the Maxwell Equations can be used to calculate the thermal emittance and absorptance of metal surfaces prepared in such a way that the emittance is equal to the emissivity. Davisson and Weeks have applied this approach, relating the total thermal radiation to the bulk resistivity and the temperature, finding the total thermal emittance to be given by⁴

$$\epsilon = 0.751(rT)^{1/2} - 0.632(rT) - 0.670(rT)^{3/2} - 0.607(rT)^2 \quad (1)$$

for $rT < 0.1$, where r is the electrical resistivity in $\Omega\text{-cm}$ and T is the temperature. Equation (1) and its derivation will be discussed further in Chapter II where the theory is discussed in detail.

A number of experiments have been done to test the validity of the theory of Davisson and Weeks, most recently the work of Ramanathan et. al.⁵ who studied the total hemispherical

emittances of Cu, Al and Ag. Their results for Cu, presented in Figure (1), show a major disagreement between theory and experiment for $T > 300^{\circ}\text{K}$. In this thesis the emittance of Cu is measured and the results are found to be in good agreement with those of Ramanathan. In Chapter III, a simple theoretical model is presented which gives better agreement between theory and experiment than the Davisson and Weeks theory. Chapter II discusses the basic radiative processes, the radiative properties of a black body and the vocabulary necessary to discuss thermal radiation. Chapter III discusses the theory of thermal emittance for the Drude Free Electron model. The experimental apparatus and procedure is described in Chapter IV, and the data analysis and conclusions are discussed in Chapter V.

-5-

Figure 1. Total hemispherical emittance of copper as measured by Ramanathan et al.⁵ as a function of temperature (●) and theoretical expression for emittance by Davisson and Weeks⁴ (Equation (1) (—)).

CHAPTER II

NOMENCLATURE

A) BASIC RADIATIVE PROCESSES

Consider a mechanically isolated body in a vacuum. Thermal energy can be exchanged with its surroundings only through the mechanism of absorption and emission of thermal radiation. For a body in thermal equilibrium with its surroundings, that is, at the same temperature, the rates of absorption and emission of energy must be the same. When a body is not in equilibrium with its environment, the rate of energy transfer through radiation, or radiant heat transfer, is the difference between the rate of absorption of energy from the environment and the rate of emission of thermal radiant energy to the environment. The rates of energy transfer, for both the equilibrium and non-equilibrium cases, are controlled by the thermal radiative properties of the body.

When electromagnetic radiation is incident upon a body, some of the radiation is reflected; some transmitted through the body; and some is absorbed. By energy conservation the sum of the reflected, transmitted and absorbed fluxes must be equal to the incident flux. We can therefore write

$$1 = \rho + \alpha + \tau \quad (2)$$

-7-

where ρ is the reflectance, α is the absorptance and τ is the transmittance of the body. Each of these quantities is the ratio of the flux of interest to the incident flux, e.g. $\rho = (\text{reflected flux/unit area}) / (\text{incident flux/unit area})$.

For a body which is opaque, the transmittance is zero and equation (2) becomes

$$1 = \rho + \alpha. \quad (3)$$

Radiation which is reflected or transmitted by a body has no effect upon the thermal energy of the body, while absorbed radiation will cause an increase in the temperature of the body. The process of absorption therefore allows the background radiation to interact with the thermal energy of the body.

The process of thermal emission of radiation allows the thermal energy of the body to interact with the background radiation, and emission of radiation by a body causes its temperature to decrease as it loses thermal energy.

B) BLACK BODY RADIATION

In order to understand how real bodies interact with radiation, we shall first describe an idealized body, the black body. A black body is a perfect absorber and emitter of radiation. When radiation is incident upon a black body, it is totally absorbed; there is no transmission or reflection.

A black body is also the most efficient emitter of radiation, emitting the maximum flux possible in each frequency interval for a body at a given temperature. The spectral distribution of the black body flux emitted per unit area in a direction normal to the surface is given by the Planck formula

$$M_{\omega} = \left(\frac{1}{2\pi c} \right)^2 \frac{\hbar \omega^3}{e^{\hbar \omega / kT} - 1} \quad 1/\pi \quad (4)$$

and the maximum flux is emitted for the frequency $\omega_{\max}$ given by Weins Law

$$\omega_{\max} = 3.676 \times 10^{11} T. \quad (5)$$

The total radiant energy emitted per unit area in a direction normal to the surface of the black body is found by integrating over all frequencies, giving

$$I = \int_0^{\infty} \left(\frac{1}{2\pi c} \right)^2 \frac{\hbar \omega^3}{e^{\hbar \omega / kT} - 1} d\omega = \sigma T^4 \quad (6)$$

where σ is the Stephan-Boltzman constant. These expressions can be found from a discussion of cavity radiation and are derived in many modern physics texts.

C) GEOMETRIC AND FREQUENCY DEPENDENCE

It is useful to define modifiers of the radiative properties, absorptance and emittance, which will describe the geometric and frequency dependences of these properties.

"Spectral" refers to the property of interest as a function of frequency, such as the spectral emissivity

$$\epsilon(\omega) = \frac{(\text{emitted flux at frequency } \omega/\text{unit area})_{\text{real body}}}{(\text{emitted flux at frequency } \omega/\text{unit area})_{\text{black body}}} \quad (7)$$

"Total" is the value of the property, weighted by the black body distribution, integrated over all frequencies and divided by the integrated black body spectrum, such as the total emissivity

$$\epsilon(t) = \frac{\int_0^\infty M_\omega \epsilon(\omega) d\omega}{\int_0^\infty M_\omega d\omega} \quad (8)$$

"Normal" refers to the property of interest for radiation incident or emitted normal to the surface, such as the normal emissivity ϵ_n .

"Directional" refers to the property of interest as a function of direction, specified by the polar and azimuthal angles (ϕ, θ) , such as the directional emissivity $\epsilon(\phi, \theta)$.

Note that $\epsilon(0,0) = \epsilon_n$. Also note that since emissivities are defined per unit area, the intensity emitted at the azimuthal angle ϕ "as a result of" directional emissivity is $\epsilon(\phi, \theta) \cos \phi$, because of the projection of the area goes as $\cos \phi$.

-10-

"Hemispherical" refers to the value of a property integrated and averaged over a complete hemisphere divided by the black body spectrum integrated and averaged over a complete hemisphere, such as the spectral hemispherical emissivity:

$$\epsilon_h(\omega) = \frac{\int_0^{2\pi} \int_0^{\pi/2} M_\omega \epsilon(\omega; \phi, \theta) \cos \phi \sin \phi \, d\phi d\theta}{\int_0^{2\pi} \int_0^{\pi/2} M_\omega \cos \phi \sin \phi \, d\phi d\theta} \quad (9)$$

These modifiers can be suitably combined to describe such properties as the total normal emissivity; the directional spectral emissivity; and the property which is measured by the experimental technique used in this work, the total hemispherical emissivity

$$\epsilon_{t,h} = \frac{\int_0^\infty \int_0^{2\pi} \int_0^{\pi/2} M_\omega \epsilon(\omega; \phi, \theta) \cos \phi \sin \phi \, d\phi d\theta d\omega}{\int_0^\infty \int_0^{2\pi} \int_0^{\pi/2} M_\omega \cos \phi \sin \phi \, d\phi d\theta d\omega} \quad (10)$$

D) KIRCHHOFF'S LAW

The last relation needed to characterize the radiative properties is Kirchhoff's Law which states that

$$\alpha(\omega, \phi, \theta) = \epsilon(\omega; \phi, \theta) \quad (11)$$

For a black body at temperature T , in thermal equilibrium with thermal black body radiation also at temperature T , Kirchhoff's

-11-

Law must hold in order to maintain equilibrium and conserve energy. When not in equilibrium, and in cases where the background radiation is not black body, Kirchhoff's Law is still valid when applied to the directional spectral emissivity and absorptivity, but is not valid in general for other cases such as the total hemispherical emissivity and absorptivity. We can however under certain conditions write

$$\alpha = \epsilon \quad (12)$$

where α and ϵ can be any absorptivity and emissivity. Where Kirchhoff's Law is used in this work its validity will be justified.

From Kirchhoff's Law

$$1 - \rho = \alpha = \epsilon \quad (13)$$

and this relation allows the emissivity to be calculated since ρ can be found from the Maxwell Equations.

CHAPTER III

THEORY

In Chapter II, the basic concepts of reflectivity, absorptivity and emissivity were introduced and simple physical arguments were used to find relationships between them. In this chapter a simple theoretical model for the thermal emissivity of a Drude Free Electron metal is constructed and in Chapter IV this theory is compared with the experimental emittance of polished copper.

A) IR PROPERTIES OF COPPER

1. The Drude Free Electron Model

In the limit of the classical skin effect, where the electrons mean free path, l , is much less than the skin depth, δ ; the frequency dependent conductivity is given by

$$\sigma(\omega) = \sigma_0 / (1 + i\omega\tau) \quad (14)$$

where σ_0 is the dc conductivity;

$$\sigma_0 = \omega_p^2 \tau / 4\pi \quad (15)$$

and ω_p is the plasma frequency; δ is the imaginary part of the propagation constant and is the distance at which the field amplitudes are $1/e$ of their surface values and τ is the relaxation time. The relaxation time, τ , is the average

time between collisions suffered by the conduction electrons. The expression for the relaxation time must therefore take into account the various scattering mechanisms effecting the conduction electrons. Two scattering mechanisms will be considered here: the bulk scattering of the conduction electrons, which can be described by the Drude theory, and diffuse surface scattering of the conduction electrons by the metal surface. The effective relaxation time, τ , in terms of the bulk relaxation time, τ_b , and the diffuse scattering relaxation time, τ_d , is

$$1/\tau = 1/\tau_b + 1/\tau_d . \quad (16)$$

The bulk relaxation time, in the Drude model, is

$$\tau_b = \frac{m}{ne^2 r} , \quad (17)$$

where m is the electron mass, n is the density of conduction electrons, e is the electronic charge and r is the resistivity. Since the resistivity, r , is a function of temperature, the bulk relaxation time, τ_b , will also be a function of temperature, $\tau_b(T)$, as will the effective relaxation time, $\tau(T)$.

An estimate for τ_d can be made because when electrons scatter diffusely from the surface there is one collision in the time it takes for the electron to traverse twice the

-14-

skin depth δ . Thus

$$\tau_d = 2 \left(\frac{c}{\omega_p} \right) / v_F \quad (18)$$

where c/ω_p is the extreme relaxation limit for the skin depth and v_F is the Fermi velocity. The precise value for τ_d is^{6,7}

$$\tau_d = \frac{8}{3} \left(\frac{c}{\omega_p v_F} \right) . \quad (19)$$

The relaxation time for both bulk and diffuse surface scattering is

$$\frac{1}{\tau} = \frac{ne^2 r}{m} + \frac{3\omega_p v_F}{8c} \quad (20)$$

2. Fresnel Equations

By solving the Maxwell Equations for a plane wave incident upon a plane surface, which separates two media, one with index of refraction unity and the other with complex index of refraction

$$N=n+ik \quad (21)$$

satisfying the boundary conditions that the perpendicular components of $\underline{D}$ and $\underline{B}$ and the normal components of $\underline{E}$ and $\underline{H}$ are continuous across the interface, a set of equations known as Fresnel Equations is found for the reflectivity. These equations express the reflectivity in terms of n and k and the polarization of the incident wave. In Figure 2 the two linear polarizations of interest are presented graphically.

-15-

The plane of incidence is the plane containing $\hat{n}$ and $\hat{k}$, where $\hat{n}$ is the normal to the surface and $\hat{k}$ is in the direction of propagation of the wave. For parallel polarization, the incident $\underline{E}$ is contained in the plane of incidence, while for perpendicular polarization the incident $\underline{E}$ is perpendicular to the plane of incidence. Radiation which is not polarized parallel or perpendicular to the plane of incidence can be written as a linear combination of these polarizations, allowing the general case to be treated.

Figure 2. This figure shows the two polarizations of interest for reflection of electromagnetic waves from a plane interface.

-16-

Stratton⁸ solves for the Fresnel equations in the case of a metal, and these are quite complex. In the case where the Drude Free Electron model applies, however, the Fresnel Equations can be closely approximated by⁹

$$\rho_{\perp} = \frac{(n - \cos \phi)^2 + k^2}{(n + \cos \phi)^2 + k^2} \quad (22)$$

$$\rho_{\parallel} = \frac{(n - 1/\cos \phi)^2 + k^2}{(n + 1/\cos \phi)^2 + k^2} \quad (23)$$

for the cases of perpendicular and parallel polarization.

In Chapter II, it was shown that from ρ the remaining radiation properties α and ϵ can be computed. Thus, if the optical constants, n and k , of any material are known as functions of temperature and frequency, all the thermal radiative properties may, in principle, be computed. The Drude Free Electron model can be used to find expressions for n and k in terms of ω and τ , where τ is the electrical relaxation time at a given temperature T .

For metals in the IR it is customary to use the surface impedance instead of n and k . The next section introduces the surface impedance and relates it to the complex index of refraction, N .

-17-

3. Surface Impedance

The surface impedance is defined as¹⁰

$$Z(\omega, \tau) = R(\omega, \tau) + iX(\omega, \tau) = (4\pi/c) E(O)/H(O) \quad (24)$$

where R is the surface resistance, X is the surface reactance, and $E(O)$ and $H(O)$ are the values of the fields at the surface. In free space, $E=H$, and the impedance of free space is therefore:

$$Z_0 = 4\pi/c \quad (25)$$

The surface impedance appropriate for plane waves is therefore

$$Z(\omega, \tau) = (1+i) (2\pi\omega/c^2\sigma_0)^{1/2} (1+i\omega\tau) \quad (26)$$

which gives the following for the real and imaginary parts of Z/Z_0 :

$$\frac{R}{Z_0} = \left(\frac{1}{2\omega_p \tau} \right) (2\omega_p \tau)^{1/2} ((\omega^2 \tau^2 + 1)^{1/2} - \omega\tau)^{1/2} \quad (27)$$

$$\frac{X}{Z_0} = \left(\frac{1}{2\omega_p \tau} \right) (2\omega_p \tau)^{1/2} ((\omega^2 \tau^2 + 1)^{1/2} + \omega\tau)^{1/2} \quad (28)$$

At the temperatures of interest for thermal radiation $\omega \ll \omega_p$, so $R/Z_0 \ll 1$ and $X/Z_0 \ll 1$. For example, the plasma frequency of Copper is $\omega_p = 1.64 \times 10^{16} \text{ sec}^{-1}$ and at 600°K

-18-

$\omega_{\max} = 2.21 \times 10^{14} \text{ sec}^{-1}$ and $\tau \approx 10^{-14} \text{ sec}$ giving $R/Z_0 \approx 3 \times 10^{-3}$ and $X/Z_0 \approx 1 \times 10^{-2}$.

For a medium with complex index of refraction, N , the relation between N and Z/Z_0 is

$$N = Z_0/Z, \quad (29)$$

which gives for n and k

$$n = (Z_0 R) / (R^2 + X^2) \quad (30)$$

$$k = (Z_0 X) / (R^2 + X^2) \quad (31)$$

4. Absorptivity and Emissivity

Substitution of equations (30) and (31) into (22) and (23) yields the reflectivities, in terms of the surface impedance

$$\rho_{\perp} = \left| \frac{Z_0 - Z \cos \phi}{Z_0 + Z \cos \phi} \right|^2 \quad (32)$$

$$\rho_{\parallel} = \left| \frac{Z_0 \cos \phi - Z}{Z_0 \cos \phi + Z} \right|^2 \quad (33)$$

Equation (13) immediately results in the directional spectral absorptivity and emissivity

$$\alpha_{\perp}(\omega; \phi) = \epsilon_{\perp}(\omega; \phi) = \frac{4Z_0 R \cos \phi}{|Z_0 + Z \cos \phi|^2} \quad (34)$$

-19-

$$\alpha_{\parallel}(\omega; \phi) = \varepsilon_{\parallel}(\omega; \phi) = \frac{4Z_0 R \cos \phi}{|Z + Z_0 \cos \phi|^2} \quad (35)$$

Note that these expressions are independent of the azimuthal angle θ .

Because the relaxation time is the only temperature dependent variable, it gives the temperature dependence of α and ε .

These expressions for emissivity will now be applied to copper in the cases of normal and hemispherical emissivity.

B) NORMAL EMISSIVITY

For normal incidence, $\phi=0$,

$$\varepsilon_n(\omega) = \alpha_n(\omega) = \frac{4Z_0 R}{|Z + Z_0|^2} \quad (36)$$

which becomes

$$\varepsilon_n(\omega) = \alpha_n(\omega) = 4R/Z_0 \quad (37)$$

for copper in the case of thermal radiation because $|Z| \ll Z_0$.

The total normal emittance can now be calculated from the normal spectral emittance by

$$\varepsilon_{t,n} = \frac{\int_0^\infty M_\omega \varepsilon_n(\omega) d\omega}{\sigma T^4} \quad (38)$$

-20-

When the expression for $\epsilon_n(\omega)$ is multiplied by the Planck formula the integrand is quite formidable. However, the behavior of the integrand allows a simple approximation to be made. In Figure 3, the function $\epsilon_n(\tilde{\nu})$, where $\tilde{\nu}=\omega/2\pi c$, is plotted for copper at 600°K. Also plotted is the black body spectrum corresponding to 600°K. From these plots, it is apparent that the greatest contribution to the integrand comes from the flat segment of the emissivity curve, that is, for $\tilde{\nu} > \tilde{\nu}_{\text{relax}}=1/2\pi c\tau$, where $\omega\tau > 1$. Writing the normal spectral emissivity as a function of (ω, τ) the integrand will be approximated by

$$M_{\omega} \epsilon_n(\omega, \tau) \approx M_{\omega} \lim_{\omega\tau \gg 1} \epsilon_n(\omega, \tau) = M_{\omega} \frac{2}{\omega_p \tau} \quad (39)$$

where $2/\omega_p \tau$ is the extreme relaxation limit of the normal spectral emissivity. Evaluation of the integral is now trivial and the result is

$$\epsilon_{t,n}(\tau) = 2/\omega_p \tau \quad (40)$$

for the total normal emissivity. Returning to Figure 3, it is seen that this approximation scheme will cause the result to overestimate the emissivity, providing an upper bound on its value.

In light of previous theoretical work on emissivity, it is interesting to see the results obtained for the normal spectral emissivity in the non-relaxation limit, $\omega\tau \ll 1$.

Figure 3. The normal spectral emissivity of copper at 600°K computed using Equation (37) (—), the black body spectrum for 600°K, the extreme relaxation limit of the normal spectral emissivity (---) and $\tilde{\nu}=1/2\pi\epsilon\tau$.

-22-

Hagen and Rubens² derived a series expansion for the normal spectral emissivity of metals in the non-relaxation limit, $\omega\tau \ll 1$, and Foote³ used this expression to find a series expansion for the total normal emissivity. By applying the same limit to the expression for $\epsilon_n(\omega, \tau)$, the first term in the Hagen-Rubens expansion and Foote's expansion will be found. The validity of using the non-relaxation region limit for thermal emittance in the IR will also be discussed.

The non-relaxation region limit for $\epsilon_n(\omega, \tau)$ is

$$\lim_{\omega\tau \ll 1} \epsilon_n(\omega, \tau) = (2/\omega_p \tau) (2\omega\tau)^{1/2} \quad (41)$$

and this result is the first term in Hagen and Rubens' expression for $\epsilon_n(\omega, \tau)$. By equation (38) the total normal emissivity is

$$\epsilon_{t,n}(\tau, T) = \left(\frac{2}{\omega_p \tau} \right) \left(\frac{2k}{\hbar} \right)^{1/2} (\tau T)^{1/2} \quad (42)$$

which is the first term in Foote's expression for the total normal emissivity. In Figure 4, the Hagen-Rubens formula has been applied to copper at 600°K. It is plotted along with the exact expression for the normal spectral emissivity (Equation (37)) and the black body spectrum. From this graph it is apparent that the limit $\omega\tau \ll 1$ is the wrong limit to use for thermal radiation in the infra-red for metals such as copper.

Figure 4. The normal spectral emissivity of copper at 600°K computed using Equation (37) (—), the black body spectrum for 600°K, and the Hagen Rubens formula (Equation (41)) for copper (---).

-24-

C) TOTAL HEMISPHERICAL EMISSIVITY

Figure 5 shows the geometry for the radiation emitted into a solid angle $d\Omega$.

Figure 5. Geometry of emitted radiation.

Because the emitted radiation is unpolarized in general, an expression for the directional spectral emissivity of unpolarized radiation $\epsilon(\phi, \theta)$ must be constructed from the expressions for $\epsilon_{\perp}$ and $\epsilon_{\parallel}$ given in equations (34) and (35). For completely unpolarized incident radiation

$$\rho(\phi) = 1/2 (\rho_{\perp}(\phi) + \rho_{\parallel}(\phi)), \quad (43)$$

-25-

and this yields for the emissivity of unpolarized radiation

$$\varepsilon(\phi) = 1/2 (\varepsilon_{\perp}(\phi) + \varepsilon_{\parallel}(\phi)).$$

Equation (10), for the total hemispherical emissivity, therefore becomes

$$\varepsilon_{t,h} = \frac{-\int_0^{\infty} \int_0^{2\pi} \int_1^0 M_{\omega} 1/2 (\varepsilon_{\perp}(\phi; \omega) + \varepsilon_{\parallel}(\phi; \omega)) \cos \phi \, d(\cos \phi) d\theta d\omega}{\pi \sigma T^4} \quad (45)$$

This integral will be treated in two parts, one for each polarization.

The case of perpendicular polarization can be approximated by

$$\varepsilon_{t,h,\perp} = \frac{\int_0^{\infty} \int_0^{2\pi} \int_1^0 M_{\omega} \varepsilon_n(\omega) \cos^2 \phi \, d(\cos \phi) d\theta d\omega}{\pi \sigma T^4} \quad (46)$$

as $|Z \cos(\phi)| < |Z| \ll Z_0$, with ε_n given by Equation (37). Comparing this formula with Equation (38) the only difference between the two expressions is the angular integration and averaging. Doing the angular integration and using the results of integration of Equation (38) the total hemispherical emissivity for the radiation polarized perpendicular to the plane of emission is

$$\varepsilon_{t,h,\perp} = \frac{2}{3} \varepsilon_{t,n} = \frac{4}{3} \frac{1}{\omega_p \tau} \quad (47)$$

-26-

As in the case of the total normal emissivity, this result will overestimate the total hemispherical emissivity for perpendicular polarization.

For the case of parallel polarization the following equation is obtained:

$$\epsilon_{t,h;\parallel} = \frac{\int_0^\infty \int_0^{2\pi} \int_1^0 M_\omega \frac{4RZ_0}{|Z+Z_0 \cos \phi|^2} \cos^2 \phi d(\cos \phi) d\theta d\omega}{\pi \sigma T^4} \quad (48)$$

This expression cannot be simplified as readily as in the case of perpendicular polarization because, for large angles, ϕ , from the normal $|Z_0 \cos(\phi)| < |Z|$ and the Z term cannot be dropped. The function $\epsilon(\phi; \tilde{\nu}_{\max}(600^\circ\text{K})) \cos \phi / \epsilon_n(\tau(600^\circ\text{K}))$ vs. ϕ , is plotted in Figure 6, which shows that the integrand is approximately constant and equal to the normal emittance for angles less than 70° . Also, for angles greater than 85° , the emissivity drops rapidly to zero, while for angles between 70° and 85° the emissivity drops to about 90% of its normal value. The emissivity therefore can be approximated by a step function, having the normal emittance value, ϵ_n , to some cut-off angle, θ_c . Setting $\theta_c = 90^\circ$ as a first approximation yields

$$\epsilon_{t,h;\parallel} = \frac{\epsilon_n \int_0^\infty \int_0^{2\pi} \int_1^0 M_\omega d(\cos \phi) d\theta d\omega}{\pi \sigma T^4} \quad (49)$$

Figure 6. Plot of $\epsilon(\phi; \nu_{\max}(T=600^{\circ}\text{K})) \cos \phi / \epsilon_n(\tau(600^{\circ}\text{K}))$ illustrating angular dependence of the integrand in Equation (48).

-28-

$$\epsilon_{t,h;\parallel} = 2\epsilon_{t,n} \quad (50)$$

as the total hemispherical emissivity for radiation polarized parallel to the plane of incidence.

The total hemispherical emissivity is therefore

$$\epsilon_{t,h} = \frac{4}{3} \epsilon_{t,n} = \frac{8}{3} \left(\frac{1}{\omega_p \tau} \right) \quad (51)$$

in the extreme relaxation region limit, $\omega\tau \gg 1$. This result is plotted in Figure 7 for copper. Again, the approximation scheme overestimates the emissivity so the result found is an upper bound for the emissivity.

In Figure 7, the results of Davisson and Weeks theory, derived in the non-relaxation region limit, are also plotted for copper. Using the same reasoning as in the case of normal emissivity, it is observed that, for thermal radiation in the infra-red, application of the non-relaxation limit is incorrect.

In Chapter V, the experimental results for copper are compared with the theory presented here.

Figure 7. The total hemispherical emissivity of copper as a function of temperature for the theory of Davisson and Weeks (Equation (1)) and the theory developed in this thesis (Equation (51)). These curves are calculated in Appendix A.

CHAPTER IV

APPARATUS AND PROCEDURE

The transient calorimetric technique offers a relatively simple way to measure a specimen's total hemispherical emittance. In this technique a thermally isolated sample, not in thermal equilibrium with its surroundings, is brought to thermal equilibrium predominately by radiative heat transfer to the walls of a calorimeter, which is maintained at some temperature T_0 . The rate of heat transfer, measured in terms of the rate of change of the temperature of the specimen, is then equated to the rate of radiative heat transfer and the total hemispherical emittance can be found.

The success of this technique depends upon thermally isolating the sample from the surroundings so that the dominant mode of heat transfer is by radiation. To accomplish this isolation, the calorimeter is evacuated to minimize losses through the atmosphere, and the mechanical mounting is designed to minimize conduction losses through the supports. To minimize losses through the supports the samples were mounted by hanging them from .005" Chromel-Alumel thermocouple wires (2 wires) and the power to heat the sample to higher than ambient temperature was supplied by induction

-31-

heating, eliminating the need for mechanical heating connections. There are two loss mechanisms associated with gasses: convection and conduction. For residual gas pressures where the mean free path of the molecules is greater than the distance between the two surfaces exchanging thermal energy, the mechanism of convection is eliminated, leaving only the mechanism of gaseous conduction. The conduction losses are pressure-dependent, and decreasing the pressure reduces the conduction losses. Thermal radiation by the thermocouple wires and the residual gas will not be considered, as these effects are negligible.

For a sample at temperature T , of mass M , surface area A , and specific heat, $C_p(T)$, the power loss is given by the energy balance equation

$$-MC_p(dT/dt)|_T = \epsilon_{t,h}(T) \sigma AT^4 - \alpha_{t,h}(T) \sigma T_o^4 + \dot{Q}_c + \dot{Q}_g, \quad (52)$$

where $\epsilon_{t,h}(T)$ is the total hemispherical emittance at temperature T ; $\alpha_{t,h}(T)$ is the total hemispherical absorptance at temperature T ; and $\dot{Q}_c$ and $\dot{Q}_g$ are, respectively, correction terms for the heat loss by the thermocouple wires and conduction losses through the residual gas in the vacuum chamber. The terms $\dot{Q}_c$ and $\dot{Q}_g$ will be discussed in Chapter V in the section on data analysis.

Equation (52) is usually simplified by application of Kirchhoff's Law. By assuming that the background radiation

-32-

in the calorimeter is black body and by applying Kirchhoff's Law, Equation (52) becomes

$$-MC_p(T) dT/dt|_T = \sigma A \epsilon_{t,h}(T) (T^4 - T_o^4) + \dot{Q}_g + \dot{Q}_c, \quad (53)$$

and this is the form of the energy balance equation used to evaluate the data.

A) THE EMITTANCE CALORIMETER

The emittance calorimeter was constructed from a 4'id x 12" long Pyrex Conical Pipe fitted with an induction heater coil and end flanges to connect to the vacuum system (bottom) and sample holder (top). The vacuum system consisted of a LN₂ cold trap, a diffusion pump, and a mechanical roughing pump which maintained a sample chamber pressure of 1-2x10⁻⁵ torr during the experimental runs. The sample mounting flange was designed to allow repositioning of the sample in the vacuum chamber without disturbing the vacuum. This allows the sample to be positioned in the induction heater coil for heating and then be removed from the coil during measurement of the cooling rate.

The sample was supported by thermocouple wires which pass through the movable center column. This column passes through a double O-ring seal which is evacuated by a mechanical pump. (Figure 8).

Figure 8. Schematic of Emittance Calorimeter.

-34-

B) THE INSTRUMENTATION

The Chromel-Alumel thermocouples operated in the differential mode were used to determine the sample temperature and dT/dt . One of the thermocouple junctions was at the sample temperature and the other junction was maintained at a reference temperature of 0°C . The thermocouple junction at the sample was also used to support the sample. The reference junction was immersed in an ice water bath. This double immersion was found to give more stability than placing the reference thermocouple junction directly in the ice water bath.

The electronics equipment necessary to record the data included a Kiethley Model 148 Nanovoltmeter, an HP Model 3450A Digital Multifunction Meter, an HP Model 580A Digital to Analog Converter, and an HP Model 17500A chart recorder (Figure 9). The output signal of the thermocouple circuit was input to the Nanovoltmeter. The nanovoltmeter amplified this signal and output it to the digital voltmeter which digitized the signal. The digital signal was output from the voltmeter and input to the Digital to Analog Converter which converts three consecutive digits of the input signal to an analog output. By choosing the three least significant digits of the $5\frac{1}{2}$ digits input to the DAC for conversion to an analog signal, it is possible to

-35-

Figure 9. Schematic of Instrumentation used to collect data from Emittance Calorimeter.

-36-

expand greatly the resolution of the slope of the cooling curve. The two most significant digits, which are lost in this process, must be known in order to find the thermocouple output voltage and thus the temperature. The output of the DAC is sent to a chart recorder which records the time variation of the thermocouple output voltage.

Heating of the sample is done by a Lepel Model T-20-3-DF-R-S RF Generator, rated for 20Kw at 450 Hz. The output of the RF generator is coupled through a matching transformer to the 1 1/2" id. coil in the sample chamber.

C) SAMPLE PREPARATION

It has been found that the emittance is highly dependent upon the microscopic surface condition and the macroscopic shape of a specimen. Because of this dependence of emittance upon properties of the individual specimen, care must be taken in preparation, handling and description of the specimen to assure that the data are reproducible and meaningful. The preparation techniques used in this study minimize the specimen dependence of the measurements.

Ramanathan et. al.⁵ have studied the effects of surface preparation and sample shape by using a sample of high purity copper (percentage purity 99.999). They found that the best results were obtained using an electropolished sphere. Their

-37-

results also show that a carefully prepared mechanically polished flat plate gives results in good agreement with an electropolished sphere. The difficulty of surface preparation for the sphere and the agreement of the flat plate results with those of the sphere make the flat plate geometry a good experimental choice. The flat plate geometry also allows spectrally selective films to be applied easily to the specimen for emittance measurements of the films. The copper specimens used in this work were made from 1/16" flat plate OFHC copper milled into rectangles roughly 3/4" on a side. The two larger faces of these samples were then mechanically polished to optical surfaces using, in order, 600 grit dry sandpaper, 9.5 μ Alumina, 3.0 μ Alumina and finally .3 μ Alumina grit. These two surfaces are the main radiating, or emitting, surfaces. The polishing was done on a flat glass plate covered with felt grinding pads and a slurry was formed by using either water or ethelene glycol with the Alumina. The sides of the sample were polished in a similar fashion, but only down to the 9.5 μ grit. The specimens were cleaned after polishing with Benzene, Acetone and tap water.

The copper specimens used as substrates for the spectrally selective films were then coated by H. Craighead by evaporation techniques. The composite films were produced by evaporating the metal and dielectric simultaneously from

independently controlled electron beam evaporators in an oil free vacuum system at pressures of approximately 10^{-8} torr. The substrate was mounted 30 cm above the evaporation sources and could be heated to a temperature of 500°C if desired. All of the coated samples except the Al_2O_3 film on a copper substrate were made with the substrate heated to approximately 500°C . The Al_2O_3 on copper sample was produced with the temperature uncontrolled. The thin film coatings applied on the optical surfaces of the copper substrates were also of optical quality and did not require further preparation before measurement.

The sample using a quartz substrate was prepared by H. Craighead in the same manner as the samples using copper substrates and was cleaned with acetone and cotton before measurement. Figure 10 is a schematic of the evaporation equipment used to coat the samples.

D) SAMPLE MOUNTING

The sample mounting procedure was designed to minimize the heat loss through the supports and allow the temperature of the sample to be determined by a thermocouple. For the conducting samples, this minimization was accomplished by drilling a hole in one edge of the sample with a #64 drill, placing the thermocouple junction into

-39-

Figure 10. Schematic of evaporation equipment used by H. Craighead to prepare spectrally selective films.

-40-

the hole and then force fitting a copper plug into the hole. The sample was thus supported by the two .005" diameter thermocouple wires which were attached to the movable center column of the top flange of the vacuum chamber.

For non-conducting samples a copper holder was constructed in order that the induction heater could again be used. This holder consisted of front and back copper foils which were polished to optical surfaces (smallest grit used was 9.5 μ) and a copper body to hold the non-conducting sample. The emittance of this holder was measured with a copper foil in place of the dielectric sample so that the emittance of the dielectric samples could be calculated. This holder was mounted in the vacuum chamber in the same manner as the conducting samples, that is, by the thermocouple and copper plug. Stainless steel screws were used to hold the mount together.

E) OPERATION AND DATA COLLECTION

The experimental procedure used was simple and straightforward but time consuming. After mounting the sample on the thermocouple wires attached to the top flange the sample chamber was evacuated to a pressure of $1-2 \times 10^{-5}$ torr, the pressure at which the experimental measurements were done. The ice water bath, which provided the 0°C

-41-

CONDUCTING SAMPLES

NON CONDUCTING SAMPLES

Figure 11. Sample Mounting.

-42-

reference temperature, was contained in a small dewar. It was found that best stability was obtained after a twenty-four hour delay for the bath to reach equilibrium after the dewar was at room temperature. By refilling with ice daily, keeping the dewar continuously cold, the ice water bath provided a stable reference temperature.

When the ice water bath and the vacuum were ready, the sample was lowered into the induction heater coil the cooling water in the heater coil was turned on and the sample was ready to be heated. By adjustment of the power output of the induction heater the rate of heating could roughly be controlled by observation of the temperature curve on the chart recorder. When the sample reached the desired temperature it could be maintained there, if desired, by appropriate adjustment of the power output. To take data, the induction heater was turned off, the cooling water in the heater coil was turned off and the sample was removed from the coil and repositioned approximately 3" to 4" above it. As the sample cooled, temperature versus time data were recorded on the chart recorder. The nonovoltmeter was set to the most sensitive scale to assure maximum resolution and the chart speed was adjusted to give a reasonable slope to the T vs. t data. During the heating cycle the Digital to Analog Converter (DAC) was set to

-43-

convert the most significant digits from the Digital Voltmeter for recording by the chart recorder. To measure the cooling rate, the DAC was set to convert the three least significant digits for recording by the chart recorder and the two most significant digits had to be recorded by hand. This procedure allowed measurement of the voltage output of the thermocouple, and consequently, the temperature, and produced an effective zero offset which expanded the slope so that a more accurate determination of dT/dt could be made.

-44-

DAC - most significant digits
 NVM - most sensitive scale able to measure thermocouple output

DAC - three least significant digits
 NVM - most sensitive scale able to measure thermocouple output.

adjust chart speed to get reasonable slope on chart recorder.

During heating $E = (\text{chart reading}) \times (\text{full scale setting on NVM})$ where E is the thermocouple EMF.

During cooling $E = (XX + .01 \times \text{chart reading}) \times (\text{full scale setting on NVM})$

The temperature is then found from EMF vs. T table for Chromel-Alumel thermocouples.

Figure 12. Data Collection

CHAPTER V

DATA ANALYSIS AND CONCLUSIONS

This chapter is divided into two sections. The first section discusses the procedure for analyzing the data and making error estimates. The second section consists of three parts, one for each of the three classes of materials for which the emittance was measured.

A) DATA ANALYSIS AND ERROR ESTIMATES

In Chapter IV the energy balance equation relating the total power loss of the sample to the various loss mechanisms was presented. This equation will now be applied to calculate the total hemispherical emittance for the copper sample.

1) Non-radiative terms $\dot{Q}_g$ and $\dot{Q}_c$

In Chapter IV it was stated that the success of the transient calorimetric technique depends upon minimizing the heat losses by conduction through the residual gas and the sample mounts. A comparison of estimates of the magnitudes of $\dot{Q}_g$ and $\dot{Q}_c$ to the total heat loss, $\dot{Q}_g = -MC_p \dot{T}$, reveals how completely the sample is isolated and will determine if these terms must be taken into consideration.

An approximation for $\dot{Q}_g$ can be found from¹²

$$\dot{Q}_g = 2.426 \times 10^{-4} A ((\gamma+1)/(\gamma-1)) (MT_g)^{-1/2} p \Delta T \quad (54)$$

where A is the area of the surface of interest in cm²; γ is the ratio of specific heats, $\gamma = c_p/c_v$; M is the molecular weight of the gas in g/mole; T_g is the temperature at the pressure gauge in °K; p is the pressure in microns and ΔT is the temperature difference in °K between the surfaces exchanging thermal energy. For the experiment performed on copper $\dot{Q}_g < .01 \dot{Q}_t$ so the correction term can therefore be dropped.

Assuming that the temperature gradient in the thermocouple wires is linear, an approximation to the power loss in the wires is

$$\dot{Q}_c = \kappa A (\Delta T / l) \quad (55)$$

where κ is the thermal conductivity; A is the area of the wires; ΔT is the temperature difference between the ends of the wires and l is the length of the wires. For the experiment on copper $\dot{Q}_c < .035 \dot{Q}_t$ and this effect is too great to ignore, so $\dot{Q}_c$ will be kept.

2) Radiation Term $\dot{Q}_r$

For a sample with all of its surfaces prepared in the same manner, the radiation term $\dot{Q}_r$ is

-47-

$$\dot{Q}_r = \epsilon_{t,h} A \sigma (T^4 - T_o^4) \quad (56)$$

(from Chapter IV). For samples which are not prepared in the same way on all sides $\dot{Q}_r$ should reflect this variation, and take into account different emittances from the different sides. For the copper samples used in these experiments, the 1/16" edges of the samples were not as finely polished as the main radiating faces so $\dot{Q}_r$ becomes

$$\dot{Q}_r = (\epsilon_{t,h;s} A_s + \epsilon_{t,h;x} A_x) \sigma (T^4 - T_o^4) \quad (57)$$

where the subscripts s and x refer to the samples' main radiating faces and edges respectively. For the samples used in this experiment, $A_x/A_{total} \approx .15$, and the edge effects are not small enough to be ignored.

B) ESTIMATION OF ERRORS

From the results obtained by the calculations of Section A, the final energy balance equation for the copper sample is:

$$-MC_p \dot{T} = (\epsilon_{t,h;s} A_s + \epsilon_{t,h;x} A_x) \sigma (T^4 - T_o^4) + \dot{Q}_c \quad (58)$$

This formula will now be applied to calculate an estimate for the error.

For the propagation of non-correlated errors the relative error is approximated by

$$\frac{\delta \epsilon_s(x)}{\epsilon_s} = \frac{1}{\epsilon_s} \sum_i \frac{\partial \epsilon_s}{\partial x_i} \delta x_i \quad (59)$$

Solving equation (58) for ϵ_s and applying equation (59), the relative error is

$$\begin{aligned} \frac{\delta \epsilon_s}{\epsilon_s} = & \frac{4}{(T^4 - T_o^4)} (T^4 (\delta T/T) + T_o^4 (\delta T_o/T_o)) + \\ & (\epsilon_x A_x / \epsilon_s A_s) (\delta \epsilon_x / \epsilon_x + \frac{4}{(T^4 - T_o^4)} (T^4 (\delta T/T) + T_o^4 (\delta T_o/T_o)) + \\ & \frac{MC_p \dot{T}}{\epsilon_s \sigma A_s (T^4 - T_o^4)} (\delta \dot{T} / \dot{T}) + \frac{\delta \dot{Q}_c}{\epsilon_s \sigma A_s (T^4 - T_o^4)} \end{aligned} \quad (60)$$

caused by uncertainty in the measurement of T , T_o , $\dot{T}$, and ϵ_x . The quantities M , C_p , A_s , and A_x are known accurately enough to make their contributions to the error negligible.

B) EXPERIMENTAL RESULTS AND CONCLUSIONS

1) Copper

In Figure 13 the experimental results for the total hemispherical emittance of copper are plotted along with the theory of Davisson and Weeks and the theory developed in Chapter III. The error bars are computed from equation (60) with the $\delta \dot{Q}_c$ term ignored, since for $\delta \dot{Q}_c / \dot{Q}_c < .5$ the error contribution from this term is small. Appendix B contains the data from which the results in Figure 13 were found.

Figure 13. Experimental results for the total hemispherical emittance of copper (o) and the theoretical results of this thesis (Chapter III, Equation (51)) and the work of Davisson and Weeks (Chapter I, Equation (1)). The data is presented in Appendix B.

-50-

2) Solar Selective Thin Films on Copper

Solar selective thin films were applied to one face of three flat plate copper samples, and the total hemispherical emittance was measured. For these samples the energy balance equation becomes (ignoring $\dot{Q}_c$)

$$-MC_p \dot{T} = (\epsilon_s A_s + \epsilon_{Cu} A_s + \epsilon_x A_x) \sigma (T^4 - T_o^4), \quad (61)$$

where the subscripts s, Cu, x refer to the coated side, the bare copper side and the edges respectively. Solving for ϵ_s and applying equation (59), the relative error is

$$\begin{aligned} \frac{\delta \epsilon_s}{\epsilon_s} = & \frac{4}{(T^4 - T_o^4)} (T^4 (\delta T/T) + T_o^4 (\delta T_o/T_o)) + \\ & (\epsilon_{Cu} A_{Cu} / \epsilon_s A_s) (\delta \epsilon_{Cu} / \epsilon_{Cu} + \frac{4}{(T^4 - T_o^4)} (T^4 (\delta T/T) + T_o^4 (\delta T_o/T_o))) + \\ & \frac{MC_p \dot{T}}{\epsilon_s \sigma A_s (T^4 - T_o^4)} (\delta \dot{T} / \dot{T}) . \end{aligned} \quad (62)$$

assuming $\epsilon_x = \epsilon_{Cu}$ and letting $A_{Cu} = A_s + A_x$. Ignoring $\dot{Q}_c$ causes an additional 3% error in the measurement of ϵ_s .

Appendix B contains the data from which the results in Figure 14 are found.

Figure 14. Experimental results for the total hemispherical emittance of solar selective thin films. The data are presented in Appendix B.

3) Solar Selective Thin Films on Metal Films on Quartz

Because quartz is not a conductor the induction heating method cannot be used to heat the sample in the same fashion as for the copper samples. In order to make use of the emittance calorimeter for non-conducting samples, a sample holder was constructed of copper (See Chapter III-D and Figure 11). This sample holder has an opening in one face through which the quartz sample could radiate. The emittance of the holder was measured with a copper sample inserted to provide the value for ϵ_{holder} . The equation

$$-MC_p \dot{T} = (\epsilon_s A_s + \epsilon_{\text{holder}} A_{\text{holder}}) \sigma (T^4 - T_o^4),$$

is used to find the emittance of the sample where A_s is the emitting area of the sample and is the area of the hole in the face of the holder, A_{holder} is the area of the holder, and ϵ_{holder} is the emittance measured with the copper sample mounted in the holder. The experiment was run twice on this sample. In the first run, the sample was heated to 550°C and the induction heater was turned off. The data from this run suggested that the quartz sample had not reached equilibrium with the copper sample holder, so the run was repeated, this time maintaining the sample holder at 550°C for 1/2 hour before turning off the induction heater. The purpose of this procedure was to

-53-

allow the sample to reach thermal equilibrium with the sample holder. The results of this run are plotted in Figure 15 for Pt/Al₂O₃ on Pt on quartz. At this time the temperature dependence of the emittance is not understood.

-54-

Figure 15. Experimental results for the total hemispherical emittance of a solar selective thin film on a metal film on a quartz substrate. (Pt/ Al_2O_3 on Pt on Quartz. The data are presented in Appendix B.

APPENDIX A
CALCULATION OF TOTAL HEMISPHERICAL
EMISSIVITY OF COPPER FROM THEORY

The total hemispherical emissivity will now be calculated from the theory developed in Chapter III and the theory of Davisson and Weeks.

To compute the emissivity from Equation (51) the parameters ω_p , τ_b and τ_d are required, and will be determined.

The plasma frequency, ω_p , is given by¹³

$$\omega_p = 71.63 (r_s/a_0)^{-3/2} \times 10^{15} \text{ sec}^{-1}$$

where r_s is the radius of a sphere whose volume is equal to the volume per conduction electron and a_0 is the Bohr radius.

For copper $r_s/a_0 = 2.67^{13}$ which gives

$$\omega_p = 1.64 \times 10^{16}$$

The bulk relaxation time is given by¹³

$$\tau_b = (0.22 (r_s/a_0)^3 / \rho) \times 10^{-14}$$

where ρ is the resistivity in $\mu\Omega\text{-cm}$.

The diffuse relaxation time, given by equation (19) requires the Fermi velocity for copper which is $1.57 \times 10^8 \text{ cm/}$

-56-

sec.¹³ This gives

$$\tau_d = 3.11 \times 10^{-14} \text{ sec.}$$

ρ and T are needed to compute the theoretical values from the Davisson and Weeks theory. The electrical resistivity, ρ , is obtained from Goldsmith.¹¹

TABLE 1. Data for calculation of total hemispherical emissivity of copper from theory.

T (K)	ρ $\mu\Omega\text{cm}$	τ_b (sec)	τ (sec)	τ	ϵ Ch-3	ϵ D&W
300	1.70	2.46×10^{-14}	3.11×10^{-14}	1.37×10^{-14}	1.19	1.66
400	2.25	1.86×10^{-14}		1.16×10^{-14}	1.40	2.19
500	2.80	1.50×10^{-14}		1.01×10^{-14}	1.61	2.72
600	3.45	1.21×10^{-14}		8.71×10^{-15}	1.87	3.28
700	4.10	1.02×10^{-14}		7.68×10^{-15}	2.12	3.83
800	4.75	8.82×10^{-15}		6.87×10^{-15}	2.37	4.37

APPENDIX B

TABLE 2. Experimental data for total hemispherical emittance of copper.

$T(^{\circ}\text{K})$	$\dot{T}$ ($^{\circ}\text{K/sec}$)	$C(T)^{14}$ (joules/gok)	$\dot{Q}_t$ (watts)	$\dot{Q}_c$ (watts)	$\epsilon_{t,h}(T)$
820.3	2.255×10^{-1}	4.45×10^{-1}	5.408×10^{-1}	2.22×10^{-3}	2.40×10^{-2}
785.1	1.840×10^{-1}	4.41×10^{-1}	4.083×10^{-1}	2.07×10^{-3}	2.32×10^{-2}
749.9	1.456×10^{-1}	4.37×10^{-1}	3.202×10^{-1}	1.92×10^{-3}	2.19×10^{-2}
714.7	1.180×10^{-1}	4.33×10^{-1}	2.572×10^{-1}	1.77×10^{-3}	2.16×10^{-2}
679.2	9.395×10^{-2}	4.29×10^{-1}	2.027×10^{-1}	1.62×10^{-3}	2.08×10^{-2}
643.6	7.227×10^{-2}	4.25×10^{-1}	1.546×10^{-1}	1.47×10^{-3}	1.94×10^{-2}
607.8	5.471×10^{-2}	4.21×10^{-1}	1.160×10^{-1}	1.32×10^{-3}	1.89×10^{-2}
571.8	4.101×10^{-2}	4.17×10^{-1}	8.608×10^{-2}	1.17×10^{-3}	1.82×10^{-2}
535.4	3.086×10^{-2}	4.13×10^{-1}	6.415×10^{-2}	1.02×10^{-3}	1.80×10^{-2}
520.7	2.582×10^{-2}	4.12×10^{-1}	5.346×10^{-2}	9.53×10^{-4}	1.70×10^{-2}
508.4	2.315×10^{-2}	4.10×10^{-1}	4.777×10^{-2}	9.02×10^{-4}	1.69×10^{-2}
496.0	1.984×10^{-2}	4.09×10^{-1}	4.080×10^{-2}	8.50×10^{-4}	1.61×10^{-2}
471.0	1.572×10^{-2}	4.06×10^{-1}	3.211×10^{-2}	7.44×10^{-4}	1.61×10^{-2}
446.0	1.182×10^{-2}	4.03×10^{-1}	2.398×10^{-2}	6.38×10^{-4}	1.56×10^{-2}
421.0	8.133×10^{-3}	4.01×10^{-1}	1.638×10^{-2}	5.33×10^{-4}	1.43×10^{-2}

To compute the error bars the quantities δT , δT_o , $\delta \dot{T}/\dot{T}$ and $\delta \epsilon_x/\epsilon_x$ are needed. For the Chromel-Alumel thermocouples

and the total error $\delta\epsilon_s/\epsilon_s=12.4\%$. As T approaches T_o the error terms associated with T_o and ϵ_x increase and the total error increases to 14.3%.

-60-

TABLE 3. Experimental data for Pt/Al₂O₃, Ni/Al₂O₃ and Al₂O₃ on copper.

T(°K)	$\dot{T}$ Pt/Al ₂ O ₃	$\epsilon_{t,h}$ (%)	$\dot{T}$ Ni/Al ₂ O ₃	$\epsilon_{t,h}$ (%)	$\dot{T}$ Al ₂ O ₃	$\epsilon_{t,h}$ (%)
	(°K/sec)		(°K/sec)		(°K/sec)	
749.9	3.37x10 ⁻¹	8.91			1.99x10 ⁻¹	4.06
714.7	2.69x10 ⁻¹	8.57			1.61x10 ⁻¹	4.01
679.2	2.03x10 ⁻¹	7.81	6.43x10 ⁻¹	30.9	1.329x10 ⁻¹	4.18
643.6	1.54x10 ⁻¹	7.29	4.86x10 ⁻¹	29.0	1.05x10 ⁻¹	4.12
607.8	1.14x10 ⁻¹	6.75	3.63x10 ⁻¹	27.2	8.25x10 ⁻²	4.19
571.8	8.37x10 ⁻¹	6.31	2.66x10 ⁻¹	22.7	6.53x10 ⁻²	4.42
535.4	6.30x10 ⁻¹	6.34	1.79x10 ⁻¹	22.0	5.01x10 ⁻²	4.19
520.7	5.37x10 ⁻¹	6.05	1.54x10 ⁻¹	22.2	4.27x10 ⁻²	4.42
508.4	4.90x10 ⁻¹	6.20	1.40x10 ⁻¹	22.0	3.95x10 ⁻²	4.60
496.0	4.24x10 ⁻¹	5.93	1.24x10 ⁻¹	20.9	3.53x10 ⁻²	4.39
471.0	3.30x10 ⁻¹	5.87	9.33x10 ⁻²	19.1	2.78x10 ⁻²	4.59
446.0	2.50x10 ⁻¹	5.81	6.63x10 ⁻²	18.3	2.18x10 ⁻²	4.60
421.0	1.85x10 ⁻¹	5.74	4.73x10 ⁻²	18.6	1.65x10 ⁻²	4.65

used the accuracy is¹⁵

$$\begin{aligned} T < 530^{\circ}\text{K} & \quad \pm 2.22^{\circ}\text{K} \\ T > 530^{\circ}\text{K} & \quad \pm (.008T - 2.18)^{\circ}\text{K}. \end{aligned}$$

The error in measuring the slope is less than 5%, giving a maximum of $\delta T/T = .05$. L. Wojik measured the total hemispherical emittance of a copper sample which was only polished down to the 9.5 μ grit on the main radiating faces and found the emittance varied by less than 6% from the sample polished as in Chapter IV. Taking $\epsilon_x = \epsilon_s$ and $\delta\epsilon_x/\epsilon_x = .2$ in Equations (58) and (60) will give a reasonable value for the error due to the edges, which are not polished as well as the main radiating faces. For $T = 820.3^{\circ}\text{K}$ the error terms are

$$\frac{4T^4(\delta T/T)}{(T^4 - T_o^4)} = 2.17 \times 10^{-2}$$

$$\frac{4T_o^4(\delta T_o/T_o)}{(T^4 - T_o^4)} = 5.1 \times 10^{-4}$$

$$\frac{MC_p \dot{T}(\delta \dot{T}/\dot{T})}{\epsilon_s A_s \sigma (T^4 - T_o^4)} = 6.21 \times 10^{-2}$$

$$\frac{A_x}{A_s} (\delta\epsilon_x/\epsilon_x + \dots) = 3.99 \times 10^{-2}$$

-62-

TABLE 4. Experimental data for Pt/Al₂O₃ on Pt on Quartz.

T(°K)	C _p (T) ¹⁶	ε _{holder} (%)	$\dot{T}$ (°K/sec)	ε (%)
714.7	1.089	5.37	3.98x10 ⁻¹	20.1
679.2	1.072	5.18	3.14x10 ⁻¹	16.1
643.6	1.054	4.99	2.24x10 ⁻¹	13.2
607.8	1.036	4.68	1.62x10 ⁻¹	10.5
571.7	1.018	4.59	1.24x10 ⁻¹	10.3
535.4	0.993	4.51	9.00x10 ⁻²	8.67
520.7	0.982	4.30	7.13x10 ⁻²	7.94
508.4	0.972	4.32	6.98x10 ⁻²	8.83
496.0	0.963	4.20	6.16x10 ⁻²	9.08
471.0	0.944	4.08	4.78x10 ⁻²	9.14
446.0	0.916	3.89	3.65x10 ⁻²	10.1
421.0	0.890	3.76	2.67x10 ⁻²	10.0

REFERENCES

1. Planck, Sitz. Königl. Ak. Wiss., Berlin, 278(1903).
2. Hagen and Rubens, Sitz. Königl. Ak. Wiss., Berlin, 468(1910).
3. Foote, Bull. of Bureau of Standards 11, 607(1914-15).
4. Davisson and Weeks, Jour. of Opt. Soc. of Am. 8, 581(1924).
5. Ramanathan, Yen and Estalote, Applied Optics 16, 2810(1977).
6. Dingle, Physica 19, 311(1953).
7. Holstein, Phys. Rev. 96, 535(1954).
8. Stratton, Electromagnetic Theory, McGraw Hill, New York, 550ff(1941).
9. Jenkins and White, Fundamentals of Physical Optics, McGraw Hill, New York, 400(1941).
10. Donovan, Elementary Theory of Metals, Pergamon Press, 218(1967).
11. Goldsmith, Thermophysical Properties of Solid Materials, Volume 1 - Elements, WADC Technical Report, 58-476, 1960, p. 59-977.
12. Scott, Cryogenic Engineering, D. VanNostrand Co., Inc., New York, 146(1959).
13. Ashcroft and Mermin, Solid State Physics, Holt, Rinehard and Winston, New York, Chapter 1 and 2 (1976).
14. Goldsmith, Thermophysical Properties of Solid Materials, Volume 1 - Elements, WADC Technical Report 58-476, 1906, p. 59-329.
15. Hoskins Manufacturing Co., Catalog M-61 C-A 7.5M-A.P.-12-68, p. 12.
16. Touloukian and Buyco, Thermophysical Properties of Matter - Volume 5: Specific Heat - Nonmetallic Solids, IFI/PLENUM, New York(1970), p. 202ff.