GAS ABSORPTIVITY IN A COMPLETE SPECTRUM

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Necessary conditions are established for the validity of the Hottel formulas for the absorptivity relative to black radiation. The formulas are used in describing the absorption of a badly mixed medium and for nonblack incident radiation.

A formula for the absorptivity of an isothermal gas (CO_2 and H_2O) for black radiation,

$$a_0 = (T/T_0)^m \varepsilon\,[T_0,\ x(T/T_0)^u], \qquad (1)$$

is used extensively in practical computations of radiant heat exchange. Hottel proposed the formula as empirical [1]. On the basis of the simplest models of a spectrum it has been derived in [2], where it is shown that the formula can be suitable for all gases with a vibrational–rotational absorption spectrum. The necessary conditions for the validity of (1) are considered herein, the indices m, u are discussed, various problems are indicated in whose solutions (1) can be used. Our main attention is spent on the combustion products of CO_2 and H_2O.

The Hottel indices for carbon dioxide $m = 0.65$, $u = -1$ have been verified experimentally in [3]. The formula has a ±5% error for sufficiently large thicknesses in the T and T_0 temperature range equal to 555–1390°K. Analogous deductions have been made in [4] on the basis of experiments conducted for $x = 0.1$–0.4 mat, $T < 1500$ and $T_0 < 1290$°K.

For water vapor the indices $m = 0.45$, $u = -1$ have been established with a greater error. The dependence $m(T_0)$ has been noted in [5], where $m = 0.51$ for $T_0 = 645$°K, $m = 0.45$ for $T_0 = 980$°K, and $m = 0.39$ for $T_0 = 1390$°K. The value 0.45 is the mean. Some growth in m has been noted as x increases. However, the function u(x) has the strongest growth according to the theory. It has been shown in [2] that as $x \to 0$ there should be $m + u \to -1$; hence the Hottel indices are not suitable for $x < 0.1$ mat.

Necessary Conditions for the Validity of (1)

The spectroscopic formula for the absorption of black radiation is

$$a_0 = \frac{\pi}{\sigma T_0^4} \sum_j I_{0j}(T_0)\, A_j(T,\ x), \qquad (2)$$

where

$$A_j = \int_{\Delta\omega_j} [1 - \exp(-\alpha_\omega \langle T \rangle x)]\, d\omega. \qquad (3)$$

The equality $a_0 = \varepsilon(T_0, x)$ is used in going from (2) to (1). The integrated absorption must be represented as

$$A_j = \Delta\omega_j \bar{A}_j = \Delta\omega_j (1 - D_j).$$

The passage from (2) to (1) is possible if there exist:

1) An equivalent ray path identical over the spectrum

$$x' = x\,(T/T_0)^u (P_{\mathrm{eff}}/P_{\mathrm{eff}0})^n. \qquad (4)$$

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TABLE 1. The Function $\Phi(T)$ According to Exact and Approximate Formulas

T, °K	Φ	$(T/1000)^{0,68}$
1000	1,118	1
1500	1,315	1,317
2000	1,572	1,602
2500	1,870	1,865
3000	2,198	2,111

Hence

$$\bar{A}_j(T,\ x) = \bar{A}_j(T_0,\ x').$$

2) An identical dependence of the parameter $\Delta\omega_j$ in the form

$$\Delta\omega_j/\Delta\omega_{0j} = (T/T_0)^m. \tag{5}$$

To answer the question as to how these conditions are satisfied, the models of the bands can be separated into two classes.

Models for the First Class. Take account of the rotational structure of the band. Three parameters S/d, b/d, and $\Delta\omega_j$ are used in the formulas. It is essential that the parameter $\Delta\omega_j$ be the effective width $\Delta\omega_{\mathrm{eff}j}$ dependent not only on the pressure but also on the optical thickness [6]. Compliance with the condition (5) denotes the representation

$$\Delta\omega_{\mathrm{eff}\,j} = (T/T_0)^m\,\Delta\omega_{0\,\mathrm{eff}\,j}(x,\ p,\ P).$$

The dependence $\Delta\omega_{\mathrm{eff}}$ (p, P, x) is ordinarily neglected. But for large thicknesses and pressure possibly exceeding those that hold in combustion chambers, the concept of $\Delta\omega_{\mathrm{eff}j}$ becomes meaningless, and (1) is without foundation. Let us present the most widespread formulas for the transmissivity in the band for lines with a dispersion outline. According to a random model [7, 8] with an exponential and uniform line intensity distribution

$$D_j = \exp\left(-\frac{Sx/d}{\sqrt{1+\dfrac{Sx/d}{\pi b/d}}}\right); \tag{6a}$$

$$D_j = \exp\left[-\frac{2\pi b}{d}\,L\left(\frac{Sx/d}{2\pi b/d}\right)\right]. \tag{6b}$$

According to the regular Elsasser model

$$D_j = E\left(\frac{b}{d},\ \frac{Sx/d}{2\pi b/d}\right). \tag{7}$$

It is shown in [9] that for $b/d \le 0.1$ a good approximation is given by the formula

$$E \approx 1 - \operatorname{erf}\left[\pi^{3/2}\,\frac{b}{d}\,L\left(\frac{Sx/d}{2\pi b/d}\right)\right].$$

It is impossible to assume the ratio b/d constant, hence condition (4) is not satisfiable in all the models. It holds only in the extreme strong and weak lines approximations. In the weak lines case, $D_j \approx 1 - Sx/d$ in all the models. In the strong lines case, according to (6b)

$$D_j \approx \exp\left(-\sqrt{4bSx/d^2}\right).$$

According to (6a), the 4 under the radical is replaced by π. Formula (7) yields the same value for $Sx/2\pi b > 1.25$ and $2\pi b/d < 0.3$ with <10% error. The additional condition is that the dependences of the parameters S/d and b/d would be power-law and identical over the whole spectrum. The weak and strong lines approximations hence yield different indices u and n, which directly indicates their dependence on the gas thickness.

The relationships

$$S/d = S_j/\Delta\omega_j;\quad \Delta\omega_j/\Delta\omega_{0j} = \sqrt{T/T_0};\quad d/d_0 = (T_0/T)^{\eta};$$
$$\frac{b}{b_0} = \frac{P+p}{P_0+p_0}\sqrt{\frac{T_0}{T}}; \tag{8}$$
$$S_j/S_{0j} = T_0/T;$$

are used in [2, 1]. Since the dependence $\Delta\omega_{\mathrm{eff}}(p,\ P)$ has been discarded, the dependence $a_0(p,\ P)$ appears only in terms of the function b(p, P). For H_2O we take $\eta = 1$ and $u = -1$, $n = 1$, $m = 0.5$ are obtained. The strong line approximation is applicable for $x > 0.2$ mat. For $x < 0.1$ mat the indices $u = -2$, $m = 1$ are derived in [2], which agree better with experiment.

Models of the Second Class. At elevated pressures when the lines overlap sufficiently, the band contour can be described by a simple envelope. In any case the band can be reconstructed so that the function

TABLE 2. To Compute the Emissivity at T = 1873°K, x = 0.2 mat by Using (1)

i	T_i, °K	c_i	$(T_i/T)^4$	$\varepsilon(T_i, x')$	$(T/T_i)^{0,65}$	a_{0i}	$\left(\frac{T_i}{T}\right)^4 c_i a_{0i}^*$
1	973	1,3835	0,0728	0,115	1,5306	0,1760	0,0177
2	1273	—3,3868	0,2133	0,114	1,2845	0,1464	—0,1058
3	1573	3,0944	0,4974	0,102	1,1196	0,1442	0,1758

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* $\sum_i \left(\frac{T_i}{T}\right)^4 c_i a_{0i} = 0,0877$

$\alpha_\omega(\omega)$ would be smooth

$$\alpha_\omega = \alpha_0 f(y);\ y = |\omega - \omega_0|/\Delta\omega_j.$$

Under the normalization $\int_0^\infty f(y)dy = 1$ we obtain $S_j = \Delta\omega_j \alpha_0$. Exponential [10-12] and other contours [1] are used. The rotational structure drops out, hence taking account of the pressure is quite difficult. This is not essential for boiler and furnace engineering. The number of parameters in the integral (3) is reduced by one,

$$A_j = \Delta\omega_j A_j^0 (\alpha_0 x), \text{ where } \alpha_0 = S_j/\Delta\omega_j.$$

The width parameter is here independent of the gas thickness. Then the quantity A_j^0 increases without limit as $x \to \infty$ in contrast to A_j^-, if the contour has wings. Namely the wings of the band are distorted strongly hence the values of A_j^0 become meaningless as x grows. Thus, even in this class of models (1) is without foundation as $x \to \infty$. Condition (4) is satisfied if the parameter S_j, which has ordinarily been studied adequately, can be represented as

$$S_j/S_{0j} = (T/T_0)^{\varkappa - 1}. \tag{9}$$

We obtain $\alpha_0 \sim T^{\varkappa - m - 1}$, and therefore, $u = \varkappa - m - 1$. The dependence (9) is more exact than (8). The conditions for the existence of (1) are determined by the following questions: a) can the functions $S_j(T)$ and $\Delta\omega_j(T)$ be described by power-law dependences; and b) is use of indices $\varkappa$ and m averaged over the bands admissible?

Let us examine the index m. The temperature dependence of the parameter $\Delta\omega_j$ is assumed to be the same as for $\Delta\omega_{\mathrm{eff}j}$. The value m = 0.5 has been established in [2] for diatomic molecules. It has been remarked in [1] that it cannot be exact for triatomic molecules. The dependence $\Delta\omega_j \sim (1 + T/T_0)^{1/2}$ has been taken in [13] for the 4.3 and 2.7 μ bands of CO_2, but the dependence is omitted for the 2 μ band. As a rule, m = 0.5 is taken for all the bands in the literature. In our computations of the emissivity of H_2O the absorption in the bands has been described by the formula $A_j = \Delta\omega_j \ln(1 + \alpha_0 x)$. Attempts to change the index m to any side of the value 0.5 have resulted in an increase in the error. Let us turn to the index $\varkappa - 1$. Its part, equal to −1, takes account of isobaric expansion of the gas. The index $\varkappa$ determines the change in the quantity S_j referred to the constant number of the molecule $S_j \sim \Phi(T)/T$, $\Phi(T) \sim T^{\varkappa}$. It is assumed $\Phi = 1$ for the fundamental bands, and therefore, $\varkappa = 0$. As an exception, let us note [14], where it is assumed $\Phi = 1 + 2 \cdot 10^{-4}\ T$ for the 6.3 μ band of H_2O. This function is comparatively weak. For a typical nonfundamental 1.38 μ band of H_2O the formula

$$\Phi(T) = \frac{1 - \exp(-7408\,\gamma/T)}{[1 - \exp(-3652\,\gamma/T)]\,[1 - \exp(-1595\gamma/T)]}$$

is deduced in [15]. We approximated it in the 0-3000°K range by

$$\Phi = 1 + 0.00326(T/1000) + 0.13786(T/1000)^2$$

with a maximum error of 2.4% at 3000°K. If some value of the temperature T_* is selected, then for $T > T_*$ the function $\Phi = (T/T_*)^{\varkappa}$ can yield a better approximation. It is shown in Table 1 that the function (10) can be represented as $\Phi = (T/1000)^{0.68}$. In contrast to m, the index $\varkappa$ differs essentially for the bands, hence, it is more difficult to find its mean. For sufficiently small thicknesses $\varkappa \approx 0$ can be assumed. The flux on the boundary of a volume is determined by the integrated intensities S_j which are ordinarily greatest for the fundamental bands. The 6.3 and 2.7 μ water vapor bands yield around a 90% flux. For large thicknesses, on the other hand, the contribution to the radiation of the volume is determined by the width of the band. For

$x = 0.5$ the same two bands yield only around a 50% flux according to the data in [15]. The second half of the flux belongs to the bands for which $\varkappa > 0$. As is seen, the mean index $\varkappa$ should grow with the thickness. In a first approximation, $0 < \varkappa < m$ can be taken with a very rapid change in $\varkappa$ in the region of 0.1 mat. If $\varkappa = m$ is taken for $x \geq 0.2$ mat and also the Hottel values for m, then we obtain the known empirical formulas.

Absorption of a Badly Mixed Medium

The parameters S/d and b/d are functions of a point in a medium with inhomogeneous fields of the quantities T, p, P. This difficulty is bypassed by using the Curtis–Hodson approximation ([7, 8], etc.) in which the parameters are averaged with respect to the thickness

$$(S/d)_* = \frac{1}{x}\int_0^x (S/d)\,dx, \quad (Sb/d^2)_* = \frac{1}{x}\int_0^x (Sb/d^2)\,dx.$$

As before, the mean absorption in the band is determined by means of (6), (7). The mean temperature is selected so that the function $D_j(T, x)$ would be nominal under isothermal conditions. Averaging the band width is of considerable difficulty. Energy transfer on the band wings plays an exceptional part in the absorption of the intrinsic gas radiation. In this case broadening of the bands should be taken into account exactly. The role of the wings in the absorption of black flux is considerably smaller. The experiments conducted by Nevskii and his colleagues [4] are demonstrative. They found that (1) is completely applicable to a nonisothermal layer if the calculations are carried out according to a weighted-mean temperature. An attempt has been made to explain this theoretically. The temperature field was most distinct, hence it is sufficient to take a linear temperature change. The direction of the gradient has no value. In this case

$$(S/d)_* = \frac{1}{\Delta T}\int_{T_1}^{T_2} (S/d)\,dT, \quad (Sb/d^2)_* = \frac{1}{\Delta T}\int_{T_1}^{T_2} (Sb/d^2)\,dT.$$

By analogy let us take the average of the effective width

$$\Delta\omega_* = \frac{1}{\Delta T}\int_{T_1}^{T_2} \Delta\omega_j\,dT.$$

Let the common symbol R denote the parameters S/d, Sb/d^2, and $\Delta\omega_j$. Let us compare the parameter R_* with R_c calculated at the weighted-mean temperature

$$T_c = \frac{1}{x}\int_0^x T\,dx = (T_1 + T_2)/2.$$

Let us introduce the notation $z = (T_2 - T_1)/2T_c$. Analysis has shown that $R_* = R_c$ can be taken if the representations are admissible for:

$$R \sim T^{-3/2}, \ (1-z)^{-1/2} - (1+z)^{-1/2} \approx z,$$

$$R \sim T^{-1}, \ \ln\frac{1+z}{1-z} \approx 2z,$$

$$R \sim T^{-1/2}, \ \sqrt{1+z} - \sqrt{1-z} \approx z;$$

$$R \sim \sqrt{T}, (1+z)^{3/2} - (1-z)^{3/2} \approx 3z.$$

Assuming $T_c = 1000$°K, $T_2 - T_1 = 600$°K we obtain $z = 0.3$ and the errors correspond to the listed equalities in the following percentages: 6, 3.5, 1.2, and 0.4. They are within the limits of experimental error. In the strong line approximation, which is suitable for the experimental conditions, the parameter S/d does not figure separately. In this case, the greatest error 6% should be discarded. The foundation presented for (1) is of great value for practical computations.

Expansion of the Sphere of Application of (1)

The use of (1) to determine the emissivity of a dusty medium and its transmissivity relative to a black flux has been proposed in [16]. The function $\alpha_\omega(\omega)$ in the dust absorption spectrum should hence be sufficiently smooth, as ordinarily corresponds to practice. Here (1) is used in computations of the gas absorptivity for a nonblack flux. The initial expression is

$$a = \frac{1}{I} \sum_j I_j A_j (T, x).$$

The intensity of the incident flux at the center of the band (I_j) should be expressed by a smooth function of the wave number only within the band. In conformity with [16], let us represent I_j as the superposition of Planck function

$$I_j = \sum_i c_i I_{0ij} (T_i), \quad i, \ j = 1, \ 2, \ \ldots, \ k.$$

The subscript i refers to the temperature, and k the number of the strongest bands of the gas spectrum. A system of equations is obtained in the numbers c_i with matrices of the coefficients I_{0ij}. The temperatures T_i are selected so that the matrix would be nonsingular. The solution is

$$a = \frac{1}{\pi I} \sum_i \sigma T_i^4 c_i \ \frac{\pi}{\sigma T_j^4} \sum_j I_{0ij} (T_i) A_j \ (T,x) = \frac{1}{\pi I} \sum_i \sigma T_i^4 c_i a_{0i}.$$

If a black surface radiates at a temperature T the same as for the gas, then $a = \varepsilon$, $\pi I = \sigma T^4$,

$$\varepsilon = \sum_i (T_i/T)^4 c_i \, a_{0i} \, (T, \ T_i, \ x).$$

This formula permits verification of the computation scheme since the result is easily checked by means of emissivity nomograms. A computation has been carried out for carbon dioxide with x = 0.2 mat, T = 1873°K taking account of the three spectrum bands at 2.7, 4.3, and 15 μ. The quantities a_{0i} have been calculated by means of (1) for the Hottel indices. The emissivities have been determined by means of the nomogram in [17]. The numbers c_i have been found by means of the system of equations

$$\left[\exp \left(\frac{\gamma \cdot 10^4}{\lambda_j \ T_j} \right) - 1 \right]^{-1} = \sum_i c_i \left[\exp \left(\frac{\gamma \cdot 10^4}{\lambda_j \ T_i} \right) - 1 \right]^{-1}$$

$$(i = 1, \ 2, \ 3; \ \lambda_j \ \text{in} \ \mu).$$

The initial and computed values are represented in Table 2, wherein $\varepsilon = 0.0877$ has been used in place of 0.085 in the nomogram.

For not too large thicknesses in the carbon dioxide case, only one fundamental band 4.67 μ can be taken into account:

$$c = I_j / I_{0j} (T),$$

$$a = \frac{\sigma T^4}{\pi I} \cdot \frac{I_j}{I_{0j}(T)} \, \varepsilon \, (T, \ x),$$

$$a_0 = \left(\frac{T}{T_0} \right)^4 \frac{I_{0j} (T_0)}{I_{0j} (T)} \, \varepsilon \, (T, \ x) = (T/T_0)^{0,5} \, \varepsilon \, [T_0, \ x \, (T/T_0)^{-1,5}].$$

The errors of the nomogram and especially (1) restrict the possibilities of the methods shown in [16] and herein drastically.

NOTATION

x	is the ray path in mat;
p, P	are the partial and total pressure;
P_{eff}	is the effective broadening pressure;
T, T_0	are the gas and wall temperatures, °K;
T_*, T_i	are the selected temperature values;
T_c	is the weighted-mean temperature;
a_0	is the absorptivity of the gas for black radiation;
a	is the same for a flux with nonblack spectrum;
ε	is the emissivity;
m, u, n, $\varkappa$, η	are the power exponents;
I_{0j}	is the Planck function for the center of the band, cm • W/m² • sr;
I_j	is the incident flux intensity at the center of the band j, cm • W/m² • sr;

I	is the integrated incident flux intensity, $W/m^2 \cdot sr$;
A_j	is the integral absorption (equivalent width) of band f, cm^{-1};
$\overline{A}_j$	is the mean absorption in the band;
$A_j^0 = A_j/\Delta\omega_j$;	
ω	is the wave number, cm^{-1};
ω_0	is the position of the band center;
$\Delta\omega_j$	is the width parameter;
$\Delta\omega_{effj}$	is the effective width;
$\Delta\omega^{!}_{j}$	is the total width of the band j, cm^{-1};
D_j	is the mean transmissivity in the band j;
S	is the integrated line intensity, cm^{-1}/mat;
d, b	are the spacing between lines and their half-width, cm^{-1};
S_j	is the integrated intensity of the band j;
L	is the Landenburg and Reiche functions;
α_ω	is the spectral absorption coefficient, mat^{-1};
$\alpha_0 \geq (\alpha_\omega)max$;	
$\Phi(T)$	is the dimensionless function;
c_i	is the dimensionless number;
$\gamma = 1.4388$;	
R_*, R_c	are the general notation for parameters averaged over the band and for T_c;
$z = \Delta T/2T_c$;	
E	is the Elsasser function.

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