THE GRAY GAS IN HYPERSONIC FLOW

Thesis by

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ABSTRACT

The assumption that the spectral absorption coefficient is independent of frequency in problems involving radiant energy transfer in hot gases is examined. A particular case, that of the hypersonic wake, is treated in some detail, and a non-gray transfer equation involving two mean coefficients is developed. One mean absorption coefficient is related to emission, and the other to absorption.

The problems arising from lack of chemical equilibrium are discussed, and a modification of the equations used for prediction of the spectral absorption coefficient (for diatomic species) is suggested, wherein two distinct temperatures are utilized. Sample calculations for one nitrogen band have been made and the results presented graphically.

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LIST OF SYMBOLS

$A_{u\ell}$	Einstein coefficient for spontaneous emission
A	Angstrom units = 10^{-8} cm (formerly written Å)
B	integral of Planck's Function (= $\frac{1}{\pi}\sigma T^4$) (see end of this list)
B_e	rotational constant
$B_{\ell u}$	Einstein coefficient, induced absorption
$B_{u\ell}$	Einstein coefficient, induced emission
ΔB	difference of rotational constants, upper minus lower state
c	velocity of light (2.998 10^{10} cm/sec)
C	constant of integration
c_v	specific heat
D_e	rotational constant (2nd order)
e	base of natural logarithm
E	energy
E_n	exponential integral function (Eq. 26)
f	electronic oscillator strength (experimental value)
g	degeneracy (no. of physically distinguishable states with same energy)
h	Planck's constant (6.6234· 10^{-27} erg sec)
H_e	rotational constant (3rd order)
I	intensity
j	rotational quantum no.
J	emissivity
k	Boltzman's constant (1.38 · 10^{-16} ergs $^{o}K^{-1}$)

$k_{(\ )}$	with subscript - conductivity
K	mass absorption coefficient or absorption cross-section (dimensions: cm^2)
^{o}K	degrees Kelvin
ℓn	natural logarithm
L	total thickness, or characteristic depth
$\vec{n}$	unit normal vector
N	number density (cm^{-3})
$P_{v'v''}$	matrix element, square of vibrational overlap integral (dipole moment integral; Reference 28)
q	heat flux
$q_{v'v''}$	Franck-Condon factor
Q	partition function (Eq. 74)
r	radius, radial coordinate
r_o	classical electron radius ($2.82 \cdot 10^{-13}$ cm)
$\vec{s}$	linear distance coordinate along a ray
t	time (sec.)
T	temperature (^{o}K)
$T_{e''}$	electronic state term value (Reference 29)
U	internal energy
$\vec{v}$	velocity
v	vibrational quantum number
V	volume
x	coordinate along preferred direction in one-dimensional problems
NO(γ)	nitric oxide gamma bands (Reference 29)
γ	scattering function (Reference 6)

δ	an increment
θ	angular coordinate (see Figure 1)
λ	wavelength (usually cm unless specified as A or μ)
$\bar{\lambda}$	Photon mean free path
μ	cos θ
μ	viscosity (Section IV only)
μ	units - microns = 10^{-4} cm (on graphs)
μ_ω	spectral absorption coefficient ($= \rho K_\omega$) per unit wavenumber, per unit volume
ν	frequency ($\sec^{-1}$)
π	3.14 . . .
ρ	gas density, particles/cm^3
ρ_o	standard sea level value of ρ
ρ_p	photon density (Section IV only)
ρ_ν	radiation energy density (see below)
σ	Stefan-Boltzman constant (in σT^4) ($0.567 \cdot 10^{-4}$ erg/sec cm^2 $^\circ\mathrm{K}^4$)
σ_λ	scattering coefficient
$d\sigma$	element of area
τ	optical depth ($\int \rho K_\lambda \, dx$)
ϕ	angular coordinate see Figure 1
ω	wave number = λ^{-1}
ω_e	vibrational constant
$\omega_e X_e$	vibrational constant (anharmonic term)
$\omega_e y_e$	vibrational constant (third order)

$d\omega$	element of solid angle

Subscripts

e	electronic
f	wake "front" (see Figure 2)
i	dummy index
g	gas
j	rotational state
l	lower state
p	photon
r	radiation; radial
R	rotational state
T	total
u	upper state
v	vibrational state
w	wake, or wall
λ	per unit wavelength
ν	per unit frequency
ω	per unit wavenumber

Superscripts

$'$	upper state
$''$	lower state
$-$	mean value

Black body radiation: Planck's function

$$B_\nu \, d\nu = \frac{2h}{c^2} \nu^3 \left[\exp(h\nu/kT) - 1 \right]^{-1} d\nu$$

$$B_\lambda \, d\lambda = 2hc^2 \lambda^{-5} \left[\exp(hc/k\lambda T) - 1 \right]^{-1} d\lambda$$

$$B_\omega \, d\omega = 2hc^2 \omega^3 \left[\exp(hc\omega/kT) - 1 \right]^{-1} d\omega$$

$$B = \int_0^\infty B_\nu \, d\nu = \int_0^\infty B_\lambda \, d\lambda = \int_0^\infty B_\omega \, d\omega = \frac{\sigma T^4}{\pi}$$

Energy density, thermal equilibrium

$$\rho_\nu \, d\nu = \frac{4\pi}{c} B_\nu \, d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 \, d\nu}{\exp(h\nu/kT) - 1}$$

Wein's displacement law: $(\lambda T)_{max} = 0.2898$ cm°K

$\frac{hc}{k} = 1.44$ cm °K

1 ev $= 1.602 \cdot 10^{-12}$ erg

1 amu $= 1.492 \cdot 10^{-3}$ erg

1 Joule = 1 watt sec $= 10^7$ erg

Avogadro's No: $6.025 \cdot 10^{23}$ (gm mole)$^{-1}$

I. INTRODUCTION

The rapidly increasing importance of radiation in the field of gas dynamics has brought forth a number of excellent papers on the problem of accounting for the effects of energy transfer by this mode (e.g., see References 1, 11, and 14). However, for the most part grayness is assumed in treating this phenomenon -- that is, the absorption coefficient is assumed to be independent of wave-length for the purpose of predicting the energy transfer (including absorption phenomena). The intent here is to examine this assumption in some detail and to determine at least qualitatively the effect it has on the solution of the transfer equation.

Along with the gray gas assumption, the assumption of local thermodynamic equilibrium is almost universal. This assumption means that at any given instant (or location) the flow field can be described by a single characteristic temperature, and further that the local radiant intensity is proportional to the Planck value for that temperature. Even when substantial chemical non-equilibrium is assumed, the radiation is treated from the local thermodynamic equilibrium point of view, and only one temperature is used (usually the kinetic temperature).

It is not intended here to minimize the other difficulties to be encountered in dealing with radiant transfer, e.g., the problem of averaging over the angle θ, but merely to concentrate for the moment on these two aspects of the gray assumption. It should be pointed out that in most engineering problems the greater difficulties lie in getting any reasonable mean value of the absorption coefficient for the gases of interest.

II. THE TRANSFER EQUATION

In dealing with problems involving the transfer of energy by radiation, the quantity usually considered is the spectral intensity, I_λ, which may be defined, for volumetric emitters (i.e., hot gases) as the following limit[1]*

$$I_\lambda = \lim \left| \frac{dE_\lambda}{\rho\, dV\, d\omega\, d\lambda\, dt} \right|_{dV, d\omega, d\lambda, dt \longrightarrow 0} \tag{1}$$

where dE_λ (or more precisely, d^7E_λ) is the energy flux from an element of volume dV, in an element of solid angle $d\omega$ (about some direction L), in the increment of wavelength $d\lambda$ about a wavelength λ, in an increment of time dt, from a substance of density ρ, in a direction θ with respect to some as yet undefined coordinate system. The corresponding definition for emission from a surface[2] (which is more commonly used) is

$$I_\lambda = \lim \left| \frac{d^6E_\lambda}{\cos\theta\, d\sigma\, d\omega\, d\lambda\, dt} \right|_{d\sigma, d\omega, d\lambda, dt \longrightarrow 0} \tag{2}$$

where $d\sigma$ is the element of surface area, and θ is the angle with respect to $\vec{n}$, the unit normal to $d\sigma$. In most practical problems one is ultimately desirous of calculating the energy flux across some bounding surface of a volume of gas; hence the two definitions become quite compatible when the unit volume is expressed in terms of the element of surface area $d\sigma$ and an angle θ with respect to the unit normal $\vec{n}$ to $d\sigma$, i.e., (see Figure 1)

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* Superscripts refer to references listed at the end of the text.

$$dV = d\sigma \cos\theta \, ds \tag{3}$$

It is an experimental fact that the above limits do exist (provided, of course, that the elements of volume, time, etc., are properly chosen; Osborn and Klevens[3] show that the element of volume must have characteristic dimensions larger than the greatest wavelength to be considered; correspondingly then, dt must not be less than this longest wavelength divided by c, the velocity of light, etc.) The spectral intensity is typically a function of the temperature, location, direction, frequency, and, of course, the species.

The transfer equation is simply a statement of the conservation of energy[4] in terms of I_λ,

$$(\partial I_\lambda/\partial \vec{s}) = \rho J_\lambda - \rho K_\lambda I_\lambda \qquad \text{(Bouguer's law)} \tag{4}$$

that is, the change in I_λ over a distance $d\vec{s}$, in the direction of $\vec{s}$, equals the gain from emission minus the loss from absorption. Here J_λ is the emissivity, per unit mass, and K_λ is the mass absorption coefficient. As will be shown later, J_λ and K_λ are related to the Einstein coefficients for spontaneous emission, and induced emission and absorption[5]. As written above, Eq. 4 does not show directly that both the emissivity and the absorption coefficient are lumped parameters which include scattering terms as well as the so-called true emission and absorption. The complete statement is[2,6,7]

$$\frac{1}{c}\frac{DI_\lambda}{Dt} = \frac{1}{c}\frac{\partial I_\lambda}{\partial t} + \frac{\partial I_\lambda}{\partial s} = \rho\left[J_\lambda + \frac{\sigma_\lambda}{4\pi}\int_{\omega'} \gamma I_\lambda \, d\omega' - (K_\lambda + \sigma_\lambda) I_\lambda\right] \tag{5}$$

where σ_λ is a scattering coefficient and $\Upsilon(\vec{r}, \omega \rightarrow \omega')$ is a scattering function. In the case of surfaces the scattering terms become reflection terms. The time derivative term is rarely considered since in most problems it is negligible. This can easily be seen if one notes that the ratio of the time derivative term to the space derivative term is a ratio of velocities: $\left(\partial s/\partial t\right)/c$. The $\frac{\partial s}{\partial t}$ term is some characteristic physical velocity, and c is the velocity of light. Thus unless one is dealing with a problem involving relativistic velocities (i.e., velocities comparable to the speed of light) the time derivative term is negligible. Furthermore, in the usual hypersonic problem the scattering terms are small compared to the energy production and absorption terms and are also neglected. Induced emission is small and is lumped into the absorption term, although it may be accounted for separately quite easily (see Appendix I). Scattering terms become important, for example, when one is considering a cold gas irradiated by a hot source, such as is the case with the earth's atmosphere under the influence of the sun.

The first observation to be made about Eq. 4 is that in perfect thermal equilibrium the derivative is identically zero and hence

$$J_\lambda \equiv (K_\lambda I_\lambda)_{\text{Equilibrium}} \equiv K_\lambda B_\lambda \qquad (6)^*$$

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* More precisely $J_\lambda = \eta_\lambda^2 K_\lambda B_\lambda$ where η_λ = the refractive index. (Kirchoff's law).

where B_λ is the Planck function given by

$$B_\lambda d\lambda = \frac{2hc^2}{\lambda^5} \frac{d\lambda}{\exp(hc/k\lambda T) - 1} \tag{7}$$

This function, which is the quantum-mechanically correct equilibrium intensity distribution, is well verified experimentally (especially for enclosures with solid surfaces). Planck's function[5] will not be derived here but will constitute a basic assumption. Equation 4 may now be written as

$$\frac{\partial I_\lambda}{\partial \vec{s}} = \rho K_\lambda (B_\lambda - I_\lambda) \tag{8}$$

It should be noted that in the general case the ratio

$$j_\lambda / K_\lambda \equiv \mathcal{J}_\lambda \tag{9}$$

is referred to as the source function[2]. In perfect thermal equilibrium it is identical with B_λ. The distance element $d\vec{s}$ in Eq. 8 is written with a vector sign to emphasize that it is the distance along some particular direction. Although in some problems $d\vec{s}$ may be conveniently identified with a radius vector r in a spherical polar coordinate system[8], more commonly it is written as

$$d\vec{s} = -\sec\theta \, dx = -(dx/\mu) \tag{10}$$

where x is an appropriately chosen linear coordinate. This relation is especially useful when (as frequently happens) a coordinate system may be selected such that the temperature is a function of only one coordinate (x). This one dimensional case is referred to as the "plane parallel atmosphere"[2]. The transfer equation is written as

$$\mu \frac{\partial I_\lambda}{\partial \tau_\lambda} = I_\lambda - B_\lambda \tag{11}$$

where

$$\tau_\lambda - \tau_{1,\lambda} = \int_{x_1}^{x} \rho(\xi)\, K_\lambda(\lambda,\xi)\, d\xi \tag{12a}$$

or

$$d\tau_\lambda = \rho K_\lambda\, dx \tag{12b}$$

Eq. 11 is probably the most common simple statement of the transfer equation. The quantity τ_λ is referred to as the optical depth (note that it is along the preferred direction x). Eq. 11 is a linear differential equation for I_λ with the general solution[4, 6]

$$I_\lambda = \left[C_1(\tau_{1,\lambda}) - \int_{\tau_{1,\lambda}}^{\tau_\lambda} B_\lambda(t)\, e^{-t/\mu} \frac{dt}{\mu} \right] e^{\tau_\lambda/\mu} \tag{13}$$

where $C_1(\tau_{1,\lambda})$ is determined by the boundary condition at $\tau_\lambda = \tau_{1,\lambda}$. To illustrate the basic exponential nature of the absorption process, let $C_1(0) = 0$ and consider a region of uniform temperature. Eq. 13 then may be integrated to give

$$I_\lambda = \frac{-B_\lambda}{\mu} \int_0^{\tau_\lambda} e^{-t/\mu}\, dt \cdot e^{\tau_\lambda/\mu} = B_\lambda \left(1 - e^{\tau_\lambda/\mu}\right) \tag{14}$$

or using Eq. 10 freely

$$I_\lambda = B_\lambda \left(1 - e^{-\rho K_\lambda x}\right) \tag{15}$$

That is, as one moves into a layer of gas in a direction θ the radiant intensity of a wavelength λ, in the direction θ, is 0 at the boundary and approaches the equilibrium value B_λ exponentially with increasing optical depth $\rho K_\lambda \vec{s}$. Obviously, the physical depth s at which the equilibrium value is essentially reached depends directly on the magnitude of the absorption coefficient K_λ. In cases involving enclosures (e.g., furnaces) where the walls are in equilibrium with the gas, equilibrium densities are closely approached, but it is rare in hypersonic aerodynamics that a gaseous layer is of sufficient optical depth to achieve this. Note that the depth s required (at a given value of ρ) varies inversely with K_λ. For example, from References 9 and 10, the ρK_λ term varies from 7 cm^{-1} at λ = 2150 A to 10^{-3} cm^{-1} at λ = 2050 A, back to 5 cm^{-1} at λ = 2250 A, and to less than $10^{-4} cm^{-1}$ for $\lambda > 2900$ A [A = Angstrom = 10^{-8} cm] (See also Figure 7.) These values are for NO(γ) band emission in air at one atmosphere and at 2000°K. In other words, over a relatively short wavelength interval of a few hundred angstroms the absorptivity may vary by four or five orders of magnitude. As temperature and density increase the variation of ρK_λ becomes less pronounced, but is always considerable when compared to that encountered in enclosures. Even gaseous bodies as large as the sun show considerable deviation from the Planck function. In fact, it is the non-grayness of the sun and the other stars that permits determination of their composition (i.e., by observation of distinct absorption and emission lines).

III. THE GRAY GAS; PLANCK'S MEAN

If the assumption that K_λ is independent of wavelength is made, the solution of Eq. 11 is considerably simplified. Let K_λ be a function only of the temperature T

$$K_\lambda = K(T) \tag{16}$$

Then Eq. 11 may be integrated with respect to wavelength

$$\frac{\mu}{\rho K} \frac{\partial I}{\partial x} = I - B \tag{17}$$

where

$$I = \int_0^\infty I_\lambda \, d\lambda \tag{18}$$

and

$$B = \int_0^\infty B_\lambda \, d\lambda = \frac{\sigma T^4}{\pi} \tag{19}$$

Since in all practical cases K_λ is a strong function of λ, a suitable mean value must be chosen. The absorption coefficient is directly related to the energy emitted by the gas (in equilibrium) by virtue of Eq. 6. The total emitted energy will be correctly given then by the mean value of K_λ if that value K is defined by

$$\int_0^\infty J_\lambda \, d\lambda = \int_0^\infty K_\lambda B_\lambda \, d\lambda = KB \tag{20}$$

where

$$B = \int_0^\infty B_\lambda \, d\lambda = \frac{\sigma T^4}{\pi} \tag{21}$$

Hence the definition of K (a function of T) is given by

$$K(T) = \frac{\int_0^\infty K_\lambda B_\lambda \, d\lambda}{\left(\frac{\sigma T^4}{\pi}\right)} \tag{22}$$

With this definition, K is referred to as the Planck mean absorption coefficient. The solution to Eq. 17 then is simply

$$I = \left[C_1(\tau_1) - \int_{\tau_1}^{\tau} \frac{\sigma T^4}{\pi} e^{-t/\mu} \frac{dt}{\mu} \right] e^{\tau/\mu} \tag{23}$$

To get the heat flux q to a surface (this is the end product usually desired) it is necessary to return to the definition of I for a surface, Eq. 2. Since the heat flux is the energy crossing a surface, per unit area, per unit time, it is given by

$$q = \int_0^\infty d\lambda \int_{4\pi} d\omega \, I_\lambda \cos\theta \tag{24}$$

Usually the heat flux q is broken up into two parts -- the flux towards the wall, q^-, and the flux away from the wall, q^+.[10] Using this notation, the heat flux to the wall for the plane parallel atmosphere is given by*

$$\begin{aligned} q^- &= 2\pi \left\{ \int_0^{-1} c(\tau_1) e^{\tau/\mu} \mu \, d\mu - \int_{\tau_1}^{\tau} \frac{\sigma T^4}{\pi} \left[\int_0^{-1} e^{-\frac{(t-\tau)}{\mu}} d\mu \right] dt \right\} \\ &= 2\pi C_1(\tau_1) \int_0^1 e^{-\tau/\mu} \mu \, d\mu + 2 \int_{\tau_1}^{\tau} \sigma T^4 \left[\int_0^1 e^{-\frac{(\tau-t)}{\mu}} d\mu \right] dt \end{aligned} \tag{25}$$

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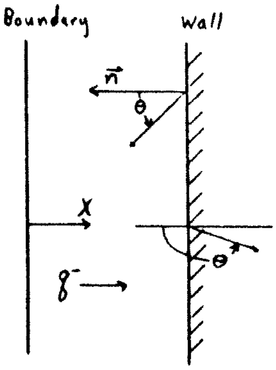
*Here, as is common in re-entry problems, it is assumed that only one boundary consists of a wall, the other being either a transparent shock, or at ∞.



Note that because x is oppositely directed from $\vec{n}$, the limits on θ for the q^- integration are π and $\pi/2$; hence μ is bounded by -1, 0. This sign convention is the usual one. For q^+ the limits are 1, 0.

By introducing the exponential functions[2]

$$E_n(x) = \int_0^1 \mu^{n-2} e^{-\frac{x}{\mu}} \, d\mu \tag{26}$$

Eq. 25 may be written

$$q^- = 2\pi C_1(\tau_1) E_3(\tau) + 2\pi \int_{\tau_1}^{\tau} \frac{\sigma T^4}{\pi} E_2(\tau - t) \, dt \tag{27}$$

If the layer is also isothermal so that T is not a function of τ, then the flux is

$$q^- = 2\sigma T^4 \left[E_3(\tau - \tau_1) - \frac{1}{2} \right] + 2\pi C_1(\tau_1) E_3(\tau) \tag{28}$$

Similar expressions may be derived for q^+. The exponential functions are tabulated in Reference 2. In the solution of problems involving transfer of energy in a hypersonic flow field, an expression similar to Eq. 27 is commonly used, e.g., see References 12, 13, and 14.

Note that for the isotropic case (intensity independent of μ) the relation between q and I is

$$q^\pm = 2\pi \int_0^{\pm 1} I^\pm \mu \, d\mu = \pi I^\pm \tag{29}$$

Hence

$$I = \frac{1}{\pi} q \tag{30}$$

is frequently used.

If Eq. (28) is applied to a very thin layer of gas, of thickness $L = \tau_2 - \tau_1$, then, using the asymptotic expansion[2] for $E_3(L)$, and letting $C_1(\tau_1) = 0$, the usual expression[7] for the emissivity of such a layer is obtained

$$\begin{aligned} q^- &= 2\sigma T^4 \left[\tfrac{1}{2} - \rho K L + \cdots - \tfrac{1}{2}\right] \\ &= -2\sigma T^4 \rho K L \end{aligned} \tag{31a}$$

This relation is frequently used to define an emissivity per unit length, $\epsilon' = \epsilon/L = 2\rho K$, so that q^- is sometimes written as

$$q^- = -\epsilon' \sigma T^4 L = \epsilon \sigma T^4 \tag{31b}$$

The Planck mean absorption coefficient is valid for at least general cases:

(a) if the variation of K_λ with λ is small in the region of interest, or

(b) if $I_\lambda \approx B_\lambda$ in the region of interest, or

(c) if $\rho K_\lambda s$ is so small for all wavelengths that absorption can be completely neglected.

If the condition for case (c) above is satisfied, then it can be seen from Eq. 28 that error involved in using Eq. 31, for $\rho KL \leqq \frac{1}{2}$, say, is less than about 30%.

IV. THE GRAY GAS; ROSSELAND'S APPROXIMATION

Another commonly used gray approximation is the Rosseland approximation. In this instance the gas is assumed to be optically very thick. In this case, $I_\lambda(T) \approx B_\lambda(T)$ at each point in the field (except near boundaries). The transfer equation, Eq. 11, is written as

$$\frac{\mu}{\rho K_\lambda} \frac{\partial I_\lambda}{\partial x} = I_\lambda - B_\lambda \tag{32}$$

If this equation is integrated over all frequencies to give a gray equation

$$\frac{\mu}{\rho \bar{K}} \frac{\partial I}{\partial x} = I - B \tag{33}$$

then the correct mean value of ρK_λ is given by

$$\frac{1}{\rho \bar{K}} \frac{\partial I}{\partial x} = \int_0^\infty \frac{1}{\rho K_\lambda} \frac{\partial I_\lambda}{\partial x} \, d\lambda \tag{34}$$

Knowledge of I_λ depends on the solution of Eq. 32; however, for the optically thick case it may be reasonably assumed that $I_\lambda(T)$ is similar to $B_\lambda(T)$. Hence B_λ is substituted for I_λ in Eq. 34, yielding

$$\frac{1}{\rho \bar{K}} \frac{\partial B}{\partial x} = \int_0^\infty \frac{1}{\rho K_\lambda} \frac{\partial B_\lambda}{\partial x} \, d\lambda \tag{35}$$

Now, since T is a function only of x (again, for the plane parallel atmosphere), Eq. 35 may be multiplied by $(\partial T/\partial x)^{-1}$ (noting that B is a function only of T)

$$\frac{1}{\rho \bar{K}} \frac{dB}{dT} = \int_0^\infty \frac{1}{\rho K_\lambda} \frac{\partial B_\lambda}{\partial T} \, d\lambda \tag{36}$$

or

$$\frac{1}{K} = \frac{\pi}{4\sigma T^3}\int_0^\infty \frac{1}{K_\lambda}\frac{\partial B_\lambda}{\partial T}\,d\lambda \tag{37}$$

Here, B(T) and $B_\lambda(T)$ are known functions of T, hence K can be obtained as a function of T. A more precise derivation of this quantity is given in Reference 2, as well as a discussion of several other mean values of K_λ related to the two just discussed (e.g., Chandrasekher's mean, and Unsold's mean).

Although Rosseland's mean has been applied to problems involving the flow of hot gases about bodies (e.g., Reference 15), it is much less likely to apply than Planck's mean, which is used for optically thin cases.

Consistent with the above definition, in which it is basically assumed that optical mean free path is comparable to the molecular mean free path, is the Rosseland approximation to the radiant transfer equation. A heuristic deviation, as outlined in Reference 6, is based on the assumption that the radiation can be represented by a "photon gas", and the heat transfer described by Fourier's law in analogy to the kinetic theory of gases. The heat flux then is given by

$$q = -k_T\left(\frac{\partial T}{\partial x}\right) \tag{38}$$

where $k_T = k_g + k_p$, k_g being the ordinary molecular conductivity and k_p being the photon conductivity. The conductivity is given by

$$k_p = \mu_p c_v \tag{39}$$

where μ_p is the viscosity and c_v specific heat of the photon gas. The viscosity then is

$$\mu_p = \frac{1}{3} \rho_p \bar{v} \bar{\lambda} \tag{40}$$

where, for the photon gas

ρ_p = photon density

$\bar{v}$ = c = velocity of light

$\bar{\lambda}$ = $1/\rho\bar{K}$ = photon mean free path.

The specific heat of the photon gas (for radiative equilibrium) is

$$C_v = \left.\frac{\partial u}{\partial T}\right|_{vol} = \frac{1}{\rho_p} \frac{\partial}{\partial T}\left(\frac{4\pi}{c} \frac{\sigma T^4}{\pi}\right) \tag{41}$$

Thus

$$C_v = \frac{16 \sigma T^3}{\rho_p c} \tag{42}$$

and

$$k_p = \frac{1}{3} \frac{\rho_p c}{\rho \bar{K}} \frac{16 \sigma T^3}{\rho_p c} = \frac{16 \sigma T^3}{3 \rho \bar{K}} \tag{43}$$

Therefore, the Rosseland approximation to the radiant transfer equation is

$$q_p = - \frac{16 \sigma T^3}{3 \rho \bar{K}} \frac{\partial T}{\partial x} = - k_p \frac{\partial T}{\partial x} \tag{44}$$

This is the expression used, for example, in Reference 15. A much more elegant derivation is given in Reference 16.

V. THE NON-GRAY GAS -- THE THIN LAYER

The basic problem in dealing with radiation from hot air in hypersonic flow is that the absorption coefficient of air varies strongly with frequency[9, 10], and both shock layers and wakes tend to be optically thin. Yet at the high velocities (say greater than 25,000 ft/sec.) radiation provides a significant mode of energy transport[14, 17]. The proper accounting of this phenomena, including absorption, becomes essential to the solution of the shock layer problem[14]. Unfortunately, because of practical limitations, it is essential to use some sort of frequency averaged absorption coefficient -- usually taken to be the Planck mean value. To examine the general validity of this approximation would require an impractically large digital computer program if a frequency dependent absorption coefficient were to be used. However, there are some particular cases[18] in which a simpler approach may be used.

In Reference 18 the particular problem treated is that of the wake behind a hypersonic re-entry body[20]. The wake is considered to be a long (semi-infinite) cylinder of radius r_f, and to be at a uniform temperature T_w. Using an expression for the heat flux similar to that given in Reference 8, the flux to a point on the centerline of the wake at the beginning of the wake (i.e., near the base of the body) is (see Figure 2)

$$q_r = -\int_0^\infty d\lambda \int_0^{2\pi}\int_0^{\pi/2}\int_0^{r_1(\theta)} \rho K_\lambda B_\lambda e^{-\int_0^r \rho K_\lambda dr'} \sin\theta \cos\theta \, dr\, d\theta\, d\phi \quad (45)*$$

It is assumed that the boundary of the wake is perfectly transparent. The solution of Eq. 45 is[18]

$$q_r = \sigma T_w^4 \left[1 - 2E_3(\rho K r_f)\right] \quad (46)$$

where K is the Planck mean absorption coefficient. For a typical wake[20] the temperature may be of the order of 2000°K to 4000°K out to some hundreds of body diameters. The density in the wake is low $\left[(\rho/\rho_0) = 10^{-3}\right.$ for the case examined in Reference $\left.18\right]$, and the wake is narrow--r_f being about equal to the body radius, or less, for a considerable distance. Hence, using Kivel and Bailey[19] it is easily seen that the wake is optically thin, at least when the Planck mean absorption coefficient is used ($\rho K r_f \approx 10^{-4}$ for $r_f \approx 1$ foot). The thin layer approximation to Eq. 46 is exactly that obtained for the plane layer (Eq. 31) with L replaced by r_f

$$q_r \doteq 2\rho K r_f \sigma T_w^4 \quad (47)$$

Furthermore, it was established in Reference 18, by expanding the exponential integral E_3 in Eq. 46, subtracting the right hand side of Eq. 47, and ratioing the difference to Eq. 47, that the error involved

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* Note from Figure 2 that r is the radial coordinate in a set of spherical polar coordinates, $r_1(\theta)$ is the value of r at the outer boundary of the wake, and r_f is the value of $r_1(\theta)$ at $\theta = \pi/2$. The value of r_f was taken to be one foot simply because this is the value used in Reference 20.

in neglecting absorption is of the order of

$$\frac{\delta q_r}{q_r} \doteq \frac{1}{2} \tau_f \left[1 - \ln(\tau_f) \right] \doteq \tau_f = 10^{-4} \tag{48}$$

that is, one hundredth of one per cent.

Now, in the above development the mean value of the absorption coefficient was taken to be Planck's mean -- this being essentially the value reported in Reference 19. However, if one examines the spectrum of air[10] for temperatures of the order of 2000°K to 4000°K, it is readily apparent that virtually all of the energy emitted comes from the infra-red bands of nitric oxide. The primary band is at about 5.5 μ, and the first overtone at 2.8 μ. About 85 % of the total energy is emitted in the 5.5 μ band, and about 10 % in the secondary band (see Figure 3). These are relatively narrow bands occurring well off the black body peak which, at 3000°K, lies at about 1 μ. The mass absorption coefficient* of the primary band is[10]

$$\rho_0 K_\lambda \doteq 10^{-2} \text{ cm}^{-1} \tag{49}$$

It is apparent that this band will suffer absorption much more strongly than would be anticipated from the Planck mean value of 10^{-4} cm^{-1}. Because of the relative narrowness of the bands it is possible to develop a form of the transfer equation which will show approximately the magnitude of the above effect.

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* The mass absorption coefficient of a given species -- neglecting certain pressure effects -- is normally independent of the density, ρ. In a mixture of gases, however, the species concentration, ρ_i/ρ, will depend in general on ρ; hence so will K_λ. Usually this dependence is very weak. The absorption coefficient in Reference 10 is normalized to the sea-level value.

The transfer equation is

$$\frac{\partial I_\lambda}{\partial r} = \rho K_\lambda B_\lambda - \rho K_\lambda I_\lambda \tag{50}$$

This equation may be formally integrated with respect to frequency to give

$$\frac{\partial I}{\partial r} = \rho \overline{K}_1 B - \rho \overline{K}_2 I \tag{51}$$

where the two mean coefficients are defined by

$$\rho \overline{K}_1 = \frac{1}{B} \int_0^\infty \rho K_\lambda B_\lambda \, d\lambda \tag{52a}$$

and

$$\rho \overline{K}_2 = \frac{1}{I} \int_0^\infty \rho K_\lambda I_\lambda \, d\lambda \quad . \tag{52b}$$

Using these two means, the solution of Eq. (51) is

$$I = \left\{ c_1 + \int_{\tau_0}^{\tau} \frac{\rho \overline{K}_1}{\rho \overline{K}_2} B e^t \, dt \right\} e^{-\tau} \tag{53}$$

where

$$\tau - \tau_0 = \int_{r_0}^{r} \rho \overline{K}_2 \, dr' \quad . \tag{54}$$

That is, there are basically two averages involved -- one is an emission mean, the other is an absorption mean. The fact that these mean values are generally different reflects the fact that, basically, hot gases rarely attain true thermal equilibrium. Unfortunately, the precise evaluation of $\rho \overline{K}_2$ depends on the solution to the problem. However, for the case where K_λ is virtually constant over some wave length range, $\delta \lambda_i$, and is zero outside of that range (a square pulse), both $\rho \overline{K}_1$ and $\rho \overline{K}_2$ may be evaluated. The evaluation of $\rho \overline{K}_2$ rests on the observation that if the absorption coefficient is essentially zero over any wave length interval, then the emission in that interval is also zero. Hence, if the only source of radiation is the gas, then I_λ will be zero at all frequencies at which K_λ is zero. Eq. (52b) then may be written

$$\rho\overline{K}_2 = \frac{\int_0^\infty \rho K_\lambda I_\lambda \, d\lambda}{\int_0^\infty I_\lambda \, d\lambda} = \frac{\int_{\lambda_i - \frac{1}{2}\delta\lambda_i}^{\lambda_i + \frac{1}{2}\delta\lambda_i} \rho K_{\lambda_i} I_\lambda \, d\lambda}{\int_{\lambda_i - \frac{1}{2}\delta\lambda_i}^{\lambda_i + \frac{1}{2}\delta\lambda_i} I_\lambda \, d\lambda} , \qquad (55)$$

and, if K_{λ_i} is approximately constant, then

$$\rho\overline{K}_2 = \rho K_{\lambda_i} . \qquad (56a)$$

On the other hand, B_λ is defined for all values of λ, and $\rho\overline{K}_1$ is just the Planck mean. This mean is approximately given by

$$\rho\overline{K}_1 = \rho K_{\lambda_i}\left(\frac{B_{\lambda_i}\,\delta\lambda_i}{B}\right) \qquad (56b)$$

for sufficiently small $\delta\lambda_i$. For the case considered above, $\rho_0\overline{K}_1$ is 10^{-4} cm^{-1}, and $\rho_0\overline{K}_2$ is 10^{-2} cm^{-1}. Now, for the isothermal case, with a null boundary condition, the solution (Eq. 53) becomes

$$I = \frac{\overline{K}_1}{\overline{K}_2}\,\frac{\sigma T_w^4}{\pi}\left(1 - e^{-\rho\overline{K}_2 r}\right) , \qquad (59)$$

and for the thin gas this result simplifies to

$$I = \rho\overline{K}_1 \frac{\sigma T_w^4}{\pi}\, r , \qquad (60)$$

that is, to a form involving only Planck's mean, as it should. On the other hand, as r ⟶ ∞ the intensity becomes

$$I = \frac{\bar{K}_1}{K_2} \frac{\sigma T_w^4}{\pi} = 10^{-2} \frac{\sigma T_w^4}{\pi} \quad . \tag{61}$$

Thus, if the gas emits only in some narrow band of frequencies, then the maximum integrated intensity is limited by absorption to a value much less than the black body value, as is intuitively obvious. Atomic lines (the sodium D line, for example) frequently reach the local black body limit, but rarely provide even a small fraction of σT^4. Actually, however, no substance can emit only between specific narrow limits. Heisenberg's uncertainty principle requires a non-zero probability of emission for all frequencies. Furthermore, air is a complicated mixture of species and has bands covering virtually all wavelengths. Consequently the upper bound attained above is not correct for sufficiently large r. Therefore, consider as the next approximation the case where a substance emits in a number of distinct bands, i. e.,

$$\begin{aligned} &\lambda_1 - \tfrac{1}{2}\delta\lambda_1 \leq \lambda \leq \lambda_1 + \tfrac{1}{2}\delta\lambda_1 , && K_\lambda = K_{\lambda_1} \\ &\lambda_2 - \tfrac{1}{2}\delta\lambda_2 \leq \lambda \leq \lambda_2 + \tfrac{1}{2}\delta\lambda_2 , && K_\lambda = K_{\lambda 2} \\ &\lambda_3 - \tfrac{1}{2}\delta\lambda_3 \leq \lambda \cdots \text{ etc.} \end{aligned} \tag{62}$$

If the bands are reasonably distinct (do not overlap), then there will be no interaction between them* (note that the basic transfer equation is monochromatic), and one can therefore write a series of (independent) transfer equations. These will all have the same form as Eq. (51), and the solutions will all be of the same form as Eq. (53). Up to this point, the angular dependence of the transfer equation (i. e., Eq. 51) has been

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* Strictly speaking this statement will not be true in a gas with collisions, since the collisions act to distribute the energy within the molecule over all frequencies.

ignored. However, assuming isotropy, this dependence may be integrated out also. The net result of the above operations is to give the result, for the wake problem

$$q_r(T_w) = -\sigma T_w^4 \left\{ \left(\frac{\bar{K}_1}{\bar{K}_2}\right)_1 \left[2E_3(\rho \bar{K}_{1,1} r_f) - 1\right] + \left(\frac{\bar{K}_1}{\bar{K}_2}\right)_2 \left[2E_3(\rho \bar{K}_{1,2} r_f) - 1\right] + \cdots \right. \qquad (63)$$

To illustrate, consider a special case where there are only two such bands. One is the strong narrow band previously considered, where

$$\left(\bar{K}_1/\bar{K}_2\right)_1 = 10^{-2} \qquad (62a)$$

and

$$\rho_0 \bar{K}_{1,1} = 10^{-4} \text{ cm}^{-1} \qquad (62b)$$

Let the other band be a continuous gray band covering all frequencies (except those of the narrow band above) such that

$$\left(\bar{K}_1/\bar{K}_2\right)_2 = 0.99 \qquad (65a)$$

$$\rho_0 \bar{K}_{1,2} = 10^{-6} \qquad (65b)$$

that is, 99 % of the total emitted energy ($\bar{K}_{1,1} + \bar{K}_{1,2}$) lies in the narrow band, and the ratio of the narrow band absorption coefficient, $\bar{K}_{2,1}$ to the background band absorption coefficient $\bar{K}_{2,2}$, is

$$\frac{\bar{K}_{2,1}}{\bar{K}_{2,2}} = \frac{10^{-2}}{10^{-6}} = 10^4 \qquad (66)$$

Eq. (63) may be written for this case as

$$\frac{q_n(T_w)}{\sigma T_w^4} = -\left\{10^{-2}\left[2E_3(\tau_f)-1\right] + 0.99\left[2E_3(0.01\,\tau_f)-1\right]\right\} \tag{67}$$

where

$$\tau_f = \rho \bar{K}_{1,1} r_f \tag{68}$$

This result is plotted in Figure 4, along with the solution using Planck's mean, and the solution using only the thin gas formula. It happens that for the sample wake $(\rho/\rho_0) = 10^{-3}$ and hence the actual optical thickness is only

$$\left(\rho/\rho_0\right) \rho_0 \bar{K}_{2,1} r_f = 10^{-3}\; 10^{-2}\; 30 = 0.3\; 10^{-3} \tag{69}$$

so that the absorption is still not significant. Note from the graph however that even for relatively small optical thicknesses (based on the Planck mean value) the error is significant, e.g., a factor of 2 or more at $\tau_f = 0.01$. At moderate thicknesses the error becomes very large.

It would of course be desirable to examine, in some similar manner, the stagnation point region. However, there the situation is not so simple. The number of important bands seems to be considerably larger, especially since fairly strong temperature gradients, as well as concentration gradients, will exist in this region when the radiation becomes really important, (e.g., see the following sections). One perturbation approach does suggest itself however. If the gas were very thin, then as a first approximation the absorption term can be dropped from the transfer equation. Thus

$$\frac{\partial I_\lambda}{\partial r} = \rho K_\lambda B_\lambda \tag{70}$$

and hence

$$I_\lambda = \int_0^r \rho K_\lambda B_\lambda \, dr = \rho K_\lambda B_\lambda r \qquad (71)$$

for the isothermal case. This result may be used to generate a simple minded perturbation solution, i.e., let

$$\frac{\partial I_\lambda}{\partial r} = \rho K_\lambda B_\lambda - \rho K_\lambda \left(\rho K_\lambda B_\lambda r \right) \qquad (72)$$

This equation is integrated to give

$$I_\lambda = \rho K_\lambda B_\lambda r - \left(\rho K_\lambda \right)^2 B_\lambda \frac{r^2}{2} \qquad (73)$$

for the isothermal case. The same result may be obtained by simply expanding Eq. (15) and retaining only the first two terms. By integrating with respect to λ, one obtains

$$I = \rho \overline{K}_1 B r - \rho \overline{K}_3 B \frac{r^2}{2} \qquad (74)$$

where $\rho\overline{K}_1$ is the Planck mean and

$$\rho \overline{K}_3 = \frac{\int_0^\infty \rho^2 K_\lambda^2 B_\lambda \, d\lambda}{\int_0^\infty \rho K_\lambda B_\lambda \, d\lambda} \qquad (75)$$

is the absorption mean as before. This procedure, of course, requires a digital computer program for evaluation. However, our simple square pulse can again be used to illustrate the effect. Let K_{λ_i} = constant in some range $\delta\lambda_i$ about λ_i. Then

$$\rho \overline{K}_3 = \frac{\int_{\delta\lambda_i} \left(\rho K_{\lambda_i} \right)^2 B_\lambda \, d\lambda}{\int_{\delta\lambda_i} \rho K_\lambda B_\lambda \, d\lambda} = \rho K_{\lambda_i} = \rho \overline{K}_2 \qquad (71)$$

as before. Thus the absorption term will tend to emphasize the contributions from the strong bands. Numerical evaluation of this method for a practical case has not been accomplished as yet. Note that the above mean is an "emissivity" mean, i. e.,

$$\rho \overline{K}_3 = \frac{\int_0^\infty \rho K_\lambda J_\lambda \, d\lambda}{\int_0^\infty J_\lambda \, d\lambda} \tag{72}$$

It assumes that the gas is sufficiently thin that the intensity is directly proportional to the emissivity.

One general conclusion may be stated from the above work: the use of **Planck's** mean always underestimates the effect of absorption.

VI. COMPUTATION OF SPECTRAL ABSORPTION COEFFICIENTS; THE EQUILIBRIUM CASE

The mass absorption coefficient (or absorption cross-section) used in the transfer equation is a computed quantity, with an experimentally measured scale factor, or strength. A brief development of the equation for the absorption coefficient associated with electronic transitions is given in Reference 25. The model used for electronic transitions is the "just overlapping line" model (the same result is obtained with the "smeared rotational line model"[25, 28]. In this model it is assumed that the rotational structure consists of a set of closely spaced, fully developed lines which may reasonably be replaced by a continuous distribution. This approximation should be especially good at the higher temperatures where the rotational modes are fully excited. Essentially, the rotational quantum number is replaced by a continuous variable. Further, the band origin is assumed to coincide with the band head (also good at high temperatures for many species). The result of these two approximations is to obtain a band for each electronic-vibrational transition which has zero intensity for all frequencies to one side of the band head frequency, jumps to a maximum value at the band head, and then decreases exponentially with frequency the other side of the band head (See Figure 7). An electronic transition occurs when electron changes its orbit about a molecule, resulting in a change of the potential well in which the atoms of the molecule are vibrating. This orbital jump forces a change in the vibrational and rotational quantum states (see Figure 5 for a typical potential diagram). A typical electronic transition band will consist of a fairly large number of such vibrational bands (e.g., typically between 10 and 1000), although most of the energy tends to be concentrated in a relatively small number of these bands.

The integrated line absorption coefficient for the given transition $v'',j'' \rightarrow v',j'$ is proportional to the number of molecules in the given lower state v'',j'' , and to the probability that such a transition will occur, $f_{v''v',j''j'}$. The fraction of molecules in the given lower state (assuming a Boltzman distribution of energies) is equal to

$$\frac{N_{v''j''}}{N} = \frac{g_{e''}\, e^{-\frac{hc}{kT} T_{e''}}}{Q_{e''}} \; \frac{g_{v''}\, e^{-\frac{hc}{kT}(\omega_{v''}-\omega_{0''})}}{Q_{v''}} \; \frac{g_{j''}\, e^{-\frac{hc}{kT} j''(j''+1) B_e''}}{Q_{j''}} \tag{73}$$

where

g_e'' = the degeneracy of the lower electronic state

g_v'' = the degeneracy of the lower vibrational state (always unity)

g_j'' = $(2j'' + 1)$ = the degeneracy of the lower rotational state

and the Q's are the partition functions of the various states, given by

$$Q_i = \sum_{i=0}^{i_{diss.}} g_i\, e^{-\frac{E_i}{kT}} \tag{74}$$

Here E_i is the energy of the ith lower state (corresponding to $j_i''(j_i''+1) B_e'' hc$; etc.). For virtually all gaseous species considered, the electronic partition function is equal to g_0 , the degeneracy of the electronic ground state of the molecule, because the other term values, $hc\,T_{e''}$ (for the upper states) are very large compared to kT. The vibrational states are non-degenerate. The rotational partition function can be nicely approximated by an integral, yielding

$$Q_{j''} = \frac{kT}{hc\,B_e''} \qquad (75)$$

The transition probability $f_{v''v',j''j'}$ is usually written as

$$f_{v''v',j''j'} = f\,p_{v'v''} \qquad (76)$$

where the $p_{v'v''}$ are the squares of the dipole moment integrals and are related to (and frequently approximated by) the Franck-Condon factors. These factors give the relative probability of a given $v'' \rightarrow v'$ transition occurring and are well tabulated in the literature for most of the transitions of interest[31, 32]. The quantity f is called the electronic oscillator strength (or "f-number") and is basically an experimentally determined number for each band considered. The mean spectral absorption coefficient for a given transition is

$$\overline{K}_{\omega_{v'v''j'j''}} = \pi n_0 \frac{g_e''}{g_0} e^{-\frac{hc}{kT}T_e''} \left[\frac{e^{-\frac{hc}{kT}(\omega_{v''}-\omega_{0''})}}{\sum\limits_{v''=0}^{v''_{diss}} e^{-\frac{hc}{kT}(\omega_{v''}-\omega_{0''})}} \right] \left[\frac{hc}{kT} \quad \frac{B_e''}{\Delta B} e^{-j''(j''+1)\frac{hc}{kT}B_e''} \right] f\, p_{v'v''} \qquad (77)$$

The rotational quantum number j" is eliminated from the above expression by using the relation

$$j''(j''+1) \doteq \frac{\omega - \omega_{BH_{v'v''}}}{\Delta B} \qquad (78)$$

where $\omega_{BH_{v'v''}}$ is called the band head wave number, and where ω is a continuous variable. The mass absorption coefficient at any given wave number ω is obtained by summing Eq. (77) over all v', v" states which contribute to the absorption at that wave number

$$K_\omega = \pi n_0 \frac{g_{e''}}{g_0} e^{-\frac{hc}{kT} T_{e''}} \left[\frac{hc}{kT} \frac{B_{e''}}{\Delta B}\right] \frac{f}{Q_{v''}} \sum_{v'} \sum_{v''} p_{v'v''} \, e^{-\frac{hc}{kT}\left(\omega - \omega_{BH_{v'v''}}\right)\frac{B_{e''}}{\Delta B}} \, e^{-\frac{hc}{kT}(\omega_{v''} - \omega_{0''})} \qquad (79)$$

This is equated to the absorption coefficients given in References 10, 19 for example, simply by multiplying it by the number density of the given species. In Reference 10 a factor of $\left(1 - e^{-\frac{hc\omega}{kT}}\right)$ is inserted in order to account for the effects of induced emission; however, this term is generally very small (see Appendix 1) for wave numbers of interest.

VII. COMPUTATION OF SPECTRAL ABSORPTION COEFFICIENTS; THE NON-EQUILIBRIUM CASE

In all the above discussion, as is practically universal in all similar discussions, the assumption of local thermodynamic equilibrium is explicit in that only one quantity identified as temperature appears. All the modes of absorption of energy are assumed to be excited to the same degree, even though chemical equilibrium may not be assumed. For example, in Reference 21 an accounting is made of the fact that an excess of molecules (of N_2, O_2, NO) may be present because of dissociative relaxation phenomena, but only a single temperature is used (i. e., the kinetic temperature). On the other hand, in solving the basic non-equilibrium flow field problem (especially the very high altitude or low density problem) the effects of vibrational relaxation may be accounted for as well as the dissociation[22, 23]. It is interesting that while in the solution of problems in chemical relaxation and in spectroscopic work with flames[24] and shock tubes[27] the use of several independent temperatures is common, very little effort has been made to predict spectral structure utilizing these several temperatures. There is one very recent paper on this topic, Reference 33. This lack of effort is probably due for the most part to a rather substantial lack of basic physical theory on such processes (as they relate to spectra),[20] and also in part to the fact that when these processes become significant (in re-entry), the overall level of radiant energy is quite low. As is evident from Eq. (73) of the previous section, the temperature dependence of the absorption coefficient comes in <u>only</u> through the Boltzmann factors which describe the relative populations of the various quantum states. The transition probability factors come from the solution of the wave equation which in no way requires the specification of a temperature. In the solution of the non-equilibrium chemistry problem, however, it is by just these same Boltzman factors that the various temperatures are defined. Therefore, to be consistent with the assumptions made in calculating these various temperatures, Eq. (77) must be written as

$$K_{\omega_{v'v''j''j'}} = \pi n_0 \left\{ \frac{g_e'}{g_0} e^{-\frac{hcT_e'}{kT_e}} \right\} \left\{ \frac{e^{-\frac{hc}{kT_v}(\omega_{v''}-\omega_{0''})}}{\sum_{v''=0}^{v''_{diss}} e^{-\frac{hc}{kT_v}(\omega_{v''}-\omega_{0''})}} \right\} \left\{ \frac{hc}{kT_R} e^{-j''(j''+1)\frac{hc}{kT_R}B_0''} \right\} f\, p_{v'v''} \qquad (80)$$

where T_e, T_v, and T_R are, respectively, the electronic temperature, the vibrational temperature, and the rotational temperature. If the induced emission is to be accounted for, then Eq. (88), Appendix I, must be used. The basic absorption process here is the electronic jump. The effect of the vibrational and rotational transitions in this process is essentially to distribute the transitional energy over a broad frequency range, rather than to add to probability of the transition occurring. Using the above concept, and data obtained from References 29 and 30, the absorption coefficients for the N_2 (2+) band were calculated for three different cases: (1) $T_R = 14000^\circ K$, $T_e = T_v = 2000^\circ K$; (2) $T_R = T_v = T_e = 2000^\circ K$; (3) $T_R = T_v = T_e = 14000^\circ K$. In addition the emissivity, J_ω, was calculated for cases (1) and (3). It should be noted that the calculations were made by slide rule so that the accuracy is correspondingly limited. The $p_{v'v''}$ matrix was obtained from Reference 30, the oscillator strength, f, from Reference 10, and the various molecular constants from Herzberg[29]. The choice of bands was arbitrary, and was based mostly on the availability and compactness of the $p_{v'v''}$ matrix.

Case (1) corresponds approximately to conditions on the stagnation streamline just behind the shock (see Figure 6). The shock separation distance was chosen to be 4 cm. From Reference 22 this case corresponds to a shock radius of 60 cm. The altitude is 250,000 ft. and the Mach number is about 22. The electronic and vibrational temperatures are assumed equal, while the rotational temperature is equated to the kinetic temperature (these are the usual assumptions made in solving the chemistry problem. Rotational relaxation times are much less than vibrational relaxation times, but not much information is available on the electronic relaxation rates.) The vibrational temperature was obtained by a simple scaling[35] of the results of Reference 22. Note that the $p_{v'v''}$ matrix used is not the Franck-Condon array, but rather includes the effect of variation of the dipole moment with internuclear separation[28, 30].

It can be seen both from the graphs (Figures 7 - 11) and from Eq. (80) that the chief difference between cases (1) and (2) is in the distribution of intensity, along with a slight change in peak intensity values (about a factor of 10). On the other hand case (3) is drastically different from (1) and (2), being about 10^{15} times stronger. This result is traced to two different effects. First, because the lower state ($B^3\pi_g$) in this transition is not the ground state, the electronic temperature enters exponentially through the Boltzmann factor, which gives the relative number of molecules in this state. Second, the Planck function now corresponds to a 14000°K source rather than a 2000°K source (a fourth power factor from this) and, in addition, the change in

T has shifted the band from one side of the black body curve over to the center (peak). Note the difference in the two black body curves of Figures 8 and 11.

Although the effect of non equilibrium conditions was to drastically change the radiation for the particular cases considered above, it is not possible to draw any general conclusions for the whole flow field without carrying out more detailed calculations. Note, for example, from Figure 6, that the electronic-vibrational temperature of O_2 may substantially exceed the kinetic temperature of the flow, and tends to lag above it as the translational temperature relaxes toward the equilibrium value. According to Reference 21, binary scaling causes the net non-equilibrium effects to be approximately independent of altitude, and indeed, if a species concentration is plotted vs. $\rho_\infty t$, ρ_∞ being the freestream density and t the transit time behind the shock, $\left\{ t = \int_0^x \frac{dx}{|\vec{v}|} \right.$; o = shock point, x = distance along streamline $\left. \right\}$, a curve which is independent of altitude is obtained[35].

Several other questions arise in connection with these non-equilibrium cases, e.g., questions concerning the validity of the Boltzmann distribution function, especially when the so called "Collision limiting" is important. More fundamentally, it is not clear that the dipole moment integrals or Franck-Condon factors are useful under these (non-equilibrium) conditions. These factors are based on the Born-Oppenheimer approximation (i.e., separation of variables in the solution of the wave equation). The fact that the r-centroid factors[30] can significantly modify the Franck-Condon arrays means that there is some measurable interaction between the modes. Even though the temperature does not enter into the solution of the wave equation, the internuclear potential certainly does, as well as perturbation potential terms due to local radiation fields (in fact it is the latter that gives rise to the dipole moment integrals), and these terms may be functions of the excitation level of the various modes. Even in the equilibrium case the interaction terms can be fairly significant for certain molecules (e.g., those in which one of the atoms is a hydrogen atom)[36, 37]. It is possible that the interaction terms may become more important under non-equilibrium conditions.

VIII. SUMMARY

The use of the Planck mean absorption coefficients always underestimates the effects of absorption. The introduction of two distinct mean values, one for emission and one (or more) for absorption, can significantly change the result when considering absorption processes.

Similarly, under certain flow conditions, the use of distinct electronic, vibrational, rotational, and kinetic temperatures can significantly modify the calculation of the absorption coefficient. This occurs in part by modifying the population of the excited states, and in part by modifying the black body function.

It is planned to investigate both of these non-gray aspects of the radiation transfer problems further. In particular, an effort is being made to determine whether the multiple absorption coefficient concept is useful in the stagnation region. Also, the various effects of considering relaxation phenomena will continue under investigation.

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APPENDIX

THE EINSTEIN COEFFICIENTS AND INDUCED EMISSION

Consider a system of N particles (atoms or molecules) in a radiation field of density ρ_ν. At any instant of time, N_ℓ of these particles may be in a low level energy state ℓ corresponding to some set of quantum numbers e'', v'', j'', ..., and N_u particles may be in a higher energy state u corresponding to a set of quantum number e', v', j', ..., such that the difference in energy of the two states is

$$E_{\ell u} = E_{e'v'j'} - E_{e''v''j''} = h\nu_{\ell u} \qquad . \qquad (81)$$

The probability that a particle in the excited state u may spontaneously drop to the energy level ℓ, in unit time, is called $A_{u\ell}$, the Einstein coefficient for spontaneous emission. The probability that a particle in the upper state u may collide with a photon of frequency $\nu_{\ell u}$ and consequently drop to the energy state ℓ, in unit time, is $\rho_{\nu_{\ell u}} B_{u\ell}$. Note that the photon emitted by the particle will have the same frequency and direction as the colliding photon. $B_{u\ell}$ is the Einstein coefficient for induced emission. The probability that a particle in the state ℓ will collide with a photon of frequency $\nu_{\ell u}$ and jump to the upper state u, thereby absorbing the colliding photon, in unit time, is $\rho\nu_{\ell u} B_{\ell u}$, where $B_{\ell u}$ is the Einstein coefficient for induced absorption. These coefficients are intrinsic properties of the particles, hence they are independent of the temperature, the number of particles, and the radiation density. They are, however, related to each other. Since they are intrinsic properties of the particles, they may be evaluated under any convenient set of conditions, e.g., thermal equilibrium. This evaluation yields the following relation between these coefficients

$$A_{u\ell} = \frac{8\pi}{c^3} h \nu_{\ell u}^3 B_{u\ell} \tag{82}$$

and

$$g_\ell B_{\ell u} = g_u B_{u\ell} \tag{83}$$

Now while the Einstein coefficients are not functions of temperature, the ratio N_ℓ / N_u certainly is. The absorption coefficient which appears in the transfer equation (Section II) is proportional to the difference of the products N_ℓ $B_{\ell u}$ and N_u $B_{u\ell}$, i.e.,

$$K_\nu \sim \left(N_\ell B_{\ell u} - N_u B_{u\ell} \right) = N_\ell B_{\ell u} \left(1 - \frac{N_u}{N_\ell} \frac{g_\ell}{g_u} \right) \tag{84}$$

Assuming the states are populated with a Boltzman distribution, Eq. (84) is equal to

$$K_\nu \sim N_\ell B_{\ell u} \left(1 - e^{-\frac{h\nu_{\ell u}}{kT}} \right) \tag{85}$$

where the term in the brackets accounts for the effect of induced emission. The black-body function

$$B_\nu \, d\nu = \frac{2h}{c^2} \frac{\nu^3 . d\nu}{\exp(h\nu/kT) - 1} = \frac{2h}{c^2} T^4 \frac{x^3 \, dx}{\exp(hx/k) - 1} \tag{86}$$

is a function of T and x = (ν/T); hence at any given temperature T the equilibrium distribution of radiation energy is a known function of x. Therefore, since the term in brackets in Eq. (85) is also a function only of x, its equilibrium value is known for every point on the black body curve. For example, the peak of intensity of the black body function is at $\lambda T = 0.29$ cm°K. At this point the exponential factor has the value

$$(1 - e^{-(1.44/0.29)}) = 0.993 \qquad (87)$$

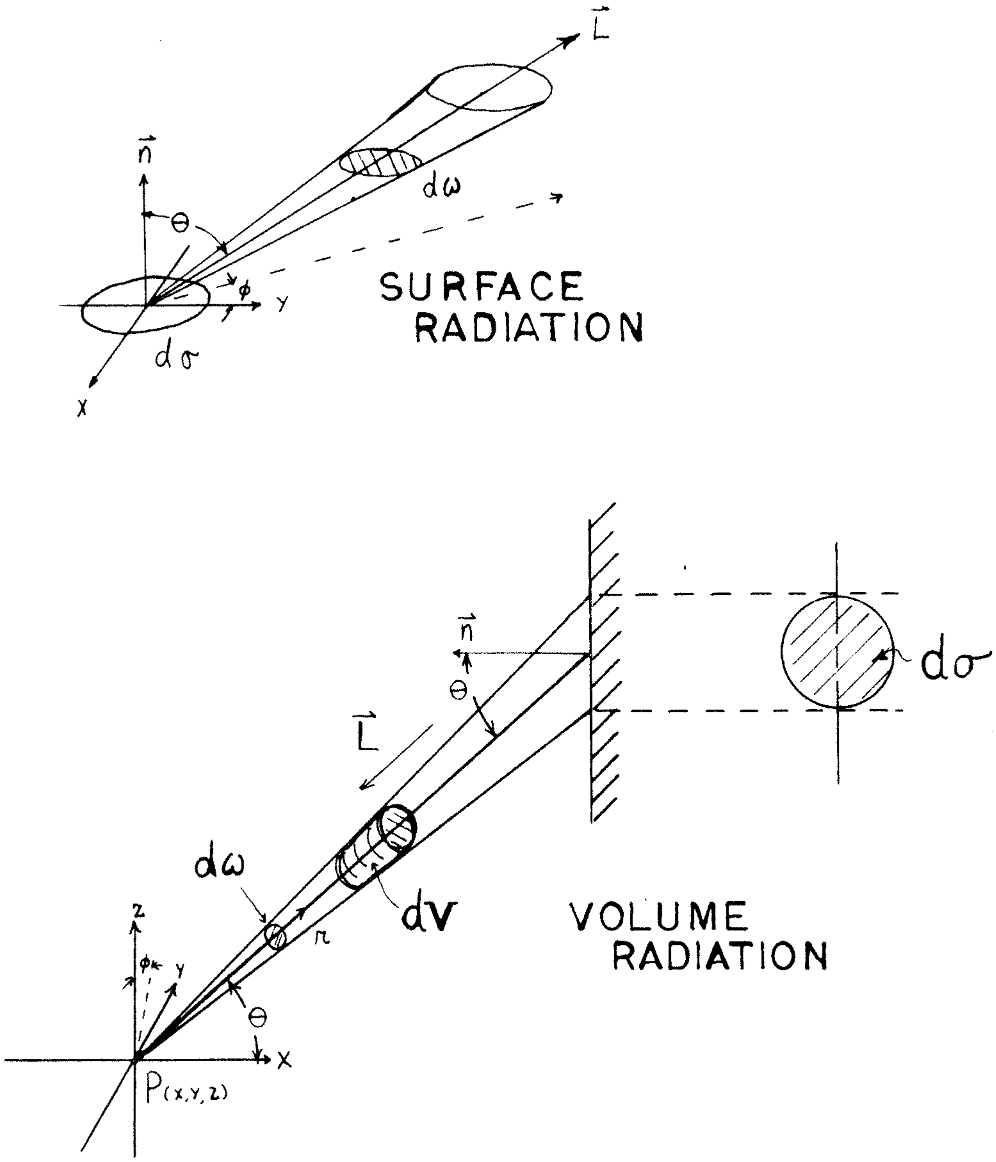
that is, induced emission is less than one per cent of induced absorption at the black body peak. Toward the blue it is even less, while toward the red it gradually increases; however, by the time the induced emission equals 10 per cent of the induced absorption, the black body intensity has fallen to about 10^{-4} parts of the peak value.

Practically speaking, the effects of induced emission cannot be separated from the effects of induced absorption -- one always measures the difference. Lowering the temperature of the system being measured will minimize the effect, as well as minimizing the effect of spontaneous emission, but this is not always either possible or even desirable. In any case, the net absorption coefficient is what is needed in the transfer equation.

Note that under non-equilibrium conditions, the relative magnitude of the induced emission term may be either increased or depressed, depending on the population ratio N_u/N_ℓ . In most (but not all) situations in hypersonic flow, this ratio tends to be less than equilibrium, thus depressing the induced emission. The absorption coefficient is related to the Einstein coefficients, under non-equilibrium conditions, by

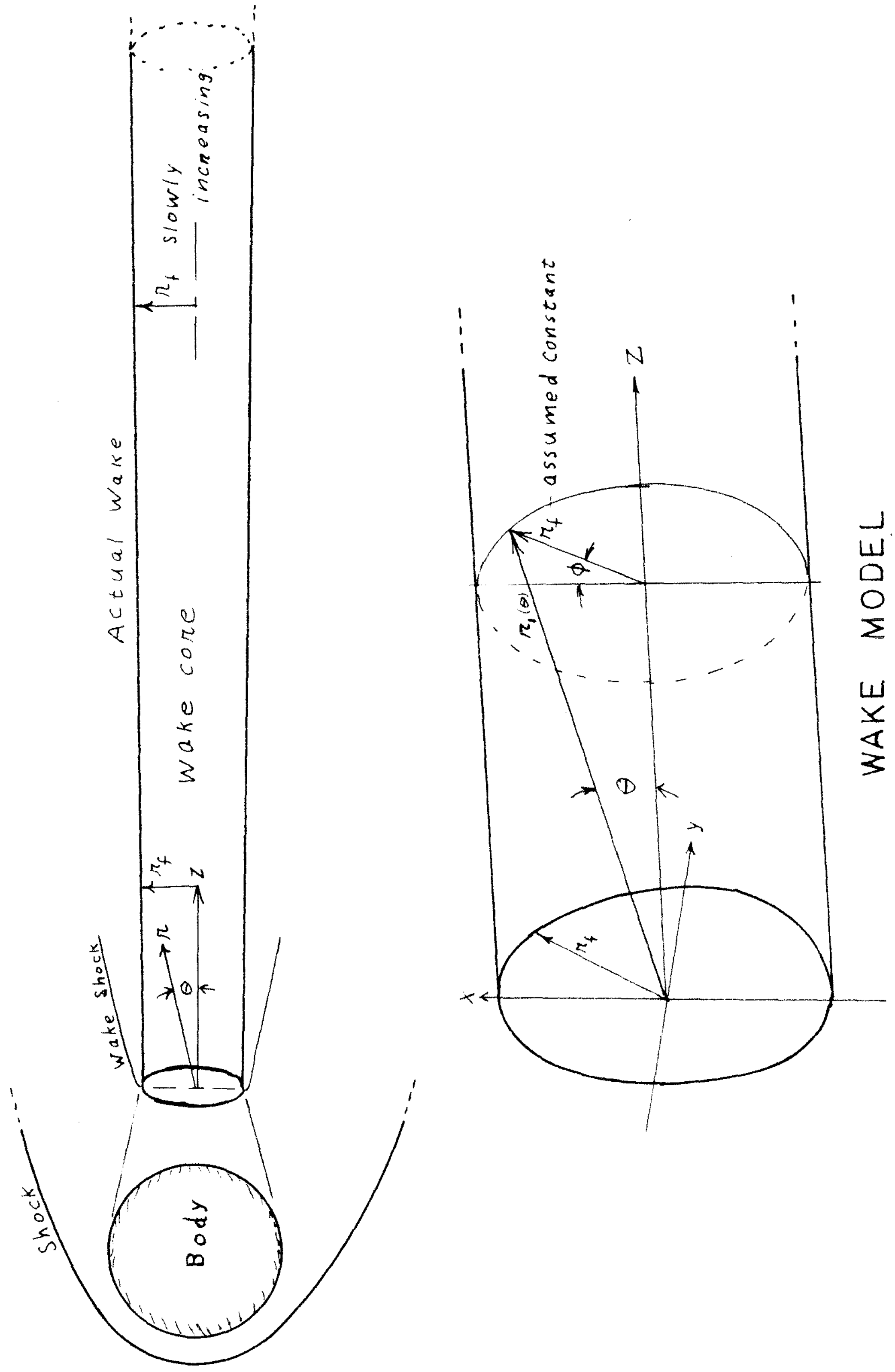
$$K_\nu \sim N_l B_{lu}\left[1 - \left\{ e^{-\frac{hc\,\delta T_{e''}}{kT_e}} \right\}\left\{ e^{-\frac{hc\,\delta \omega_{v''}}{kT_v}} \right\}\left\{ e^{-\frac{hc\,\delta \omega_{j''}}{kT_R}} \right\} \right] \tag{88}$$

where $\delta T_{e''}$, $\delta \omega_{v''}$ and $\delta \omega_{j''}$ are the differences of the term values for the electronic, vibrational, and rotational upper and lower states.



$\vec{L}$ is taken as the distance into the volume from the surface, by convention

FIG. 1



WAKE MODEL

FIG. 2

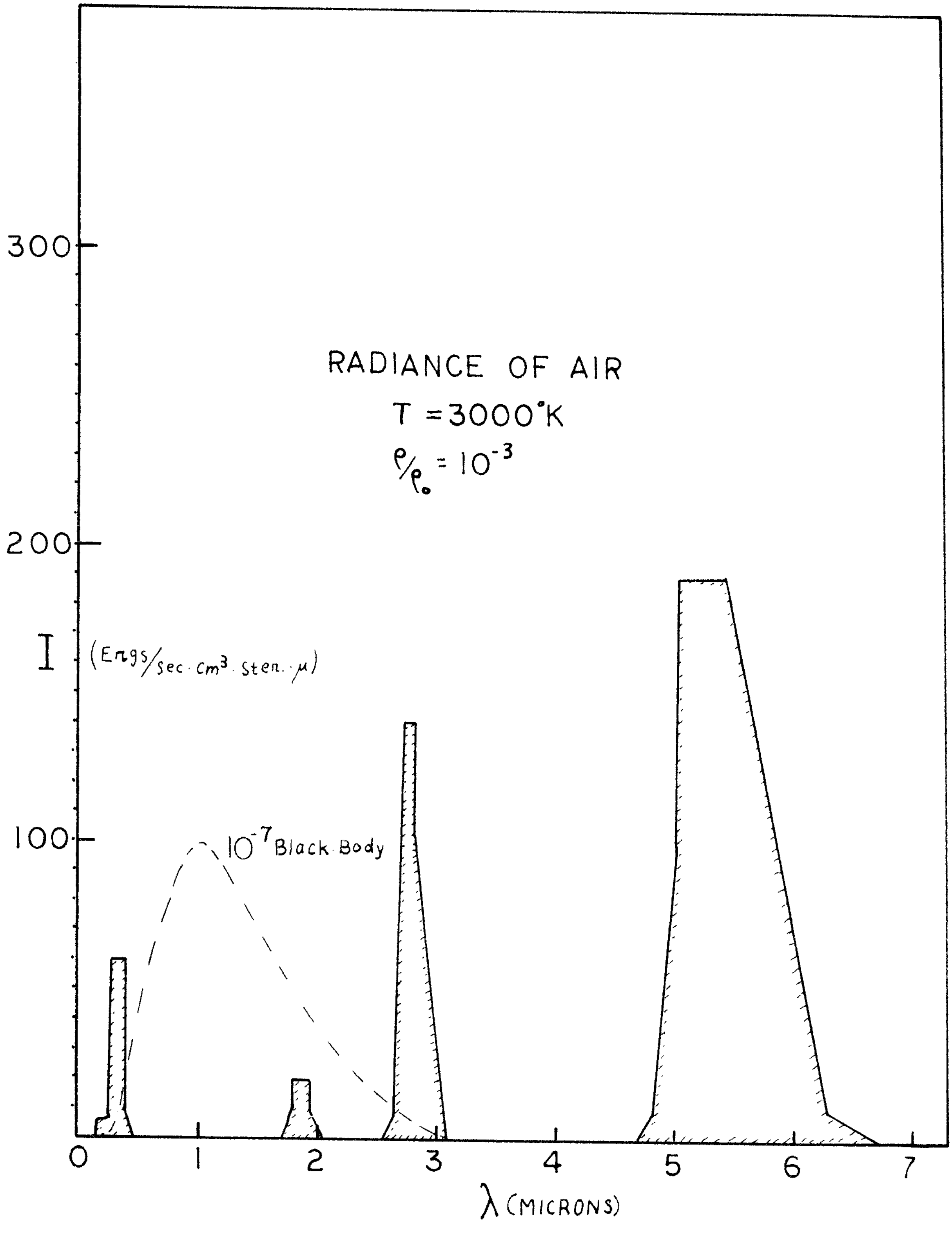

RADIANCE OF AIR
T = 3000°K
ρ/ρ₀ = 10⁻³
300
200
100
I (Ergs/sec·cm³·Ster.·μ)
10⁻⁷ Black Body
0
1
2
3
4
5
6
7
λ (MICRONS)

FIG. 3

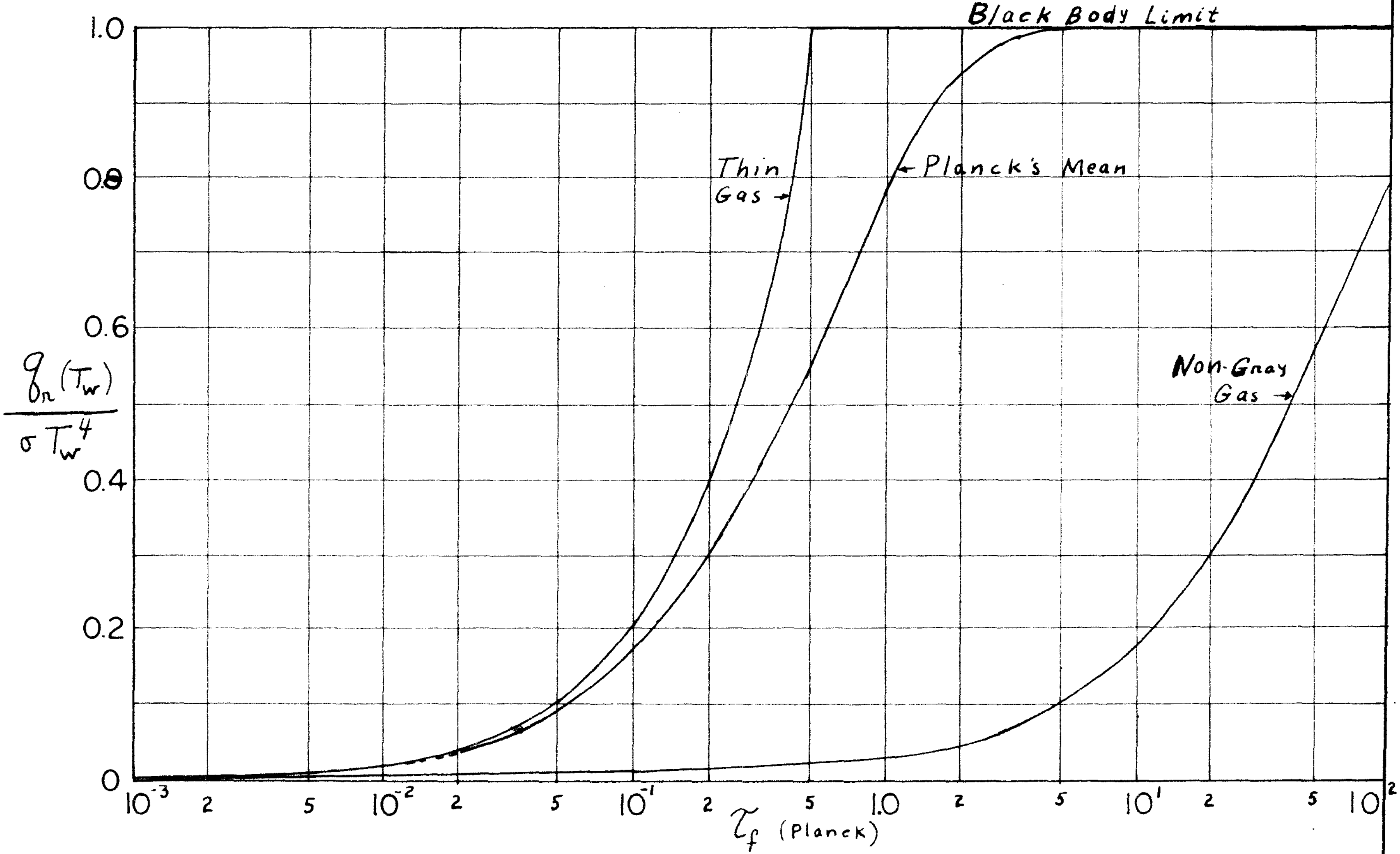
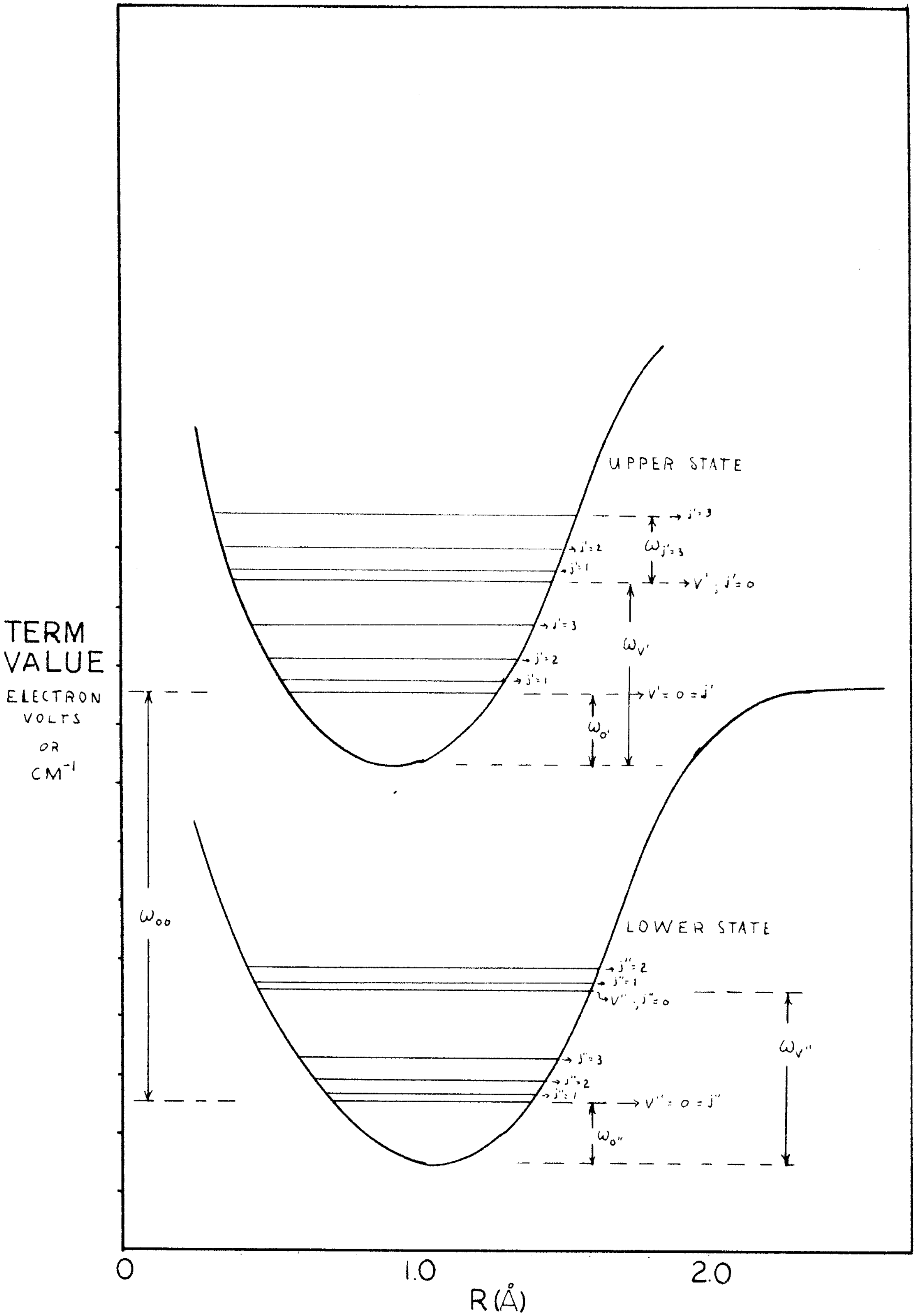

Black Body Limit
Thin Gas
Planck's Mean
Non-Gray Gas
$\frac{q_r(T_w)}{\sigma T_w^4}$
1.0
0.8
0.6
0.4
0.2
0
10^{-3}
2
5
10^{-2}
2
5
10^{-1}
2
5
1.0
2
5
10^{1}
2
5
10^{2}
τ_f (Planck)

FIG. 4



TYPICAL POTENTIAL DIAGRAM

FIG. 5

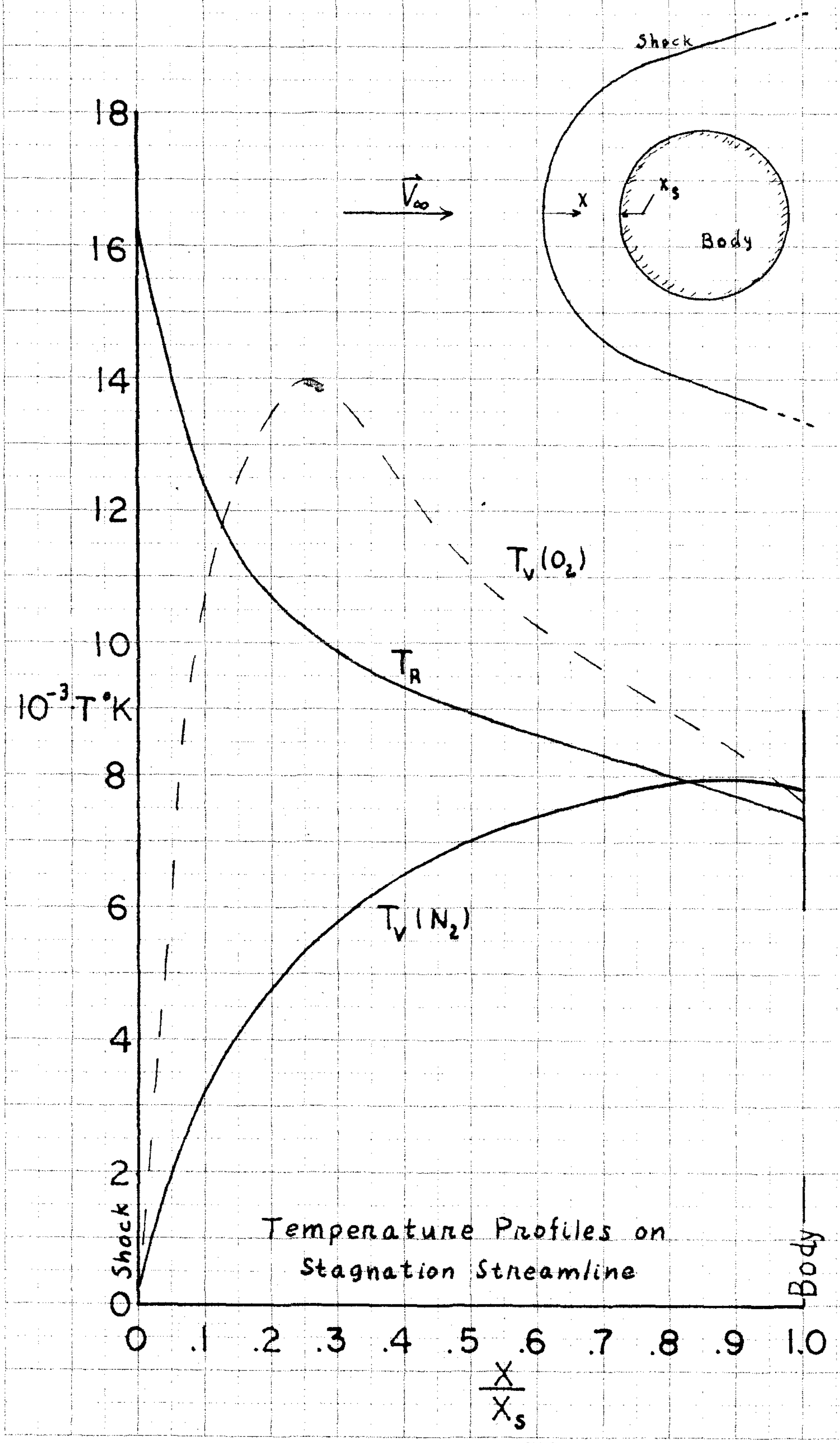
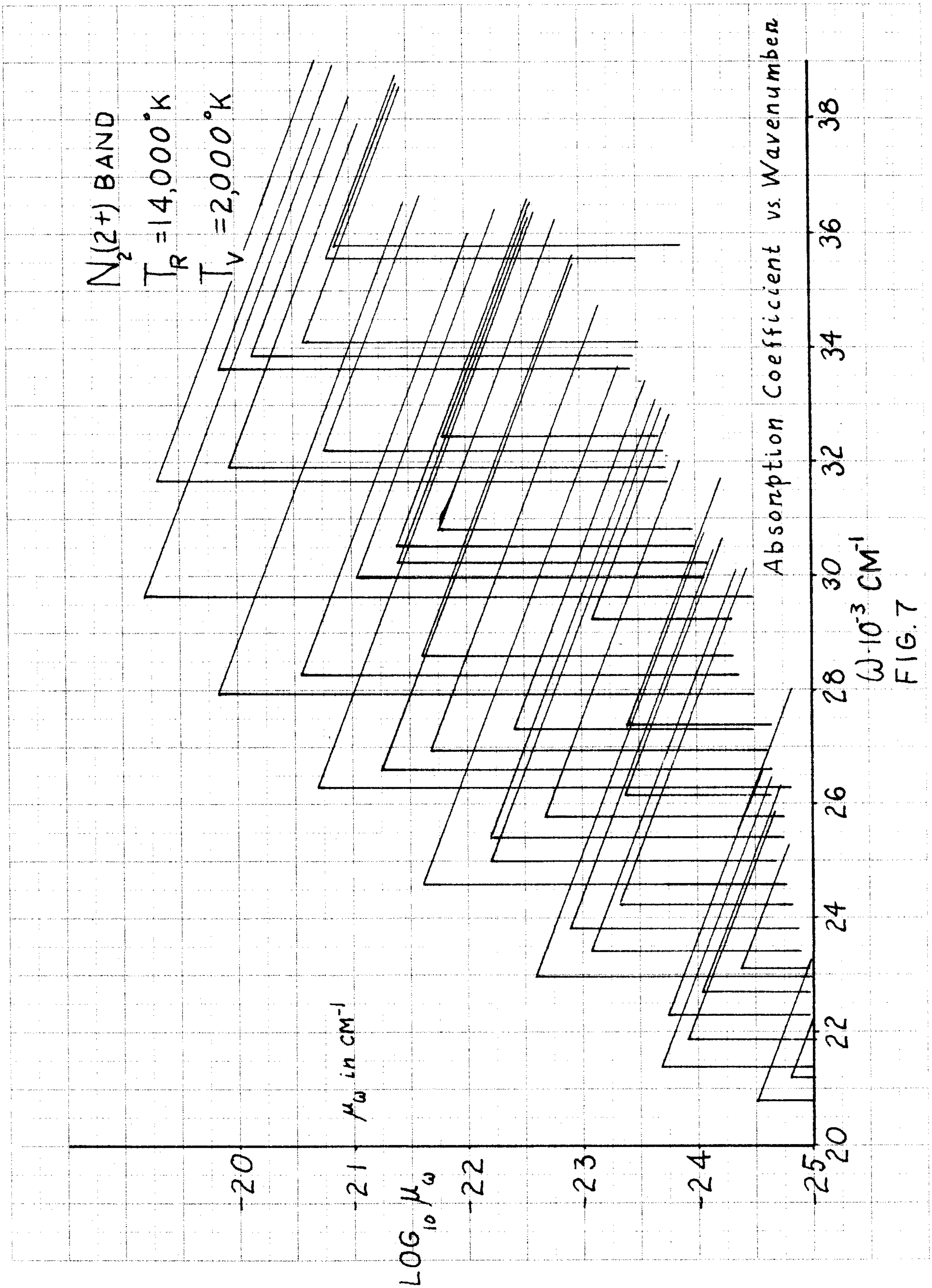

Shock
$\vec{V}_\infty$
X
X_s
Body
18
16
14
12
10
$10^{-3} \cdot T\,°K$
8
6
4
2
0
$T_V(O_2)$
T_R
$T_V(N_2)$
Shock
Body
Temperature Profiles on
Stagnation Streamline
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
$\frac{X}{X_s}$

FIG. 6



Absorption Coefficient vs. Wavenumber

FIG. 7

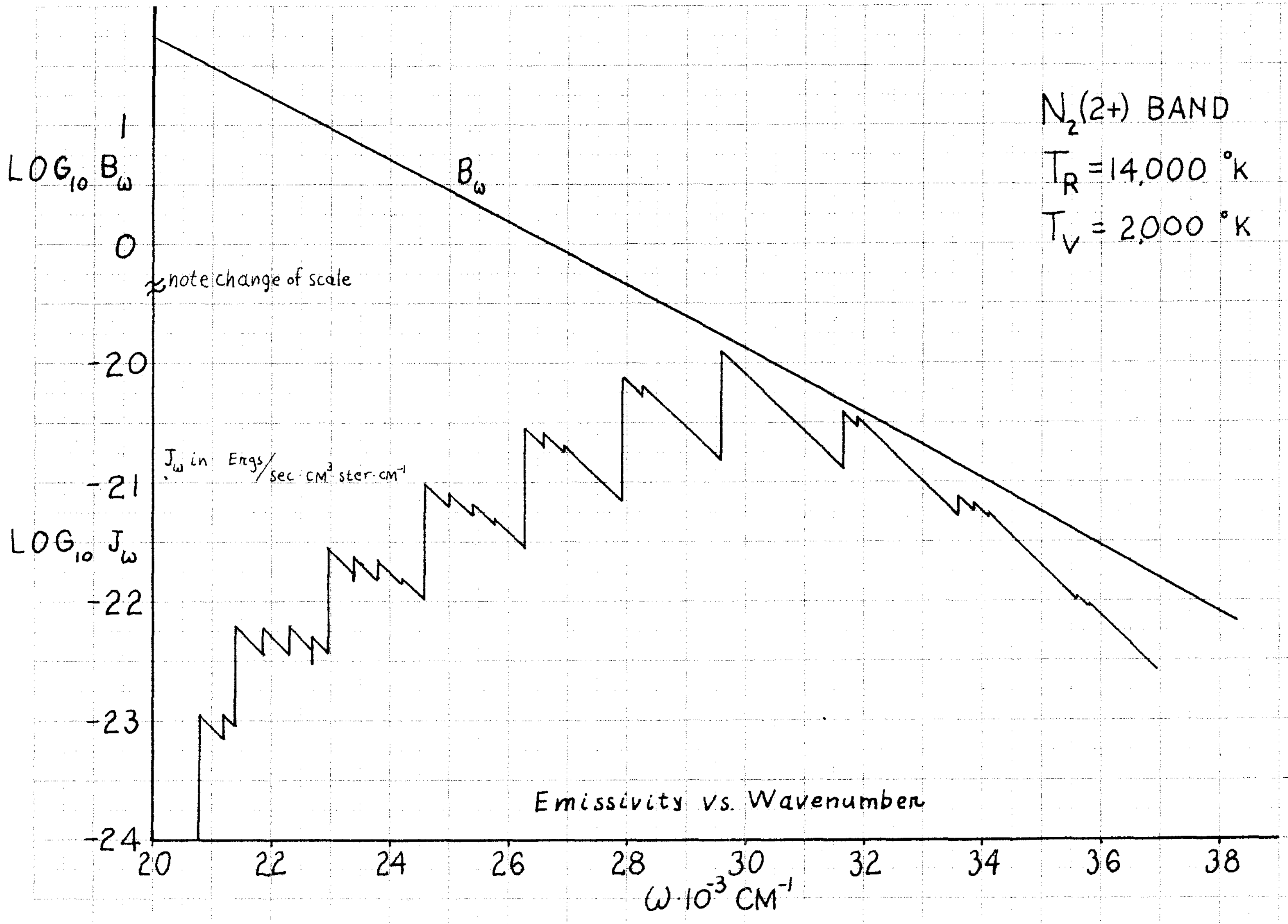
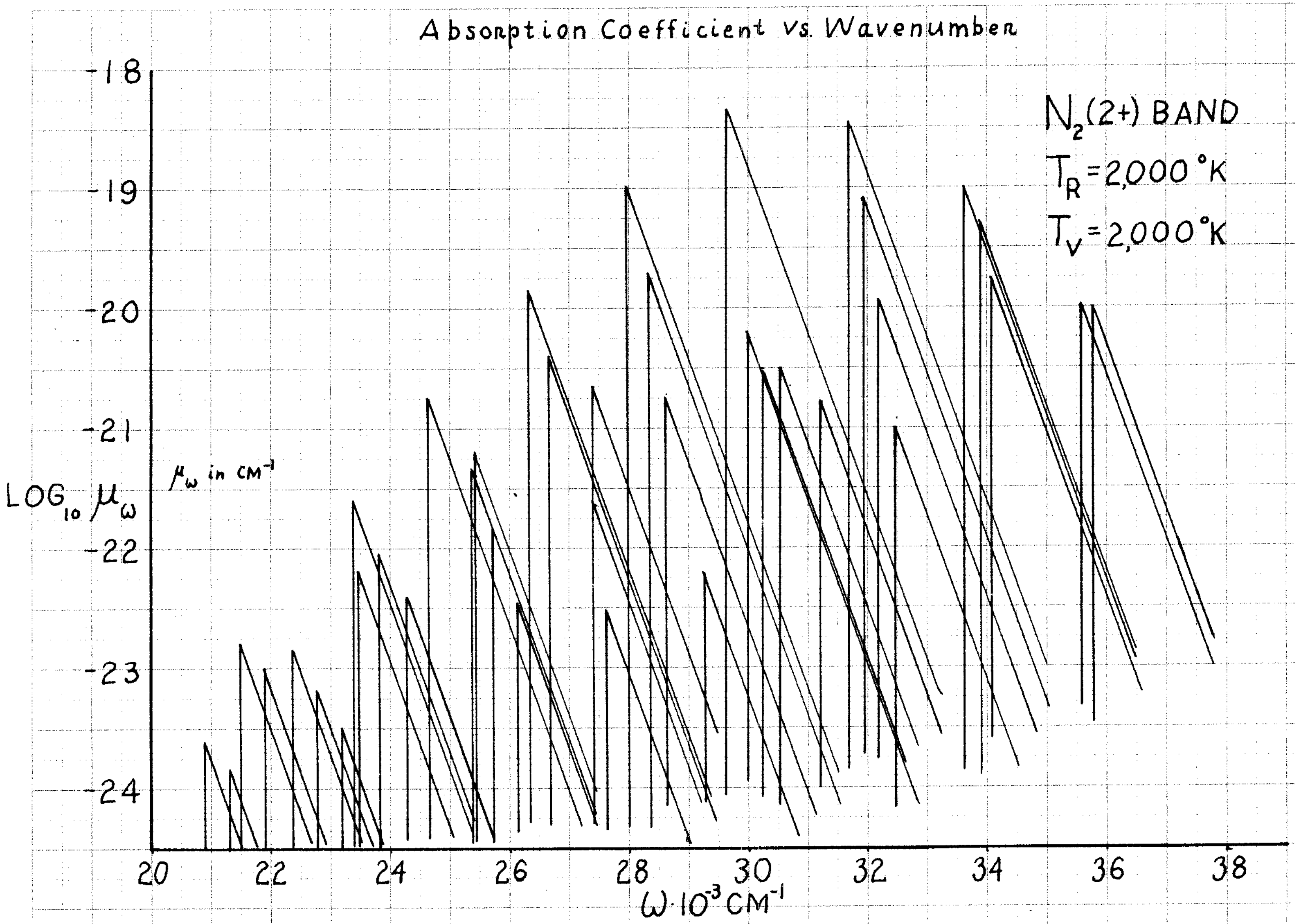
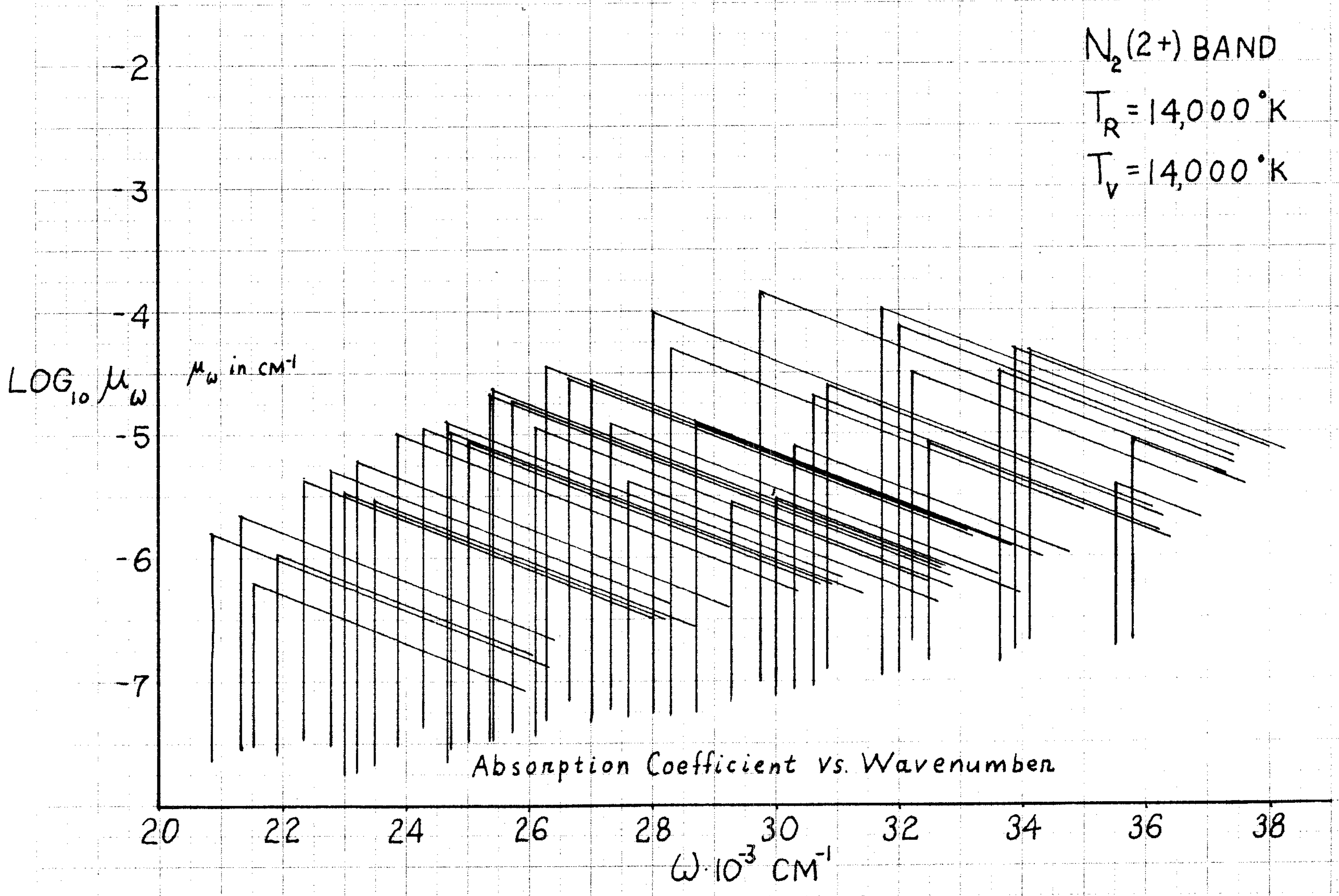

$N_2(2+)$ BAND
$T_R = 14,000$ °K
$T_V = 2,000$ °K
B_ω
$LOG_{10}\ B_\omega$
1
0
≈ note change of scale
J_ω in Ergs/sec·CM³ ster·cm⁻¹
$LOG_{10}\ J_\omega$
-20
-21
-22
-23
-24
20
22
24
26
28
30
32
34
36
38
$\omega \cdot 10^{-3}\ CM^{-1}$
Emissivity vs. Wavenumber

FIG. 8



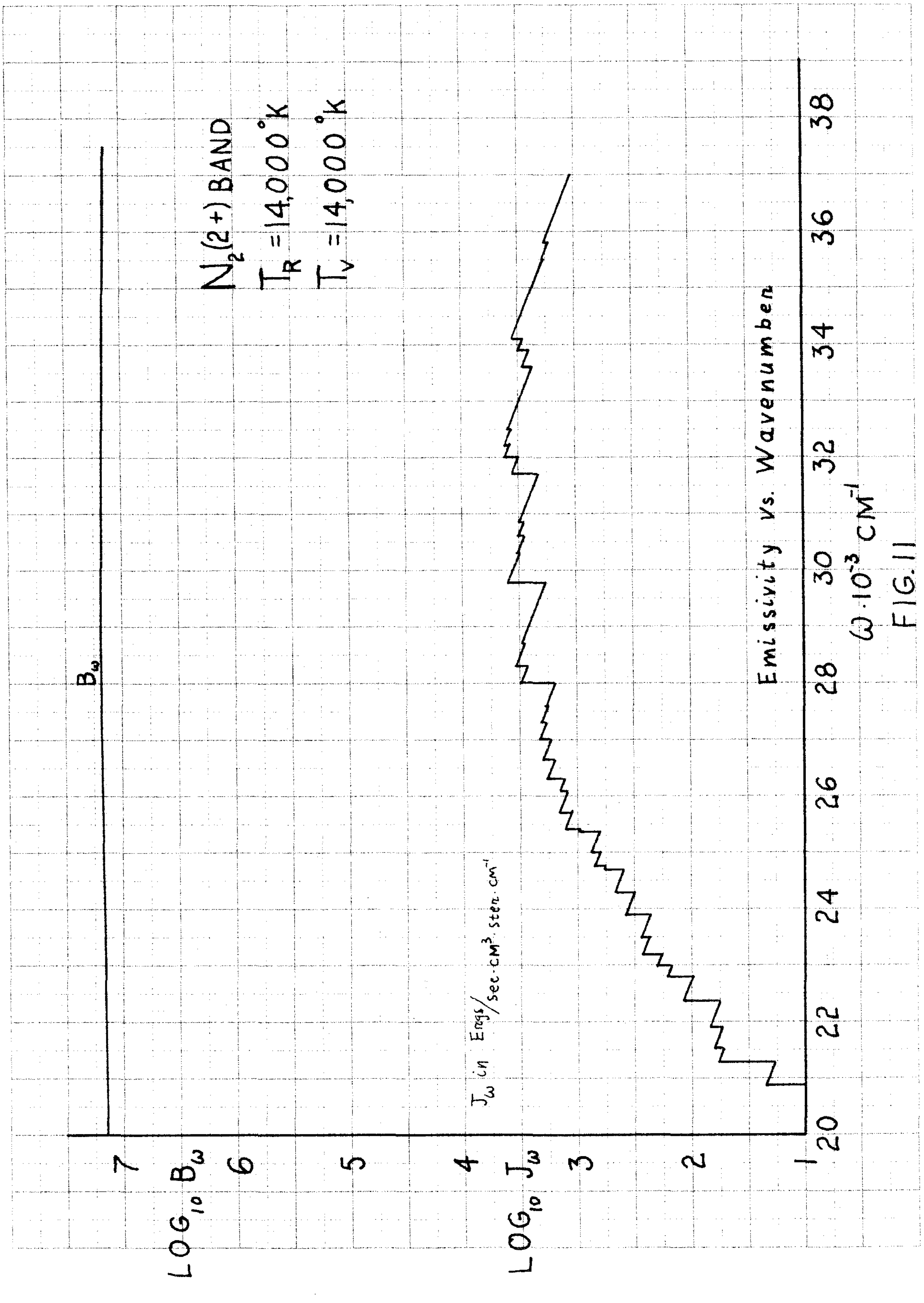
Absorption Coefficient vs. Wavenumber

FIG. 9



Absorption Coefficient vs. Wavenumber

FIG. 10



Emissivity vs. Wavenumber

FIG. 11