EMISSIVITY OF CARBON DIOXIDE

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This paper presents a new correlation for the emissivity of carbon dioxide gas, suitable for extrapolating existing nomograms to large optical thickness values and high temperatures.

Two routes have been followed in improving nomograms for the emissivity of carbon dioxide gas and expanding the range of application. One route is traditional, and consists of direct measurement of gas radiation over the complete spectrum, while the second is based on progress in applied spectroscopy. A new nomogram was obtained by computation in [1, 2], but did not account for a number of experimentally determined spectroscopic constants for the gas. It spans a region of the arguments up to 2473°K, 10 mbar, and 0.1-∞ bar. The calculation makes use of tables of line envelopes and mean distances between lines for three strong band spectra over 5 cm^{-1} [3]. Weak bands are taken into account in a first approximation, and then neglected. These tables were obtained earlier by quantum mechanical calculations. Comparison with Hottel's and other data has shown some noticeable discrepancies. Work to construct new nomograms has been endorsed by Hottel [4].

Putting aside the matter of reliability of the original data for the new nomogram, we note that it has shortcomings arising from three other causes.

1. The temperature exceeds 2500°K in the combustion chambers of MHD generators and in other new technology. There is almost no information on emissivity for such high temperatures.

2. In one engineering method of calculation [5] dimensionless fluxes are calculated using infinite series, whose terms contain emissivities for increasing optical thickness values. There are neither nomograms nor formulas for determining series of terms for x > 10 mbar.

3. It is desirable to express the emissivity in analytical form, not in the form of graphs or tables. The use of a computer is thereby simplified. The Shak formula is limited to optical thickness values of 0.4 mbar [6]. At present one can use Legendre polynomials [1, 2]. However, the range of use corresponds to the nomogram, and extrapolation is impossible.

In this paper we propose a new formula for the emissivity of carbon dioxide gas. It is simple, is physically well founded, and therefore suitable for extrapolation of existing data. The structural simplicity of the formula allows it to be used without information concerning numerous weak bands for which data in the literature is nonexistent or unreliable.

In the first form of this formula we have used the Leckner nomogram [1, 2] as a base. It is the only one constructed from spectroscopic data.

A second form of the formula gives a good description of the Hottel nomogram.

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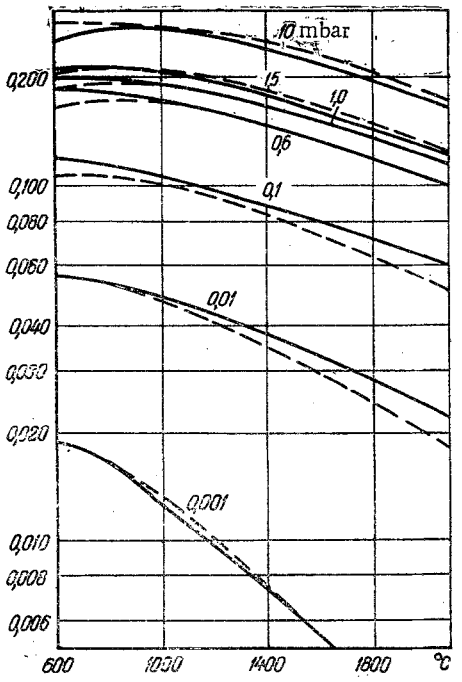


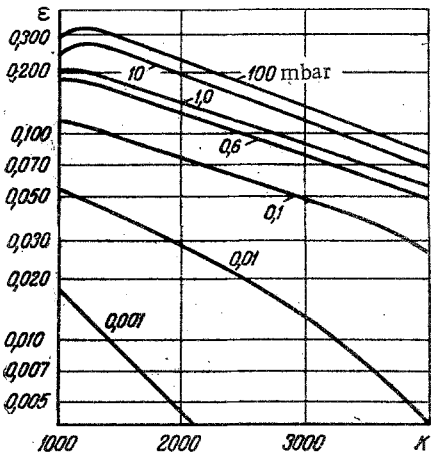


Fig. 1. Emissivity according to the first form of Eq. (1): broken lines — according to [1, 2]; solid lines — present authors' results.

Fig. 2. Emissivity at high temperatures, using the first form of Eq. (1).

The derivation of the formula has been described in [7]. Some of coefficients of the formula are altered in accordance with the nomograms. In the first form the reference points are the values of the Leckner nomogram at 2373°K. Thus, extrapolation of the data at higher temperatures up to 4000°K is a good approximation. We obtain:

$$\varepsilon = \frac{\alpha k}{g\theta^u}\left[1-\exp\left(-\frac{g\theta^u x}{k\sqrt{1+z_* dkg\theta^u x}\sqrt{T/273}/P_*}\right)\right],$$

$$k = \sqrt{\ln(4{,}9+1{,}1gx\theta^u)}, \quad u = \chi - m - n, \quad m = 0{,}65,$$

$$\chi = m\,\mathrm{th}\,[\exp(10x)-1], \quad \theta = T/1000, \quad T = t+273, \tag{1}$$

$$z_* d = \exp\left[0{,}107+0{,}813\theta_* - 0{,}583\theta_*^2\right], \quad \theta_* = t/1000,$$

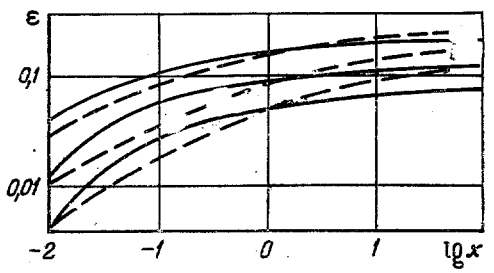
$$\lg\alpha = 1{,}9746 - 0{,}8332\theta_* + 0{,}0569\theta_*^2,$$

$$g = 276 \ (\mathrm{m\,bar})^{-1}, \quad n = 2{,}1. \tag{2}$$

Here x is in mbar. The emission coefficient α $(\mathrm{mbar})^{-1}$ determines the emissivity for low values of x: $\varepsilon \to \alpha x$, if $x \to 0$. Equation (2) is a good approximation to numerical values of α from [8] at $t \geq 600°C$. Therefore the region of the nomogram at small optical thickness is reproduced without correlation. The quantity $z_* d$ reflects an increase in the number of lines with increase of temperature and a corresponding decrease in the distance d between the lines. For $x \geq 30$ mbar we have $P_* = 1$ with negligible error:

$$\varepsilon = \alpha k \theta^{-u}/g.$$

The coefficient α, which is strongly temperature dependent, should not play an appreciable role at large values of optical thickness. Its effect here is partially compensated by the number n appearing in the exponent u.



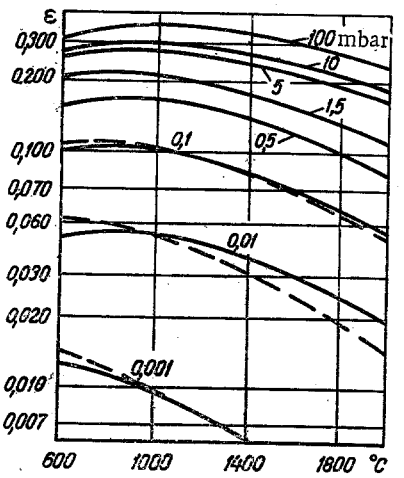


Fig. 3

Fig. 4

Fig. 3. Emissivity for complete overlap of lines (we put $P_* = \infty$) in the first form of Eq. (1). The solid lines are the present authors' results, and the broken lines are from independent calculation in [9]. A curve from [10] at 2000°K in the section 0.1-1 mbar coincides with the broken line.

Fig. 4. Emissivity for second form of Eq. (1). The broken lines are from the Hottel nomogram; the curves for 0.5 and 1.5 mbar coincide.

Figure 1 compares the results of using Eq. (1) with the Leckner curves. For x > 10 mbar our values of emissivity are apparently low. First, we neglected absorption in the spectral windows arising from distant wings of strong lines. There are no quantitative estimates of this factor in the literature.

Secondly, in the Leckner computations, and therefore, in ours also, absorption in a number of component spectral bands was neglected, which also leads to increased emissivity at large values of optical thickness and high temperatures. A calculation using Eq. (1) at temperatures up to 4000°K is shown in Fig. 2.

If we put $P_* = \infty$ in Eq. (1), we obtain a so-called upper bound for the emissivity corresponding to complete overlap of lines.

In this case a nomogram going up to 4000°K has been published in [9]. It was obtained by computation, employing an independent method. A comparison with our results is shown in Fig. 3. While there is general agreement in the levels of the curves, we note a difference in their curvature in the region 0.01-0.1 mbar. Figure 3 also shows a curve from a third independent source [10] at T = 2000°K and x = 0.1-1 mbar; it corresponds to the curve from [9].

The Leckner nomogram is in need of refinement, and we therefore developed a second form of Eq. (1), based on the Hottel nomogram. The changed parameters are:

$$g = 156.11\ (\text{mbar})^{-1};\quad n = 1.5;$$

$$z_* d = 1.8362\,\{0.39 + 0.0964\,(\theta_* - 0.6) + 0.32\exp[-6\,(\theta_* - 0.6)]\}.$$

The emission coefficient was taken from Shak [6], considered to be more consistent with the Hottel nomogram, in comparison with Eq. (2). Here we use the approximation

$$\lg \alpha = 1.5386 - 0.43955\theta_* - 0.038935\theta_*^2 + 0.0081\theta_*^3.$$

A comparison of the results with Hottel's curves is shown in Fig. 4.

The formulas obtained are suitable for any values of pressure, including low pressure (< 0.1 bar). In this case the Voigt line shape may differ considerably from a dispersion profile. Another formula will be used for absorption in a narrow band.

The effect of pressure is expressed as a correction

$$c = \varepsilon(P_*)/\varepsilon(P_* = 1).$$

The function c(x, T, P_*) in our formulas has a maximum if we vary x or T, holding the other arguments constant. This is in agreement with contemporary theory. We make a number of comments with regard to published data.

In Hottel's outdated graph for the correction factor c, assumed in Russian literature, there is no maximum with regard to optical thickness, and no temperature dependence. In a new edition [11] Hottel locates several curves of Edwards at 294 and 1111°K. The corrections are a maximum in the regions 0.03 and 0.3 mbar, respectively. This agrees with our data. In [12] neither of the two maxima is present, and the effect of temperature is very minor. In terms of absolute values, our maximum corrections exceed the values published in [13, 12]. This means that we have taken lower values of b/d. Finally, we note a difference in expressing the effect of pressure P_*. Because of our use of the concept of effective pressure we can consider the formula for P_* quite independently. According to a recommendation of Leckner [13] and several American authors, we can use the formula

$$P_* = P + 0.28p.$$

NOTATION

b and d, line half-width and average distance between lines, cm^{-1}; g and z*, correlation parameters; m, emissivity determining the thermal broadening of spectral band; x, exponent determining variation of integral intensity of a band with temperature, calculated in terms of a single molecule; m and x are averaged over bands; n, exponent accounting for partial isobaric gas expansion; p, P, and P_*, partial, total, and effective pressures, bar; T and t, absolute temperature and temperature on centigrade scale; k, width of equivalent rectangular band accounting directly for the shape of the actual envelope, dimensionless; x, optical thickness, mbar; c, correction to emissivity at pressure P_* differing from unity; α, emission coefficient, which is the same as the mean Planck mean absorption coefficient, $mbar^{-1}$; ε, emissivity of the gas, dimensionless. $\theta = T/1000$; $\theta_* = t/1000$.

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