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THERMAL RADIATION BY COMBUSTION GASES

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Abstract— Generalized expressions for the calculation of the emissivity, absorptivity, and other relevant radiation properties of molecular gases are given. New rational correlations for the properties of H_2O, CO_2, CO, NO, SO_2 and CH_4 are shown to be readily applicable to combustion gas radiation problems. Hand calculations are shown to be easily made for any arbitrary mixture of the above gases, and a simple computer routine for high-speed computation is described. Tabular and graphical aids giving the engineer physical insight into the radiation heat-transfer characteristics of the gases considered are presented and explained.

NOMENCLATURE

A,	total band absorption;
B,	rotational constant;
b,	pressure broadening parameter;
C,	band absorption correlation constant;
c,	speed of light;
d,	line spacing,
f,	fractional function of the first kind (external fraction);
g,	statistical weight;
h,	Planck's constant;
I,	spectral directional intensity;
k,	Boltzmann constant;
L,	path length, mean beam length;
M,	number of gases;
N,	number of bands;
P,	total pressure of mixture;
$P_{e,i}$,	broadening pressure effective on the ith species;
P_i,	partial pressure of the ith species;
q,	heat flux;
S,	mean line intensity;
T,	temperature;
v,	vibrational quantum number;
u,	a dimensionless grouping defined by equation (7);
x_i,	mole fraction of species i.

Greek letters

α,	integrated band intensity;
α_ν,	spectral absorptivity;
α_T,	total absorptivity;
β,	line width parameter;
Γ,	gamma function;
δ,	vibrational transition;
ε,	emissivity;
ε_T,	total emissivity;
ζ,	line effect integral, equations (28) and (31);
η,	line width to spacing ratio;
θ,	polar angle between ray and normal;
κ,	absorption coefficient;
μ,	micron, 10^{-4} cm;
ν,	wavenumber;
ξ,	line intensity integral, equations (27) and (30);
π,	3·1415927 . . . ;
ρ,	density of the mixture;
ρ_i,	density of the ith absorbing gas;
σ,	Stefan–Boltzmann constant;
τ,	transmissivity;
τ_H,	optical depth at band head or most intense spectral location;
Φ,	temperature dependent function for line width parameter;
ϕ,	azimuthal angle;

Ψ, temperature dependent function for integrated band intensity;
ω, bandwidth parameter.

Subscripts
e, equivalent or effective;
c, center;
H, head or center of the band;
i, ith gas;
j, jth band;
k, kth vibrational quantum number;
l, lower;
mix, mixture;
n, pressure broadening exponent;
o, standard or reference state;
P, Planck;
Q, from spectral quadrature;
s, surface;
T, total;
u, upper;
z, coordinate;
$*$, representing a dimensionless band absorption ratio;
$-$, negative direction;
v, spectral.

INTRODUCTION

HEAT transfer at high temperatures is effectively carried out by thermal radiation without the necessity for concurrent mass and momentum transfer required by Reynold's analogy for a turbulent convective heat-transfer process. For example, combustion gases in fossil-fuel fired power plants may be cooled in a radiative section without excessive slagging of the transfer surface and without significant pressure drop. Heat radiation is not only an effective mode of energy transfer. It may be a revealing mode of information transfer as well. Information about the amount, composition, and temperature of combustion gases can be inferred from radiation measurements. Both sorts of application have relevance to pollution control as well as to the aerospace, heat-power, and chemical process industries. For example, the rate of formation of nitric oxide in burner flames is affected by the temperatures at which combustion is carried out, which in turn can be affected by radiation heat transfer. In order to employ creatively thermal radiation for either heat or information transfer, it is necessary to know the radiation characteristics of combustion gas mixtures.

Mixtures of carbon dioxide and water vapor, the predominant products of fossil-fuel combustion, can be treated on a total basis using the emissivity charts of Hottel and the H_2O–CO_2 mixture correction chart (e.g. [1]). The possibility of treating a multi-component mixture by such a method is precluded by the lack of other mixture correction charts. The complex form which such charts would have to take for multicomponent mixtures makes such an approach dubious. For CO_2–H_2O mixtures one can also carry out spectral calculations using detailed information about the mean line intensity and mean line-width-to-spacing ratio at each spectral location (perhaps every 5 cm^{-1} wavenumbers from 100 to 10000 cm^{-1}) for each gas. Much spectral data exists for H_2O and CO_2 (e.g. [2, 3]). A third alternative, which can be employed for a variety of gas mixture components, is to use wide-band absorption relations as shown by Hines and Edwards [4]. Empirical band absorption correlations for several gases have appeared and were summarized in a previous paper [5].

It was recently pointed out [6] that previous band absorption correlations have not been based upon a rational prediction of mean line width to spacing ratio. The existing empirical correlations for band absorption are thus somewhat questionable, particularly for extrapolation beyond the range of conditions pertaining to the measurements.

It is the purpose of this paper to present new rational correlations for band absorption of several combustion gas products, to show how the new correlations compare with existing data, and to show how they may be readily used to find radiation characteristics of combustion gas mixtures.

THEORY

Molecular gas radiation properties are complex due to the many orders of magnitude of variation in the spectral absorption coefficient with wavenumber over the infrared spectrum associated with heat radiation at combustion gas temperatures (say wavenumbers from 100 cm^{-1} to 10000 cm^{-1}, that is, wavelengths from as long as 100 microns to as short as 1 micron). In regions of intense absorption, called absorption bands, the radiation is attenuated by e^{-1} in a millimeter or less while a hundred or two wavenumbers away, in regions called windows, a distance of kilometers may be required. Moreover, even within the absorption band variations of an order of magnitude or more may occur over as short a spectral increment as one or two wavenumbers. The selectivity manifested by the wide bands is due to interaction of the infrared radiation with vibrational modes of energy storage by the molecules. The selectivity within the bands is due to interaction with rotational modes of energy storage giving rise to line structure in the vibration-rotation band. Account of the line structure can be taken approximately by use of a narrow band model, for example, the Goody model [7]. The absorptivity of a homogeneous gas path of length L is for the ith species and jth band

$$\alpha_{\nu,i,j} = 1 - \exp\left\{\frac{-(S/d)_{i,j}\rho_i L}{\left[1 + \dfrac{(S/d)_{i,j}\rho_i L}{\beta_{i,j}P_{e,i}}\right]^{\frac{1}{2}}}\right\} \tag{1}$$

where $(S/d)_{i,j}$ is the mean intensity to line spacing, ρ_i is density of the absorber, $\beta_{i,j}$ is π times the mean line width to spacing ratio for a dilute mixture at one atmosphere pressure, and $P_{e,i}$ is an equivalent broadening pressure in atmospheres. The quantities (S/d) and β are imagined to vary with wavenumber ν only slowly over the extent of an entire band and not from line to line. The equivalent broadening pressure is written

$$P_{e,i} = [P/P_0 + (P_i/P_0)(b_i - 1)]^n \tag{2}$$

where P_0 is one atmosphere, P is the total pressure, P_i is the partial pressure of the absorbing gas in question and b_i is the self-broadening coefficient, somewhat greater than unity for CO_2, CO, etc., and up to 5 or more for H_2O.

For overlapping bands the transmissivity $1 - \alpha_\nu$ is very nearly the product of the transmissivities of each band [4].

$$\alpha_{\nu,\text{mix}} = 1 - \prod_{i=1}^{M}\prod_{j=1}^{N}(1 - \alpha_{\nu,i,j}). \tag{3}$$

The product is over all bands of all species.

A wide band model may then be used to prescribe how $(S/d)_{i,j}$ and $\beta_{i,j}$ vary with wavenumber ν. An exponential band model [8] has been used successfully when $\alpha_{\nu,i,j}$ is of secondary importance to the band absorption

$$A_{i,j} \equiv \int_0^\infty \alpha_{\nu,i,j}\,d\nu. \tag{4}$$

In the exponential model three crude band shapes are allowed, one for a symmetrical band with center $\nu_{c,i,j}$,

$$(S/d)_{\nu,i,j} = \frac{\alpha_{i,j}}{\omega_{i,j}}\exp\left[-2|\nu - \nu_{c,i,j}|/\omega_{i,j}\right], \tag{5a}$$

another for a band with an upper wavenumber head at $\nu_{u,i,j}$,

$$(S/d)_{\nu,i,j} = 0,\ \nu > \nu_{u,i,j},$$

$$(S/d)_{\nu,i,j} = \frac{\alpha_{i,j}}{\omega_{i,j}}\exp\left[-(\nu_{u,i,j} - \nu)/\omega_{i,j}\right], \quad \nu < \nu_{u,i,j}, \tag{5b}$$

and the third for a band with a lower wavenumber head at $\nu_{l,i,j}$,

$$(S/d)_{\nu,i,j} = 0,\ \nu < \nu_{l,i,j},$$

$$(S/d)_{\nu,i,j} = \frac{\alpha_{i,j}}{\omega_{i,j}}\exp\left[-(\nu - \nu_{l,i,j})/\omega_{i,j}\right], \quad \nu > \nu_{l,i,j}. \tag{5c}$$

An exponential band absorption correlation is then simply a prescription of values of $\alpha_{i,j}$, $\beta_{i,j}$ and $\omega_{i,j}$ vs. temperature. The parameter α is the integrated band intensity, the integral of

$(S/d)_{v,i,j}$ over all v, and was formerly called C_1 [8,5]. The band width parameter ω is the width of the spectral interval in which S/d is greater than $1/e$ of its maximum value. The parameter ω was formerly called C_3, and the grouping $[4\alpha\omega\beta]^{\frac{1}{2}}$ was called C_2. These former designations were for simplicity in application and to emphasize the entirely empirical nature of the correlations then made.

Consider a vibration–rotation band arising due to transitions in the energy states of species i. The vibrational state before absorption of a photon of thermal radiation is described by the set of vibrational quantum numbers $(v_1, v_2, \ldots, v_k, \ldots, v_m)$. After absorption of the photon it is $(v_1 \pm \delta_1, v_2 \pm \delta_2, \ldots, v_k \pm \delta_k, \ldots, v_m \pm \delta_m)$. A set of δ's (and associated algebraic signs) therefore describes the transition giving rise to the jth absorption band of species i. For simplicity in notation the i, j subscripts are temporarily dropped. The integrated intensity is the sum of all those transitions of the jth type. Approximating the molecular behavior with harmonic-oscillator type wave functions gives the following general expression for $\alpha(T)$.

$$\alpha(T) = \alpha_0 \frac{[1 - \exp(-\sum_{k=1}^{m} \pm u_k\delta_k)]\Psi(T)}{[1 - \exp(-\sum_{k=1}^{m} \pm u_{0,k}\delta_k)]\Psi(T_0)} \tag{6}$$

where

$$\begin{aligned} u_k &= hc\nu_k/kT \\ u_{0,k} &= hc\nu_k/kT_0 \\ (T_0 &= 100°\text{K for convenience}) \end{aligned} \tag{7}$$

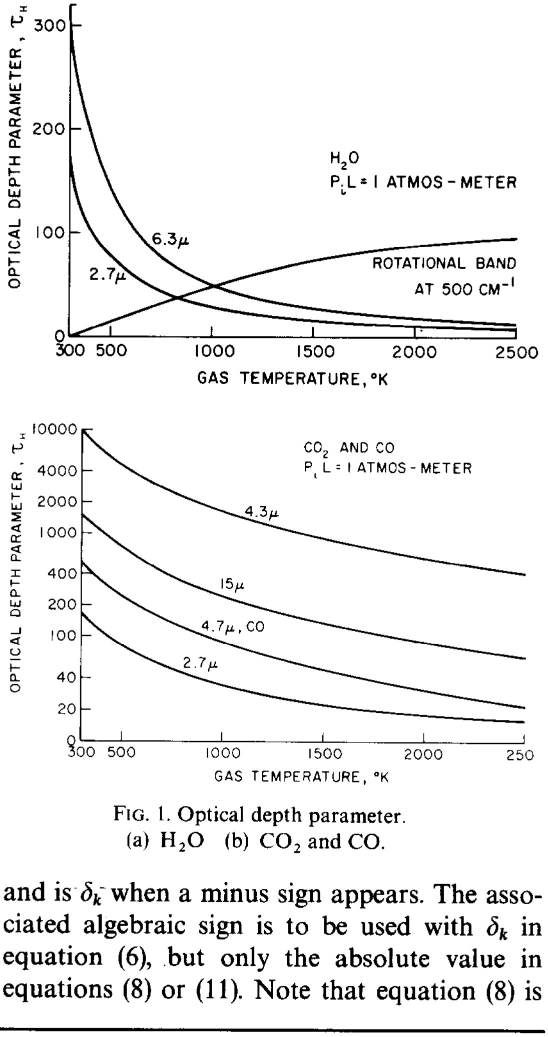

FIG. 1. Optical depth parameter.
(a) H_2O (b) CO_2 and CO.

The statistical weight g_k is unity for non-degenerate vibrations, 2 for the v_2 mode of CO_2, 2 for the v_2 vibration of CH_4, and 3 for the v_3 and v_4 modes of that molecule. The value of $v_{0,k}$ is zero if a plus sign is associated with δ_k in the upper state $(v_1 \pm \delta_1, \ \ldots, \ v_k \pm \delta_k, \ \ldots)$ and is δ_k when a minus sign appears. The associated algebraic sign is to be used with δ_k in equation (6), but only the absolute value in equations (8) or (11). Note that equation (8) is

$$\Psi(T) = \frac{\displaystyle\sum_{k=1}^{m} \sum_{v_k=v_{0,k}}^{\infty} \frac{(v_k + g_k + \delta_k - 1)!}{(g_k - 1)!\, v_k!} e^{-u_k v_k}}{\displaystyle\sum_{k=1}^{m} \sum_{v_k=0}^{\infty} \frac{(v_k + g_k - 1)!}{(g_k - 1)!\, v_k!} e^{-u_k v_k}}. \tag{8}$$

more general than previously published relations [9]. For example, an error was made in [10] when v_k was summed from 0 to ∞ instead of from $v_{0,k}$ in the numerator. The quantity α_0 must be determined experimentally for each of the j bands of each of the i species.

For a rigid rotator it has been shown [8, 11] that the bandwidth parameter is approximately

$$\omega \doteq 0{\cdot}9\Gamma^2(3/4)(2kTB/hc)^{\frac{1}{2}} = \omega_0(T/T_0)^{\frac{1}{2}} \qquad (9)$$

where B is the rotational constant. There are thus grounds for taking ω proportional to $T^{\frac{1}{2}}$. Again the constant of proportionality is best determined from experimental data for each i j combination.

The line width parameter β may be calculated in the strong line limit as [12]

$$\beta(T) = \beta_0(T_0/T)^{\frac{1}{2}}\,\frac{\Phi(T)}{\Phi(T_0)} \qquad (10)$$

where

$$\Phi(T) = \frac{\left\{\displaystyle\sum_{k=1}^{m}\sum_{v_k=v_{0,k}}^{\infty}\left[\frac{(v_k+g_k+\delta_k-1)!}{(g_k-1)!\,v_k!}\,\mathrm{e}^{-u_k v_k}\right]^{\frac{1}{2}}\right\}^2}{\displaystyle\sum_{k=1}^{m}\sum_{v_k=v_{0,k}}^{\infty}\frac{(v_k+g_k+\delta_k-1)!}{(g_k-1)!\,v_k!}\,\mathrm{e}^{-u_k v_k}} \qquad (11)$$

Note that the summation goes from $v_{0,k}$ to ∞ in both the numerator and denominator. Equation (11) is a more general expression than that given previously in [12] for $g_k = 1$ and $v_{0,k} = 0$. One would expect that β_0 would vary with species i and band type, that is, several but not necessarily all bands of a given species may have the same value of β_0.

Two particular bands of H_2O require special treatment. One is the pure rotational band of H_2O ($\delta_k = 0$; $k = 1, 2, 3$). It is believed that a theoretical solution cannot be recommended at this time, although some progress has been made [13, 14]. The older empirical correlation forms have been retained. The second is the 2·7μ H_2O band which consists of three overlapping bands. Here the $\alpha_{j'}$, for each type of transition $j' = 1, 2, 3$ is computed according to equations (6)–(8) and summed. Values of $\beta_{j'}$ are likewise computed according to equation (10) and (11), and averaged as follows:

$$\beta = \left\{\sum_{j'=1}^{3}(\alpha_{j'}\beta_{j'})^{\frac{1}{2}}\right\}^2 \Bigg/ \left\{\sum_{j'=1}^{3}\alpha_{j'}\right\}. \qquad (12)$$

Table 1 shows newly recommended values of $\alpha(T)$, $\beta(T)$ and $\omega(T)$ for the major absorption bands of several species present in fossil fuel combustion products. Figures 1 and 2 show how τ_H and β vary with T for some of the more important bands. The quantity τ_H is the optical depth at the head or center of the band in the most intense region of absorption according to the band model employed

$$\tau_{H,i,j} = \frac{\alpha_{i,j}\rho_i L}{\omega_{i,j}}\ \text{(dimensionless)}. \qquad (13)$$

In the case of the pure rotational water vapor band τ_H at $\nu = 500\ \text{cm}^{-1}$ is graphed. If this value is larger than 3, the infrared from 0 to 500 cm^{-1} is regarded as black, and the tail of the band is treated as a separate band with a lower limit at 500 wavenumbers.

For purposes of calculating band absorption and total emissivity or absorptivity, a universal band absorption curve of growth is presented

Table 1. Exponential wide band model parameters

Gas	Vibrations	Bands	Pressure parameters		Spectral location			Band absorption parameters		
	ν_k (cm^{-1})	$\delta_1, \delta_2, \ldots$	n	b (T_0 = 100°K)	ν_l (cm^{-1})	ν_c (cm^{-1})	ν_u (cm^{-1})	α_0 (cm^{-1}/gm m^{-2})	β_0	ω_0 (cm^{-1})
1. H_2O	$m = 3$	1. Rotational								
	$\nu_1 = 3652$		1	$8{\cdot}6(T_0/T)^{\frac{1}{2}} + 0{\cdot}5$	0*			5200·0*	0·14311*	28·4*
	$\nu_2 = 1595$	0,0,0								
	$\nu_3 = 3756$	2. 6·3 μ		$8{\cdot}6(T_0/T)^{\frac{1}{2}} + 0{\cdot}5$		1600		41·2	0·09427	56·4
	$g_1 = 1$	0,1,0	1							
	$g_2 = 1$	3. 2·7 μ								
	$g_3 = 1$	0,2,0						0·19		
		1,0,0	1	$8{\cdot}6(T_0/T)^{\frac{1}{2}} + 0{\cdot}5$		3760		2·30	0·13219	60·0
		0,0,1						22·40		
		4. 1·87 μ	1	$8{\cdot}6(T_0/T)^{\frac{1}{2}} + 0{\cdot}5$		5350		3·0	0·08169	43·1
		0,1,1								
		5. 1·38 μ	1	$8{\cdot}6(T_0/T)^{\frac{1}{2}} + 0{\cdot}5$		7250		2·5	0·11628	32·0
		1,0,1								
2. CO_2	$m = 3$	1. 15 μ								
	$\nu_1 = 1351$	0,1,0	0·7	1·3		667		19·0	0·06157	12·7
	$\nu_2 = 667$	2. 10·4 μ								
	$\nu_3 = 2396$	−1,0,1	0·8	1·3		960		$2{\cdot}47 \times 10^{-9}$	0·04017	13·4
	$g_1 = 1$	3. 9·4 μ								
	$g_2 = 2$	0, −2,1†	0·8	1·3		1060		$2{\cdot}48 \times 10^{-9}$†	0·11888†	10·1
	$g_3 = 1$	4. 4·3 μ								
		0,0,1	0·8	1·3			2410	110·0	0·24723	11·2
		5. 2·7 μ								
		1,0,1	0·65	1·3		3660		4·0	0·13341	23·5
		6. 2·0 μ								
		2,0,1	0·65	1·3		5200		0·066	0·39305	34·5
3. CO	$m = 1$	1. 4·7 μ								
	$\nu_1 = 2143$	1	0·8	1·1		2143		20·9	0·07506	25·5
	$g_1 = 1$	2. 2·35 μ								
		2	0·8	1·0		4260		0·14	0·16758	20·0
4. NO	$m = 1$	1. 5·34 μ								
	$\nu_1 = 1876$	1	0·65	1·0		1876		9·0	0·18050	20·0
	$g_1 = 1$									
5. SO_2	$m = 3$	1. 19·27 μ								
	$\nu_1 = 1151$	0,1,0	0·7	1·28		519		4·22	0·05291	33·08
	$\nu_2 = 519$	2. 8·68 μ								
	$\nu_3 = 1361$	1,0,0	0·7	1·28		1151		3·674	0·05952	24·83
	$g_1 = 1$	3. 7·35 μ								
	$g_2 = 1$	0,0,1	0·65	1·28		1361		29·97	0·49299	8·78
	$g_3 = 1$	4. 4·34 μ								
		2,0,0	0·6	1·28		2350		0·423	0·47513	16·45
		5. 4·0 μ								
		1,0,1	0·6	1·28		2512		0·346	0·58937	10·91
6. CH_4	$m = 4$	1. 7·66 μ								
	$\nu_1 = 2914$	0,0,0,1	0·8	1·3		1310		28·0	0·8698	21·0
	$\nu_2 = 1526$	2. 3·31 μ								
	$\nu_3 = 3020$	0,0,1,0	0·8	1·3		3020		46·0	0·06973	56·0
	$\nu_4 = 1306$	3. 2·37 μ								
	$g_1 = 1$	1,0,0,1	0·8	1·3		4220		2·9	0·35429	60·0
	$g_2 = 2$	4. 1·71 μ								
	$g_3 = 3$	1,1,0,1	0·8	1·3		5861		0·42	0·68598	45·0
	$g_4 = 3$									

* For the rotational band of H_2O, $\alpha(T) = \alpha_0$ and $\beta(T) = \beta_0(T/T_0)^{-\frac{1}{2}}$.
Otherwise α_0, ω_0 and β_0 apply to equations (6), (9) and (10) respectively.

† Because of Fermi resonance between the ν_1 and $2\nu_2$ levels, the Ψ and Φ functions for the 1060 cm^{-1} band are to be those of the 960 cm^{-1} band; i.e. use the set of δ's for the 960 cm^{-1} band to get Ψ and Φ for either band.

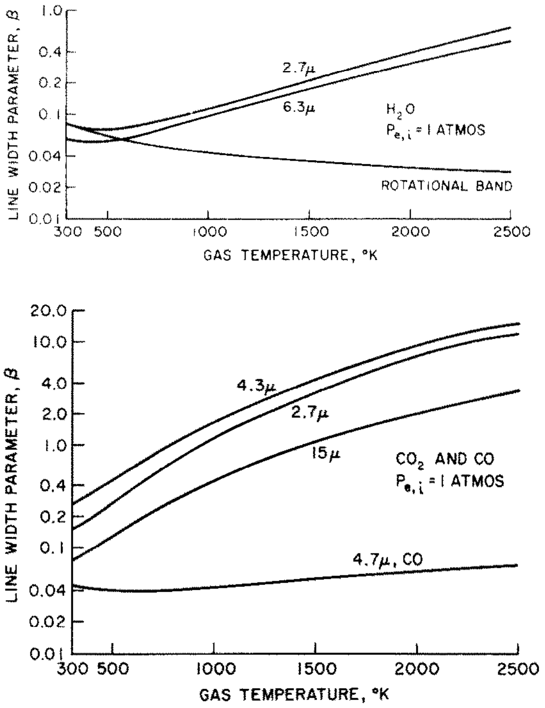

FIG. 2. Line width parameter.
(a) H_2O (b) CO_2 and CO.

in Fig. 3. The curves are $A^* = A_{i,j}/\omega_{i,j}$ vs. $\tau_{H,i,j}$ for various $\eta_{i,j} = \beta_{i,j}P_{e,i}$. They are not exact values from equation (4) but are rather those for the 4-region closed form approximations [8] to equation (4) as shown on the figure. Figure 4 may be used to identify the region in which each approximation applies. The values of α, β and ω given in Table 1 are recommended for use with the 4-region expression.

Czerney and Walther [15] present the fractional function of the first kind $f(T/\nu)$,

$$f(u) = \frac{15}{\pi^4}\int_u^{\infty} \frac{u^3\,\mathrm{d}u}{\exp(u) - 1}, \; u = \frac{hc\nu}{kT}. \qquad (14)$$

The total absorptivity of a gas at temperature T for source temperature T_s is, in the "block" approximation,

$$\alpha_i(T, T_s, \rho L, P) = \sum_j [f(\nu_{l,i,j}/T_s) - f(\nu_{u,i,j}/T_s)]. \qquad (15)$$

For the case of a nonoverlapped band one wavenumber, if prescribed, is known and the other found from

$$\nu_{u,i,j} - \nu_{l,i,j} = A_{i,j} \qquad (16a)$$

or, if $\nu_{c,i,j}$ is prescribed, both wavenumbers are found from

$$\nu_{u,i,j} = \nu_{c,i,j} + A_{i,j}/2; \; \nu_{l,i,j} = \nu_{c,i,j} - A_{i,j}/2. \qquad (16b)$$

When overlapping is discovered, that is, when one or both of $(\nu_{l,i,j}, \nu_{u,i,j})$ for one band were found to lie within the interval $\nu_{l,i',j'} < \nu < \nu_{u,i',j'}$ for another band, the minimum $\nu_{l,\min}$ is taken and the maximum $\nu_{u,\max}$, and the other values of ν_l and ν_u are discarded. Then equation (15) is employed. An example given later will illustrate this procedure.

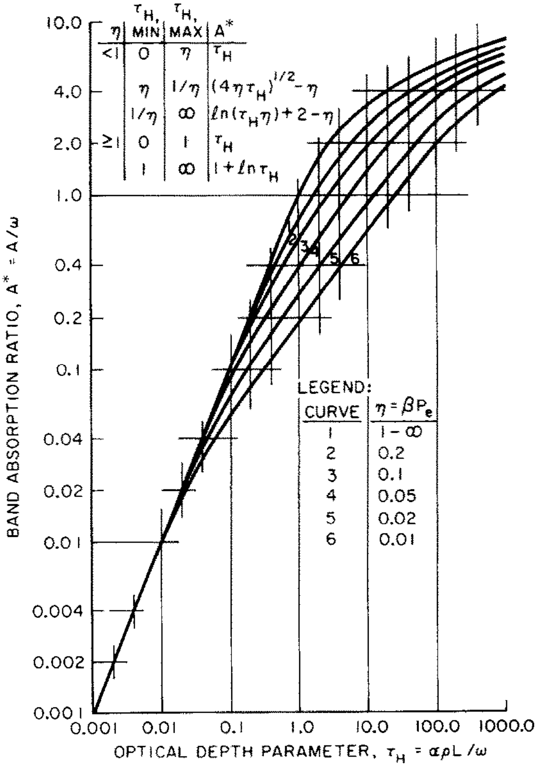

FIG. 3. Universal band absorption.

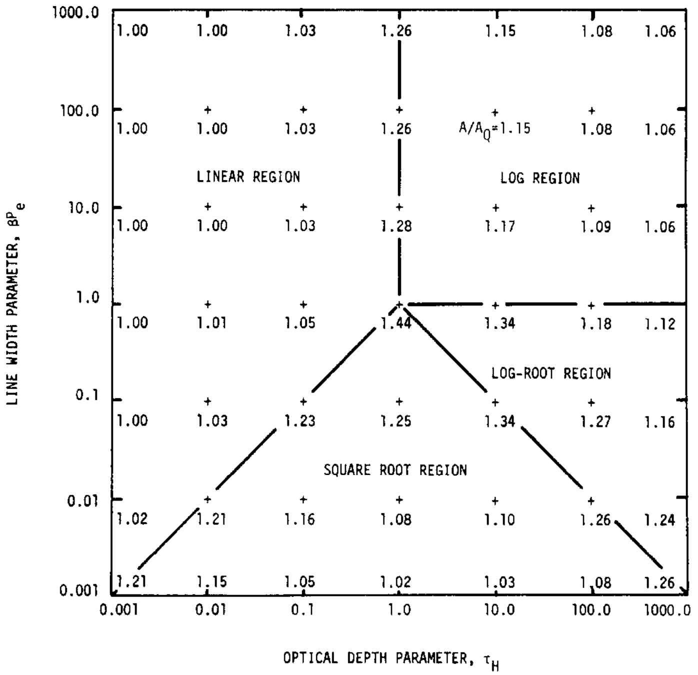

FIG. 4. Chart of the ratio of the four-region expression for band absorption to the spectrally-integrated band absorption.

Table 2. Comparisons with empirical correlations

Gas	Band	Number of data points	Investigators	Temperature range (°K)	rms discrepancy (cm^{-1}) Old corr.	rms discrepancy (cm^{-1}) New corr.	rms error (%) Old corr.	rms error (%) New corr.
H_2O	Rotational*	24	[16, 17]	300–1111	23·0	18·7	15·2	15·7
	6·3μ	48	[16, 17, 18, 19]	300–2750	23·3	23·5	18·5	18·8
	2·7μ	48	[16, 17, 18, 19]	300–2750	26·2	20·7	12·7	12·6
	1·87μ	42	[16, 17, 18, 19]	300–2250	26·5	19·3	22·5	19·9
	1·38μ	41	[16, 17, 18, 19]	300–2250	29·7	16·6	29·9	22·9
CO_2	15·0μ	95	[18, 20, 21]	300–1390	14·25	11·5	21·6	25·2
	10·4μ	51	[20]	300–1390	3·8	3·4	39·2	30·6
	9·4μ	49	[20]	300–1390	7·2	3·0	32·7	28·0
	4·3μ	94	[18, 20, 21]	300–1390	18·3	17·1	14·2	11·7
	2·7μ	84	[18, 20, 21]	300–1390	32·5	20·3	15·7	14·0
	2·0μ	52	[20]	300–1390	—	8·9	—	24·2
CO	4·7μ	82	[22, 23, 24]	300–2700	18·2	16·8	22·5	15·6
	2·35μ	14	[23]	300–1500	3·0	1·7	11·7	10·0
NO	5·3μ	178	[25, 29]	300–1200	—	12·1	—	16·7
CH_4	7·66μ	56	[18, 26, 27]	300–1000	19·0	15·0	13·5	11·5
	3·31μ	76	[18, 26, 27, 28]	300–1140	70·7	62·5	26·1	23·3
	2·37μ	50	[26, 27]	300–1140	—	28·0	—	11·8
	1·71μ	15	[26]	300– 856	—	32·8	—	22·5

* Experimental values were reported only for wavenumbers above 500 cm^{-1}. Therefore, comparisons were made using $\nu_l = 500\ cm^{-1}$ and $\alpha(T) = \alpha_0 \exp\,[-17{\cdot}6\,(T/T_0)^{-\frac{1}{2}}]$, where α_0 is given in Table 1. Both new and old correlations are empirical of the form shown in Table 1.

DISCUSSION

Comparisons with measurements for single species

Table 2 presents root mean square discrepancies between measured values of $A_{i,j}$ and results obtained from the new correlation parameters. The correlation procedure is simply to minimize the root-mean-square discrepancy of a number of data points. The RMS-discrepancy is a function of three independent variables, α_0, β_0 and ω_0. As shown in Table 2 up to 178 data points for various temperatures, pressures, and path lengths are correlated by fixing only the three parameters. For comparison, values of RMS discrepancy and error calculated using the empirical parameters are shown. A modest improvement is seen to result over the previous empirical correlations in nearly all cases.

Comparisons with measurements for mixtures

Total emissivity values are compared with experimental values reported in [4] for H_2O–CO_2 mixtures. In order to make this comparison two types of calculations were made, a band model "spectral" calculation and a "block" calculation. The former was too lengthy for hand calculation and was accordingly programmed for digital calculation. The latter was easily accomplished by hand.

The spectral calculation is simply carried out using equation (3) to find $\alpha_{\nu,\mathrm{mix}}$ and numerically summing to find the total absorptivity,

$$\alpha_{\mathrm{mix}}(T, T_s, x_i, L, P) = \int_0^1 \alpha_{\nu,\mathrm{mix}}(T, x_i, L, P)\, \mathrm{d}f(\nu/T_s) \tag{17}$$

$$\alpha_{\mathrm{mix}}(T, T_s, x_i, L, P) = \sum_{m=1}^{M_m} \alpha_{\nu_m,\mathrm{mix}}(T, x_i, L, P)\, \Delta f_m(\nu_m/T_s) \tag{18}$$

where x_i denotes the set of mole fractions describing the mixture.

A computer program TØTAL was written in FØRTRAN IV to compute the total emissivity and absorptivity. Inputs are the gas temperature, total pressure, path length, and mole fractions of gases numbered 1–6 as in Table 1. In preliminary steps, it calculates for each gas i in succession the mass length $\rho_i L$ and for each band of each gas α_{ij}, ω_{ij} and β_{ij} and $P_{e,i,j}$. The quantities $A_{i,j}$ and $A_{Q,i,j}$ are calculated, and the values of $\alpha_{i,j}$, $\omega_{i,j}$ and $\beta_{i,j}$ are corrected for the reasons explained below. In these preliminary calculations a subroutine GAS is employed which supplies the α, ω, and β values using the information contained in Table 1. The main loop in the program chooses a wavenumber and computes the transmissivity of each gas band and takes the product over all i and j. One minus this quantity is the mean spectral absorptivity which is weighted by Δf_m and summed over the spectrum from 0 to 8500 cm^{-1}, using the trapezoidal rule for simplicity.

When approximate spectral calculations are made (approximate because the model shape is an idealization of the true band shape), it is necessary to account for the fact that the values of α_0, β_0 and ω_0 given in Table 1 are meant to be used with the approximate 4-region expression for A^* given in Fig. 3. The values of α_0, β_0 and ω_0 were extracted from the data using the 4-region expressions, because it is desirable to have values which yield good results with the 4-region expressions. They are more convenient to use, whether in a hand calculation or a machine one. The 4-region expressions are analytically-derived upper limits to A_Q, the band absorption found by spectral quadrature according to equation (4). As shown in Fig. 4, A_Q is often 20 per cent lower than the 4-region value of A. If it is desired to make a spectral quadrature and obtain a value of A_Q in agreement with A and hence in agreement with the data, it is necessary to use adjusted values. The easiest procedure is to take the following values, which leave τ_H and β invariant:

$$\alpha'_0 = \alpha_0\, A/A_Q \tag{19a}$$

$$\beta'_0 = \beta_0 \tag{19b}$$

$$\omega'_0 = \omega_0\, A/A_Q. \tag{19c}$$

Note that a gas band well within the linear region of Fig. 4 requires no adjustment.

In [4] and [30] there are reported band absorption values for mixtures of gases. Total values were calculated from these. To compute total emissivity or absorptivity from the data, experimental values of band absorption for the mixture were used in the block calculation as explained above. The overlapped 2·7μ H_2O and CO_2 band was centered at 3710 cm^{-1} for the calculation. Values of absorptivity for T_s = 2200°R = 1220°K from previous computations were given in [4] and were recomputed for comparison with α_{mix} calculated according to equation (18). A temperature of 1220°K is sufficiently high for the contribution of the far infrared rotational water vapor band to be only 0·01 or less.

The comparison shown in Table 3 indicates that the hand "block" calculation gives a result which differs little from the computer spectral integration or from experiment. Table 4 shows spectrally calculated results compared with experimental values. In both Tables 3 and 4 the calculated and experimental results agree within approximately 10 per cent.

Sample block calculation of total emissivity and absorptivity of a mixture

To illustrate concretely the use of the new correlations for a combustion gas mixture, consider the following situation: A furnace gas

Table 3. Comparisons of total emissivity and absorptivity

Gas Temperature (°K)	Gas Pressure (atm)	Mole fraction of H_2O and CO_2 (remainder N_2)		Emissivity			Absorptivity 1220°K black body source		
				From [4] band absorption experimental measurement	Computed from present results		From [4] band absorption experimental measurement	Computed from present results	
		H_2O	CO_2		Spectral method	Block method		Spectral method	Block method
550	1·098	0·051	0·249	0·203	0·202	0·20	0·138	0·130	0·13
550	1·140	0·101	0·099	0·256	0·230	0·24	0·157	0·140	0·14
550	1·093	0·241	0·046	0·348	0·300	0·30	0·196	0·180	0·18
550	1·042	0·258	0·254	0·368	0·330	0·33	0·238	0·205	0·20
560	1·170	0·752	0·248	0·526	0·523	0·51	0·330	0·322	0·31
820	1·178	0·100	0·098	0·191	0·199	0·20	0·146	0·148	0·15
820	1·070	0·250	0·249	0·285	0·284	0·28	0·209	0·214	0·21

Table 4. Comparison of total band absorption for overlapped bands of a homogeneous mixture

Gas temperature (°K)	Gas pressure (atm)	Mole fraction of water vapor and CO_2 in H_2O–CO_2–N_2 mixture		Band absorption, 2·7μ	
		H_2	CO_2	Expt. [4]	Calculation equation (3)
550	1·098	0·051	0·249	241	216
550	1·140	0·101	0·099	256	224
550	1·093	0·241	0·046	241	301
550	1·042	0·258	0·254	434	350
560	1·170	0·752	0·248	618	555
820	1·178	0·100	0·098	236	231
820	1·070	0·250	0·249	324	354

at $T = 1400$°K with a mean beam length [31, 32] of $L = 3$ m and a total pressure of 1 atm radiates to a surface at $T_s = 1100$°K. The furnace gas has the following mole fractions: 0·18 H_2O, 0·06 CO_2, 0·03 CO, 0·005 CH_4, 0·002 SO_2, 0·001 NO, and the remainder N_2. It is desired to know the total emissivity $\varepsilon_T(T)$ and absorptivity $\alpha_T(T, T_s)$ of the gas mixture.

Figures 1 and 2 give $\tau_{H,i,j}$ and $\beta_{i,j}$ for the major species. The value of τ_H read from the figure is multiplied by $x_i(PL/P_0L_0)$, since the figure is for $P_0 = 1$ atm and $L_0 = 1$ m. For any case not shown in the figure, the parameters α, β and ω are obtained with the aid of Table 1, and $\tau_{H,i,j}$ is found from equation (13). The values of $\beta_{i,j}$ are multiplied by $P_{e,i}$ from equation (2) to obtain $\eta_{i,j}$.

Figure 3 yields $A_{i,j}/\omega_{i,j}$ from the known values of $\tau_{H,i,j}$ and $\eta_{i,j}$, and the band absorptions are found. The values so obtained are shown in Table 5. Also shown in the Table are the upper and lower limits for a simple block calculation using the values of $\nu_{c,i,j}$ given in Table 1 and equation (16). With these values, blocks of black bands are established as described below equation (16). Referring to Table 5, the interval $\nu = 0$ to 771 cm^{-1} is treated as black. The CO_2 band is likewise treated as black from 565 to 770 cm^{-1} and is therefore regarded as completely overlapped. The SO_2 band treated as a block from 512 to 526 cm^{-1} is similarly overlapped. The next block is found to be from 955 to 965, the next from 1055 to 1065, the next from 1145 to 1157, and the next is a major one from 1277 (CH_4, 7·7 μ) to 1919 (H_2O, 6·3 μ). The remaining blocks are similarly located as shown in Table 6.

With the values of ν bounding the blocks located, values of $hc\nu/kT$ and $hc\nu/kT_s$ are computed, and tables [15] used to determine

Table 5. Band absorptions for a gas mixture

Species i	Gas	Band j	Region	Band absorption $A_{i,j}$	Lower limit $\nu_{l,i,j}$	Upper limit $\nu_{u,i,j}$
1	H_2O	1	Rotational	771	0	771
		2	6·3μ	638	1281	1919
		3	2·7μ	590	3465	4055
		4	1·87μ	171	5265	5436
		5	1·38μ	131	7184	7315
2	CO_2	1	15μ	205	565	770
		2	10·4μ	10	955	965
		3	9·4μ	10	1055	1065
		4	4·3μ	260	2150	2410
		5	2·7μ	220	3550	3770
		6	1·9μ	8	5196	5204
3	CO	1	4·7μ	89	2098	2187
		2	2·35μ	4	4258	4262
4	CH_4	1	7·7μ	58	1277	1335
		2	3·3μ	96	2972	3068
		3	2·4μ	8	4212	4220
		4	1·7μ	2	5860	5862
5	SO_2	1	19μ	14	512	526
		2	8·7μ	12	1145	1157
		3	7·3μ	70	1326	1396
		4	4·3μ	2	2349	2351
		5	4μ	2	2511	2513
6	NO	1	5·3μ	7	1873	1880

0·18 H_2O, 0·06 CO_2, 0·03 CO, 0·005 CH_4, 0·002 SO_2 and 0·001 NO
$P = 1$ atm, $L = 3$ m, $T = 1400$°K

Table 6. Contributions of spectral blocks to total emissivity and absorptivity of a gas mixture

Block location		Emissivity (T = 1400°K)					Absorptivity (T_s = 1100°K)				
ν_l (cm^{-1})	ν_u (cm^{-1})	$\frac{kT}{hc\nu_l}$	$\frac{kT}{hc\nu_u}$	f_l	f_u	Δf	$\frac{kT_s}{hc\nu_l}$	$\frac{kT_s}{hc\nu_u}$	f_l	f_u	Δf
0	771	∞	1·2617	1·000	0·981	0·019	∞	0·9913	1·000	0·965	0·035
955	965	1·019	1·008	0·967	0·966	0·001	0·800	0·792	0·939	0·938	0·001
1055	1065	0·922	0·914	0·957	0·956	0·001	0·725	0·718	0·922	0·921	0·001
1145	1157	0·850	0·841	0·948	0·946	0·002	0·668	0·661	0·906	0·903	0·003
1277	1919	0·762	0·507	0·931	0·824	0·107	0·599	0·398	0·878	0·714	0·164
2098	2410	0·464	0·404	0·789	0·721	0·068	0·364	0·317	0·663	0·574	0·089
2511	2513	0·388	0·387	0·699	0·698	0·001	0·305	0·304	0·546	0·545	0·001
2972	3068	0·327	0·317	0·595	0·574	0·021	0·257	0·249	0·424	0·401	0·023
3465	4055	0·281	0·240	0·488	0·373	0·115	0·2206	0·1886	0·312	0·208	0·104
4212	4220	0·2310	0·2306	0·345	0·344	0·001	0·1815	0·1812	0·186	0·185	0·001
4258	4262	0·2285	0·2283	0·337	0·336	0·001	0·1795	0·1794	0·179	0·179	0·000
5196	5204	0·1873	0·1870	0·204	0·203	0·001	0·1471	0·1469	0·086	0·085	0·001
5265	5436	0·1848	0·1790	0·1963	0·1777	0·019	0·1452	0·1406	0·081	0·070	0·011
5860	5862	0·1660	0·1560	0·1380	0·1379	0·000	0·1305	0·1304	0·049	0·049	0·000
7184	7315	0·1354	0·1330	0·059	0·054	0·005	0·1064	0·1045	0·015	0·013	0·002
						ε_T = 0·362					α_T = 0·436

0·18 H_2O, 0·06 CO_2, 0·03 CO, 0·005 CH_4, 0·002 SO_2 and 0·001 NO
P = 1 atm, L = 3 m, T = 1400°K

f_l and f_u. The differences in f are summed to obtain the total emissivity and absorptivity as shown in Table 6.

In this example H_2O acting alone in the amount present would have an emissivity of 0·26, over 70 per cent of the mixture emissivity of 0·36. The H_2O and CO_2 acting together in the amounts assumed would have an emissivity of 90 per cent of the 0·36 value. In the example selected, neglect of CO, CH_4, SO_2 and NO would lead to an undercalculation of total emissivity by 10 per cent.

Treating gas absorption bands as black blocks in hand calculations is convenient for finding not just total properties but also total heat transfer rates. Because, as we have seen in the above example, most of the emission and absorption by fossil-fuel combustion gases is due to strong bands, little error is introduced in treating the gas transmissivity of a band as zero, particularly when the walls have low reflectances. Interreflections within spectral regions blocked out by the gas are attenuated. For example, under the assumption of black bands, the net transfer per unit area between the gas and a gray wall in the above example (T = 1400°K, T_s = 1100°K) is

$$q_T = \varepsilon_T(T)\,\alpha_{T,s}(T_s, T)\,\sigma T^4 - \varepsilon_{T,s}(T_s)\,\alpha_T(T, T_s)\,\sigma T_s^4 .$$

For such a wall with a 0·75 emissivity, $\alpha_{T,s}(T_s, T) = \varepsilon_{T,s}(T_s) = 0{\cdot}75$. We have found for the gas $\varepsilon_T(T) = 0{\cdot}362$ and $\alpha_T(T, T_s) = 0{\cdot}436$. Therefore, we would have $q_T = 3{\cdot}20 \times 10^4$ W/m^2. Accounting for interreflections introduces a multiplying factor of $1/(1 - \rho_s\tau)$ where τ for a single strong band is approximately ω/A [33]. In the example the gas mixture radiation properties are strongly dependent on the 6·3 μ water vapor band parameters, and for this band under the given conditions $\omega/A = 0{\cdot}33$. A better estimate of the transfer is therefore obtained by multiplying by $1/(1 - 0{\cdot}25 \times 0{\cdot}33)$ to yield $q_T = 3{\cdot}5 \times 10^4$ W/m^2.

Alternatively, a machine spectral calculation can be made as described earlier in the presentation, below equation (18). In this case the corrections indicated in equation (19) are made. The result from T0TAL is $\varepsilon_T(T) = 0{\cdot}369$ and $\alpha_T(T, T_s) = 0{\cdot}449$. These values are seen to be only 2 and 3 per cent higher, respectively, than the hand calculated values. The "block" method, while approximate, appears to give *total* values in good agreement with both more exact calculations and experiment as pointed out in [4].

Sample calculation for an inhomogeneous gas mixture

A final sample calculation shows the use of the new correlations for a nonisothermal gas mixture (nonhomogeneities in composition and pressure may be similarly accommodated). The net flux into the boundary of gas whose bounding temperatures match those of an enclosing black wall may be written as follows in terms of an effective directional emissivity [34–36].

$$q_{\text{net, in}} = (\sigma T_{\max}^4 - \sigma T_0^4)\frac{1}{\pi}\int_0^{2\pi}\int_0^{\pi/2} \varepsilon_{\text{effective}}(\theta, \phi) \cos\theta \sin\theta \, d\theta \, d\phi \qquad (20)$$

where

$$\varepsilon_{\text{effective}}(\theta, \phi) = \int_0^{\infty} \frac{\pi[I_{\text{in}}(\theta, \phi) - I_{\text{out}}]}{\sigma T_{\max}^4 - \sigma T_0^4} \, d\nu \qquad (21)$$

and

$$I_{\text{in}}(\theta, \phi) - I_{\text{out}} = B_\nu(L)\tau_\nu(L) + \int_0^L \left\{-\frac{d\tau_\nu}{dr}\right\} B_\nu(r) \, dr - B_\nu(0) \qquad (22)$$

where B_ν is the Planck black body intensity

$$B_\nu = \frac{2hc^2\nu^3}{e^{hc\nu/kT} - 1} \qquad (23)$$

and the direction θ, ϕ fixes the total path length L and the relation between the local path length r and absolute position coordinates. For example, for a parallel plate duct with separation distance δ, $L = \delta/\cos\theta$ and $y = r/\cos\theta$, where y is measured normal to the plate at which the net flux is desired.

If equation (22) is integrated by parts and substituted into equation (21) the effective directional emissivity becomes

$$\varepsilon_{\text{effective}} = \frac{\pi}{\sigma T_{\max}^4 - \sigma T_0^4}\int_0^{\infty}\int_0^L \tau_\nu(r) \times \frac{dB_\nu}{dT}\frac{dT}{dr} \, dr \, d\nu \qquad (24)$$

for an isolated band scaled values of α, β and ω can be obtained from the local values, and the double integral transformed to a single one [37–39]. However, for a gas mixture with overlapping bands, it appears that direct numerical integration is necessary.

Two alternatives present themselves [40]. One is to compute τ_ν as follows:

$$\tau_\nu = \prod_{i=1}^{M}\prod_{j=1}^{N} \tau_{\nu, i, j} \qquad (25)$$

$$\tau_{\nu, i, j} = \exp\left\{-\frac{\xi_{\nu, i, j}}{[1 + \xi_{\nu, i, j}^2/\zeta_{\nu, i, j}]^{\frac{1}{2}}}\right\} \qquad (26)$$

where

$$\xi_{\nu, i, j} = \int_0^r (S/d)_{\nu, i, j}\rho_i \, dr \qquad (27)$$

$$\zeta_{\nu, i, j} = \int_0^r \beta_{i, j} P_{e, i, j}(d\xi_{\nu, i, j}/dr) \, dr \, . \qquad (28)$$

If narrow band data is not available for the gases of concern (as is presently the case for most of the gases in Table 1), equations (5a–c) are used to obtain $(S/d)_{\nu, i, j}$, depending upon the band type.

The other alternative, which offers some computational savings at the expense of a slight loss in accuracy, is the equivalent line method:

$$\tau_\nu = \exp\left\{-\frac{\xi_\nu}{[1 + \xi_\nu^2/\zeta_\nu]^{\frac{1}{2}}}\right\} \qquad (29)$$

where

$$\xi_v = \int_0^r \left\{ \sum_{i=1}^{M} \left(\sum_{j=1}^{N} (S/d)_{v,i,j} \right) \rho_i \right\} \mathrm{d}r \tag{30}$$

$$\zeta_v = \int_0^r \left\{ \sum_{i=1}^{M} \left(\sum_{j=1}^{N} (S/d)_{v,i,j} \beta_{i,j} P_{e,i,j} \right) \rho_i \right\} \mathrm{d}r . \tag{31}$$

In either alternative the problem of correcting the 4-zone correlation parameters α, ω, β to account for the A/A_Q effect must be faced. The prescription given in equations (19a–c), while simple and adequate for isothermal gases, is not applicable to nonisothermal gases. Lacking a recorrelation of the data themselves with A_Q rather than the 4-zone A expressions, it is thought that $\omega_{i,j}$ alone can be adjusted according to equation (19c) using $(A/A_Q)_{i,j}$ from Fig. 4 based upon scaled values [39] of $\langle \tau_{H,i,j} \rangle$ and $\langle \eta_{i,j} \rangle$

$$\langle \tau_{H,i,j} \rangle = \frac{\left(\int_0^L \alpha_{i,j} \rho_i \, \mathrm{d}r \right)^2}{\int_0^L \omega_{i,j} \alpha_{i,j} \rho_i \, \mathrm{d}r} \tag{32}$$

$$\langle \eta_{i,j} \rangle = \frac{\int_0^L \eta_{i,j} \omega_{i,j} \alpha_{i,j} \rho_i \, \mathrm{d}r}{\int_0^L \omega_{i,j} \alpha_{i,j} \rho_i \, \mathrm{d}r} . \tag{33}$$

The local value of $\omega_{i,j}$ is multiplied by the single value of $(A/A_Q)_{i,j}$ according to equation (19c) and this adjusted local value is used along with the local values of $\alpha_{i,j}$ and $\beta_{i,j}$ in equations (5a–c), (27), (28), (30) and (31).

A temperature profile corresponding closely to experimental run 12–10 of [40] was selected to compare the two alternative methods. Mole fractions of H_2O, $x_1 = \frac{1}{3}$, CO_2, $x_2 = \frac{3}{10}$, and CO, $x_3 = \frac{1}{30}$, were taken. These values might result from the incomplete combustion of methane in oxygen. The temperature was assumed as follows: constant at 464°K from $r = 0$ to 27 mm, linear to 1059°K at $r = 90$ mm, constant at 1059°K to $r = 126$ mm, linearly decreasing to 753°K and 420°K at $r = 342$ mm and 459 mm respectively, and constant at 420°K until $r = 486$ mm. The results for $\varepsilon_{\text{effective}}$ for the two calculations were 0·101 and 0·100, respectively. But the former required 9·48 s of IBM 360/90 computing time, while the equivalent line method required only 7·22 s.

SUMMARY AND CONCLUSIONS

1. New rational correlations of band absorption parameters were presented and compared with existing experimental data for six species.
2. It was shown that band absorption parameters modified by A/A_Q may be used in approximate spectral calculations for either homogeneous or inhomogeneous gas mixtures. Comparisons with existing data for mixtures showed good agreement.
3. It was shown that hand calculations may be readily carried out for homogeneous gas mixtures. Such a calculation was presented for a H_2O–CO_2–CO–CH_4–SO_2–NO–N_2 gas mixture.

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RAYONNEMENT THERMIQUE DANS LES GAZ DE COMBUSTION

Résumé— On donne des expressions généralisées pour le calcul de l'émissivité, de l'absorptivité et d'autres propriétés des gaz moléculaires. De nouvelles lois relatives aux propriétés des gaz H_2O, CO_2, CO, NO, SO_2 et CH_4 sont directement applicables au problème du rayonnement des gaz de combustion. Des calculs à la main sont exécutés aisément pour un mélange arbitraire des gaz ci-dessus et on décrit une procédure simple de calcul automatique à grande vitesse. On présente et explique des tables et des graphiques qui donnent aux ingénieurs une connaissance des caractéristiques du rayonnement thermique des gaz considérés.

THERMISCHE STRAHLUNG VON VERBRENNUNGSGASEN

Zusammenfassung Es werden allgemeine Gleichungen zur Berechnung des Emissions— und des Absorptionsvermögens und anderer wichtiger Strahlungseigenschaften von molekularen Gasen angegeben. Gezeigt wird, dass neue rationale Beziehungen für die Eigenschaften von H_2O, CO_2, CO, NO, SO_2 und CH_4 sich ohne weiteres auf Probleme der Strahlung von Verbrennungsgasen anwenden lassen. Einfache Berechnungen können leicht für beliebige Mischungen der obigen Gase gemacht werden. Ein einfaches Computerprogramm für schnelle Rechnungen wird beschrieben. Tabellarische und graphische Hilfsmittel werden angegeben und erklärt. Sie geben dem Ingenieur Einblick in die Charakteristiken der Wärmeübertragung durch Strahlung für die betrachteten Gase.

ТЕПЛОВОЕ ИЗЛУЧЕНИЕ ТОПОЧНЫХ ГАЗОВ

Аннотация—Приводятся обобщенные выражения для расчета излучательной и поглащательной способности, а также некоторых других радиационных свойств молекулярных газов. Показано, что новые рациональные соотношения для свойств H_2O, CO_2, CO, NO, SO_2 и CH_4 могут быть использованы при решении задач излучения для топочных газов. Расчеты могут быть легко выполнены для любой произвольной смеси указанных газов. Кроме того, описывается простая программа для быстрого расчета на вычислительной машине. Приведенные таблицы и графики дают физико-инженерное представление о характеристиках лучистого переноса тепла в этих газах.