EXTRAPOLATION OF THE EMISSIVITY OF GASES

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A new simple equation for the emissivity of gases is derived. This is used in order to extrapolate the emissivity of water vapor to high temperatures, great optical thicknesses, and an effective pressure differing from unity.

The nomograms used for engineers' calculations of the emissivity of gases suffer from a number of disadvantages: a) certain extrapolated regions require verification, while no data are available for great optical thicknesses; assumptions made in this respect are quite unsatisfactory, published data relating to the emissivity of an infinitely thick layer are artificial, and their role in the calculations is purely formal [1]; b) the emissivity values are given for unit effective pressure; c) when computers are used, a table has to be fed into the memory of the machine, and efficient interpolation and extrapolation equations are therefore vital.

It is quite impossible to penetrate into the region of high temperatures and great optical thicknesses on any sound basis at the present time. For this purpose a large number of bands having low intensities at ordinary temperatures and optical thicknesses would have to be taken into account, and spectroscopic data for these are sparse or entirely absent. The overlapping of the bands becomes extremely important; the possibility of accounting for this depends on the accuracy of the spectral characteristics. The range of applicability of the best analytical equations in [2, 3] simply corresponds to the range of the nomograms. Graphical extrapolation of the experimental data over the whole spectrum is unreliable.

In this paper we propose a simple method of extrapolating the experimental data to temperatures, optical thicknesses, and pressures beyond the limits of existing nomograms. We shall establish an intermediate procedure for solving the problem, in which the equation fairly completely reflects the physical characteristics of the phenomenon without making detailed use of spectroscopic data. For the case of water vapor we shall show that the simple equation reproduces many of the details of the very best solutions.

In the problem under consideration we first have to specify a table of emissivity values ε_0 which we shall call exact. Let the unknown extrapolation equation have reasonably accurate derivatives in the region of a specified exact value of the function. We desire that the relative increments in emissivity given by the table and the equation should be equal to one another,

$$\Delta\varepsilon_0/\varepsilon_0 = \Delta\varepsilon/\varepsilon.$$

Let us rewrite the equation in the form

$$\varepsilon_0(x,\ P_*,\ T) = c\varepsilon_0(x_1,\ P_{*1},\ T_1),\quad c = \varepsilon(x,\ P_*,\ T)/\varepsilon(x_1,\ P_{*1},\ T_1).$$

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Here c is the unknown correction for the change in arguments; the arguments of the reference value are indicated by an index. Usually reference values are absent, or their introduction complicates the calculation. The approximate equation is then used directly.

According to new experimental data, the spectral absorption of water vapor differs from zero for all wave numbers [4]. The structure of the spectrum in the gaps between the bands (windows) is regarded as being of the bright-line type. However, there is no doubt that a continuous background does occur in the spectra of gases. This arises mainly as a result of the long-range wings of strong lines having their centers lying inside the bands. We shall consider that background exists inside the bands as well. According to the results of [4], the spectral background coefficient may be described by the equations

$$\lg k_{*\omega} = A - B(\omega - 1000)/9000, \quad A = \theta - 2,$$

$$B = 2.5 - 1.7\theta + 0.5\theta^2.$$

Here $k_{*\omega}$ in $(\mathrm{m \cdot bar})^{-1}$, $\theta = T/1000$.

In the simplified approach we have to average the absorption coefficient over the spectrum; the estimate then changes:

$$k = 6 \cdot 10^{-3}\theta^2 P_* \ (\mathrm{m \cdot bar})^{-1}.$$

The direct proportionality of the absorption coefficient to the pressure on the wings of the lines agrees with all existing theories of line broadening. The equation for the emissivity changes form

$$\varepsilon = 1 - (1 - \varepsilon_1)\exp(-kx). \tag{1}$$

The equation does not change form in the presence of a gray dispersed phase, provided that the coefficient k is correspondingly increased.

For low values of T and θ the influence of the spectral background only becomes important at the very top of the nomogram in cases of great thicknesses.

Let us consider one further effect not taken into account in previous calculations. This lies in the dimerization of the water molecules. Although the dimer concentration is usually low, the dimers may increase the integrated band intensities very considerably [5]. We find, in fact, that the intensity depends on the pressure. We attempted to estimate this dependence (averaged over the spectrum) on the basis of some rather incomplete data

$$S = S_1 M, \quad M = 1 + 20Kp, \quad \lg K = -5.65 + 1250/T.$$

At high temperatures the factor M differs very little from unity even at high partial pressures. For example, when T = 1000°K and p = 10 bar, M = 1.008. In a number of practically important cases the dimerization of the molecules may change the result considerably, and in such cases the factor M must be refined. In the present investigation we omit M.

The equation for the emissivity in the case of the vibrational—rotational spectrum (without any background) takes the form

$$\varepsilon_1 = \frac{\pi}{\sigma T^4} \sum_j I_{0j} A_j, \quad A_j = \gamma_j \bar{A}_j. \tag{2}$$

Since the background is taken into account separately, the bands do not overlap.

We shall consider that the envelope of each band corresponds to the model of a harmonic oscillator and a rigid rotator. In order to allow for the rotational structure we use the narrow-band Goody model. The absorbing power averaged over the band equals

$$\overline{A} = 2\int_0^\infty \left[1 - \exp\left(-\frac{sx/d}{\sqrt{1 + (s/d)\,x/(4b/d)}}\right)\right] dy, \tag{3}$$

$$s/d = (S/\gamma) f,\ f = y \exp(-y^2),\ y = |\omega - \omega_0|/\gamma.$$

By introducing the variable v = 1/(1 + y) the integral is transformed to a more convenient interval [0, 1]:

$$\overline{A} = 2\int_0^1 [1 - \exp(-u/\sqrt{1 + u/(4b/d)})]\, dv/v^2,$$

$$u = u_0(1/v - 1)\exp(-(1/v - 1)^2),\ u_0 = Sx/\gamma.$$

Calculations were carried out by A. V. Vinogradov, using a standard program with an error of 0.1%. For our present purposes Eq. (3) is too complicated, and the next step therefore lies in obtaining an approximation.

Absorption in a line with a Doppler contour was represented in [6] as absorption in a line with a rectangular contour

$$\overline{A} = 2b_{\text{eff}}[1 - \exp(-u_0/2b_{\text{eff}})],\ u_0 = sx/b.$$

The effective width of the rectangle increases with increasing optical thickness of the gas

$$b_{\text{eff}} = \sqrt{\ln[\exp(\pi/4) + u_0/\sqrt{\pi}]}.$$

In an analogous manner we replaced the envelope of our present band by a rectangular envelope. The absorption is then described by the equations:

$$\overline{A} = 2\gamma_{\text{eff}}[1 - \exp(-u_0/2\gamma_{\text{eff}})],\ u_0 = Sx/\gamma, \tag{4}$$

$$\gamma_{\text{eff}} = 1.11\sqrt{\ln(4.9 + 1.1u_0)}.$$

We note that the envelope based on the model of a harmonic oscillator differs considerably from the Doppler version. Nevertheless only the coefficients were altered in the equation for the width parameter γ_{eff}. Subsequently the coefficient 1.11 will be considerably altered, since the real envelopes of the bands, in turn, do not correspond to the harmonic-oscillator model. This model simply plays the role of a starting point.

We allow for the rotational structure in the band with the rectangular contour phenomenologically:

$$\overline{A}_0 = 2\gamma_{\text{eff}}[1 - \exp(-z/(2\gamma_{\text{eff}}))],$$

$$z = u_0/\sqrt{1 + u_0/(4b/d)_*},\ (b/d)_* = (b/d)\,14.7/(2\gamma_{\text{eff}}). \tag{5}$$

The latter relationship arises from the fact that the rectangle broadens while the constant number of lines remains constant. The distance between the lines increases correspondingly. The coefficient 14.7 is obtained by a fitting process. The error of the approximate equations (4) and (5) may be derived from Table 1.

The next assumption lies in regarding the integrated absorption of bands as being equal. The value of A_j in Eq. (2) is taken outside the sum

$$\varepsilon_1 = A_j \pi I,\quad A_j = \overline{A}_0\gamma,\quad I = \sum_j I_{0j}/\sigma T^4. \tag{6}$$

TABLE 1. Absorbing Power in a Spectral Band with an Envelope Based on the Model of a Harmonic Oscillator, According to the Exact and Approximate Equations (3) and (5), Respectively (columns $\bar{A}$ and $\bar{A}_0$)

$4b/d$	0,005		0,1		∞	
u_0	$\bar{A}$	$\bar{A}_0$	$\bar{A}$	$\bar{A}_0$	$\bar{A}$	$\bar{A}_0$
0,5	0,0966	0,108	0,306	0,33	0,463	0,46
10	0,4334	0,419	1,552	1,52	3,411	3,45
100	1,234	1,09	3,393	3,29	4,880	4,83
1000	2,871	2,66	4,958	5,48	5,832	5,88
10000	4,636	5,32	5,940	6,76	6,616	6,77

TABLE 2. Emissivities of Water Vapor Calculated from Eqs. (1) and (12) (allowing for the gray background of the spectrum)

x, m · bar	T, °K			
	1000	2000	3000	4000
0,01	0,0391	0,0118	0,0053	0,00470
0,1	0,144	0,0873	0,042	0,0249
0,5	0,284	0,230	0,126	0,0800
1	0,374	0,320	0,190	0,135
2	0,489	0,433	0,281	0,230
10	0,856	0,797	0,644	0,668
15	0,963	0,898	0,759	0,801

The final result confirms that the consequences of this rough assumption are not too serious. In the limit of small thicknesses $\varepsilon_1 \to \alpha x$, $\bar{A}_0\gamma \to Sx$, and hence $\pi I = \alpha/S$.

For an accurate calculation

$$\alpha = \frac{\pi}{\sigma T^4}\sum_j I_{0j}S_j,\quad \alpha_c = \frac{\pi}{\sigma T^4}\sum_j I_{0j}S_{j*}. \tag{7}$$

The total intensity of the j-th band S_{j*} diminishes by an amount $\int k_\omega d\omega$ when independent allowance is made for the background, and where the integral is taken inside the band j. We thus obtain the intensity S_j. In the complete spectrum

$$\alpha = \alpha_c - k. \tag{8}$$

Equation (1) now remains valid for any background; at its upper limit $k \to \alpha_c$, $\alpha = \varepsilon_1 = 0$, $\varepsilon = 1 - \exp(-kx)$. The correction to the quantity S is omitted from Eq. (7), since S is determined by a fitting process.

The radiation coefficients may be taken from [7, 8] and other papers. We made use of the graphical data in [8] derived from the (subsequently accepted) comparison standard. It is more convenient to express these data in analytical form

$$\lg \alpha_c = 1.7376 - 1.1374\theta + 0.158\theta^2. \tag{9}$$

Equation (6) is transformed by substituting the quantities $\bar{A}_0$ and πI from (5) and (7). The band parameters S, γ, and (b/d) in this equation are averaged over the bands. According to [9], $S \propto T^{\chi-1}$, $\gamma \propto T^m$, and for water vapor m = 0.45. We estimate the coefficient χ from the equation

$$\chi = m\,\mathrm{th}\,[\exp(10x) - 1]. \tag{10}$$

We obtain $S/\gamma = g\theta^u$, $u = \chi - m - 1$, where g is a fitting parameter. Then in accordance with [10] we have $b = b_0 P_* \sqrt{273/T}$, $b_0 = 0.0567\ \text{cm}^{-1}$, $P_* = P + 5p\sqrt{273/T}$.

The mean distance between the lines is obtained as a result of correlation:

$$d = \exp(3.0876 - 3.8744\theta + 0.9368\theta^2), \tag{11}$$

up to 2000°K it differs little from that obtained in [10]. For $T > 2100$°K the values of d based on Eq. (11) increase, which contradicts the general opinion, but is nevertheless capable of explanation.

Finally,

$$\varepsilon_1 = \frac{\alpha\gamma_{\text{eff}}}{g\theta^u}\left[1 - \exp\left(-\frac{gx\theta^u}{\gamma_{\text{eff}}\sqrt{1 + z_*\gamma_{\text{eff}} g\theta^u x d\sqrt{273/T}/P_*}}\right)\right], \tag{12}$$

$$\gamma_{\text{eff}} = C\sqrt{\ln(4.9 + 1.1gx\theta^u)},\ u = \chi - m - n.$$

The quantities α, χ, and d are calculated from Eqs. (8)-(11). In the course of fitting we obtain $g = 15\ (\text{m}\cdot\text{bar})^{-1}$, $z_* = 1.6$, $C = 1.5$, $n = 2.55$. Control results are presented in Table 2.

Equation (12) is intended for extrapolating the data to very high temperatures, as far as 4000°K. This level of temperature is encountered in the combustion chambers of MHD generators. New emissivity nomograms have limiting temperatures of 2473 and 3000°K [11, 12].

The latter is taken as a base; it is excellently described over the range of optical thicknesses 0-5 m•bar and the temperature range 1000-3000°K.

On raising the temperature to 3000°K and over, the spectral bands spread and the absorption in the windows increases rapidly. According to our own estimate, $k \propto \theta^2$. The spectral background is thus no longer negligible, but any estimation of the background is at best rough, both in magnitude and as regards dependence on wave number. It may well be that the estimate is too high. The range of applicability of the equation as regards optical thickness is reduced to ≈15 m•bar.

In traditional thermotechnical chambers the temperature rarely exceeds 2500°K. The spectral background is comparatively low and may be omitted because of its unreliable mode of estimation. The emissivity is calculated by Eq. (12), in which the values $g = 15.9\ (\text{m}\cdot\text{bar})^{-1}$, $z_* = 0.3$, $C = 1.5$, $n = 1.25$ are to be taken. The base taken in this case was the Hottel nomogram, while the radiation coefficient and the average distance between the lines were given by

$$\lg\alpha_c = 0.9856 - 0.636\theta_* - 0.0575\theta_*^2 + 0.0383\theta_*^3, \tag{13}$$

TABLE 3. Emissivity of Water Vapor Calculated by Eq. (12) [$g = 15.9\ (\text{m}\cdot\text{bar})^{-1}$, $z_* = 0.3$, $C = 1.5$, $n = 1.25$, α_c and d are calculated by Eqs. (13) and (14)]

x, m.bar	t, °C			
	600	1000	1400	2000
0,002	0,00727	0,00418	0,00239	0,00124
0,06	0,116	0,0852	0,0554	0,0322
1	0,365	0,308	0,234	0,174
4	0,527	0,452	0,346	0,259
6	0,575	0,495	0,379	0,283
8	0,608	0,526	0,403	0,300
10	0,633	0,549	0,420	0,313
100	0,820	0,729	0,561	0,414

$$\theta_* = t/1000,\ d = \exp[1.21 - 1.06(T/1000)]. \quad (14)$$

Table 3 gives some control values. The emissivity nowhere exceeds unity on raising x to 100 m•bar. However, for very great thicknesses the neglect of the spectral background certainly leads to an unestimated result.

Let us proceed to the pressure extrapolation. We determine the correction

$$c = \varepsilon(P_*)/\varepsilon(P_* = 1\ \text{bar}).$$

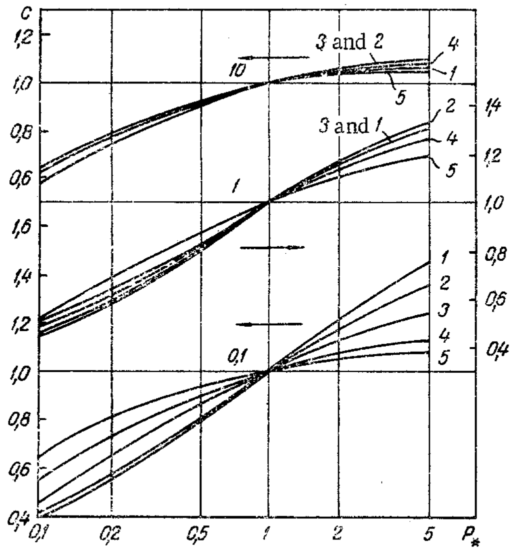

Fig. 1. Correction c to the emissivity of water vapor for the effective pressure. The groups of curves correspond to thicknesses of 10.1 and 0.1 m•bar; the serial numbers of the curves correspond to temperatures of 600, 1000, 1500, 2000, and 2500°K.

Figure 1 gives the result of the calculation in a form convenient for comparison with the latest data presented in [12]. The emissivity was calculated by means of Eq. (12), without separately allowing for the spectral background, since this was not distinguished in [12], while the temperature range in which the correction was most important lay below 1500-2000°K. Specially noteworthy is the reproduction of the extreme value of the correction c at a temperature of 600°K and thicknesses of $x \geq 1$ m•bar. No additional refinement was here applied to Eq. (12), and this fact once again indicates the correct estimation of the temperature dependence of the parameters in the equation.

We note that the value of the correction differs considerably from the previous Hottel values. The differences are explained in fair detail in [12].

NOTATION

x is the optical thickness of the gas, m•bar; p, P, and P_* are the partial, total, and effective pressure of the gas, bar; T and t are the temperatures on the absolute and centigrade scales; ε_0 and ε are the emissivities of the gas according to the nomogram and the equation, respectively; ε_1 is the emissivity of the gas for the whole spectrum, after subtracting the background; c is the correction to the emissivity of the gas associated with the change of argument; I_{0j} is the Planck function in the center of the band j, cm•W/m^2•sr; A_j is the integrated absorption in the band j, cm^{-1}; $\bar{A}$ and $\bar{A}_0$ are the absorption capacity in a spectral band, dimensionless; γ is the band width parameter, cm^{-1}; γ_{eff} is the effective width of the reconstructed band, dimensionless; S and s are the integrated intensities of the band and line, cm^{-1}/(m•bar); b and d are the half-width of line and distance between lines, cm^{-1}; ω is the wave number, cm^{-1}; ω_0 is the position of the band center; χ, m and u are exponents; α_c is the radiation coefficient and also mean Planck absorption coefficient, (m•bar)$^{-1}$; k_ω and k are the spectral and average (taken over the spectrum) absorption coefficients of the background of the band spectrum (m•bar)$^{-1}$; K is the reaction constant for the dimerization of the molecules, bar^{-1}.

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