

A relatively simple formula is presented for emissivity of carbon monoxide, useful in thermotechnical computations. The formula contains a number of new terms which are common to vibrational-rotational spectra of gases.

The thermal radiation spectrum of carbon monoxide is simple and has been studied relatively thoroughly. However, the accuracy of data in the literature on carbon monoxide radiation is inadequate from a thermotechnical standpoint. The present study will verify certain theoretical assumptions.

The emissivity of the gas at moderate optical thicknesses and temperatures is almost completely determined by the fundamental band. Experimental data on integral absorption in this band are of major importance. At room temperature we have the data of Burch and Williams [1] and Abu-Romia and Tien [2]. From [2] we will employ results at 900 and 1200°K; at 1800°K we will employ those published in [3]. The same sources were used in the calculations of [4, 5] and [6-8]. In [6-8] the spectral absorptive power in the spectral subband developing upon transition between neighboring vibrational levels was determined with a regular model. Refinements of this model, which greatly complicate an already complex calculation, do not play any significant role. Together with consideration of quite detailed phenomena, a coarse (exponential) envelope was taken for the subband branch envelopes. In our opinion, at the same level of complexity, the quantum-mechanical calculations of [9, 10] show advantages. They should be supplemented by data on rotational structure, now available in sufficient detail in ([11, 12] and others). We note that the calculation of [9] used the basic nomogram of Hottel and Sarofim [13]. Rotational structure was not considered.

Emissivity was determined with the formula

$$\varepsilon = \frac{\pi}{\sigma T^4} \sum_j I_{0j} A_j, \quad \pi I_{0j} = \frac{37.412 (\omega_j/1000)^3}{\exp(1.4388 \omega_j/T) - 1} \quad (1)$$

Here j denotes the fundamental band and its overtones considered in the calculation:

$$A_j = \int_{\text{band } j} A_\omega d\omega = \gamma_j \bar{A}_j.$$

The formulas presented above are those normally used. The methods of defining \bar{A} and γ are original.

The theoretical innovations used in the present study will be described in the following four sections.

Generalization of the Narrow-Band Statistical Model.

Statistical models differ in their choice of a distribution law for line intensity; uniform, exponential, or hyperbolic. In the last case, the probability that a line has an intensity from σ to $\sigma + d\sigma$ is inversely proportional to that quantity. With the laws mentioned, the number of weak lines increases. Comparison with experiment in [14] has shown that the third distribution is evidently the closest to the actual existing one. It was used in the

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present computation. In thermotechnical computations the second distribution is normally used, since it leads to the simplest possible formula. Spectral absorptive power has the general form

$$A_\omega = 1 - \exp(-W/d).$$

We introduce the dimensionless quantities

$$u = sx/(2\pi b), \quad N = \frac{W/d}{2\pi ub/d} = \bar{W}/(sx).$$

With the different dispersion laws we have

$$\begin{aligned} N_1 &= L(u)/u, \quad N_2 = (1 + \pi u/2)^{-1/2}, \\ N_3 &= [\exp(-4u) I_0(4u) + 2L(4u) - 1]/(4u). \end{aligned} \quad (2)$$

Justification of the formulas and curves of $\log N = f(\log u)$ are presented in the classic monograph of Goody [14]. Here we will offer an approximate formula, which generalizes all the indicated and, hence, all intermediate dispersion laws:

$$N = \left\{ \frac{(1 + \alpha)u}{\sqrt{1 + \pi u/2}} - \alpha \sqrt{\frac{2u}{\pi} \left[1 - \exp\left(-\frac{\pi}{2} u\right) \right]} \right\} / u. \quad (3)$$

For $\alpha = -0.57$ the formula corresponds to uniform line-intensity distribution. This particular case of the formula has been published previously [15]. For $\alpha = 0$ the formula corresponds to exponential distribution of line intensity. At $\alpha = 0.7$ the third distribution law is described approximately. Error in A_ω does not exceed 1%.

If the distribution law should be refined by additional collection of data, Eq. (3) could be refined by proper selection of α .

Formula for Integral Absorption in Spectral Band.

In [16] a band with an envelope modelled on a harmonic oscillator was replaced by a band with a rectangular envelope having equivalent absorption. The rectangle width then depends on optical thickness. The sense of this transformation is that in the case of the rectangular envelope the rotational structure is treated phenomenologically in correspondence with the choice of the narrow-band model. In the case of a simple rectangular model

$$\begin{aligned} \bar{A}_r &= k \sqrt{1 - \exp\left(-\frac{(u_0/k)^2}{1 + z_r u_0/(b/d)}\right)}, \\ k &= 2.22 \sqrt{\ln(4.9 + 1.1 u_0)}, \quad u_0 = Sx/\gamma. \end{aligned} \quad (4)$$

In the case of a generalized statistical model

$$\bar{A}_{st} = k [1 - \exp(-M)], \quad (5)$$

$$M = \frac{(1 + \alpha) u_0}{k \sqrt{1 + z_{st} u_0 k/(b/d)}} - \alpha \sqrt{\frac{z_{st} u_0 (b/d)}{k} \left[1 - \exp\left(-\frac{u_0}{z_{st} k (b/d)}\right) \right]}.$$

The particular case of $\alpha = 0$ was considered and used in [16].

The quantities z_r and z_{st} define the effects of pressure on absorption. They may be correlated with experimental data.

Combination of Narrow-Band Models.

With respect to narrow band models, spectroscopy has shown that the dominant influence on absorption is produced by the law of line location on the wave number axis. At room temperature in the case of carbon monoxide, molecules are excited practically only from the basic vibrational level. Line position within the band is found to be close to regular. Thus, the use of the regular narrow-band model is justified. With increase in temperature the population of upper vibrational levels grows, with a corresponding increase in intensity of hot subbands. Line location within the band (group of subbands) takes on a random character. At

sufficiently high temperature the use of a statistical model is justified.

The combination of models with increase in temperature can be represented in the form of a weighted sum of the effects described by the limiting models. For spectral absorptive power

$$A_{\omega} = \frac{1}{\xi} A_{\omega r} + \frac{\xi - 1}{\xi} A_{\omega, st}. \quad (6)$$

Here $\xi = F(T)/F(T_0)$ is the relative number of lines per unit interval of the wave number axis as compared with the number of lines at a temperature $T = 300^\circ\text{K}$.

The function $F(T)$ was first presented in [17]. In the case of a statistical model with consideration of only strong lines and the harmonic oscillator approximation

$$F = \varphi^2 [1 - \exp(-l\omega_j/T)]^{i+1}, \quad l = 1.4388 \text{ cm} \cdot ^\circ\text{K}, \quad (7)$$

$$\varphi = \sum_{v=0}^{\infty} \sqrt{\frac{(v+1)(v+2)\dots(v+j)}{1 \cdot 2 \dots j}} \exp(-v l \omega_j/T).$$

The series of Eq. (7) was approximated in the form

$$\varphi_j = 1 + a_j (T/300)^{1+i/2}. \quad (8)$$

Here $a_1 = 0.086$; $a_2 = 0.0118$; $a_3 = 0.00191$; $a_4 = 0.00033$. The error in ξ upon this replacement of Eq. (7) comprises only 1.75% at 300°K . At high temperatures it is also small.

At $T = 300^\circ\text{K}$ $\xi = 1$, the quantity A_{ω} is determined exclusively by the regular model. At very high temperatures $\xi \gg 1$ the statistical model plays the major role in Eq. (6). The weights in Eq. (6) may be assigned by a number of other methods. Since there is not sufficient data available for their selection, the combination was performed in the simplest possible manner.

The transformation from Eq. (6) to integral absorption in the spectral band is trivial for the case of rectangular envelope:

$$A = \frac{1}{\xi} A_r + \frac{\xi - 1}{\xi} A_{st}. \quad (9)$$

Width Parameter.

Edwards obtained the following value for the bandwidth parameter:

$$\gamma = \gamma_0 \sqrt{T/T_0}, \quad \gamma_0 = 0.9\Gamma^2(3/4) \sqrt{2T_0 B_e/L}.$$

With substitution $B_e = 1.931 \text{ cm}^{-1}$, $T_0 = 300^\circ\text{K}$, $\gamma_0 = 38 \text{ cm}^{-1}$. This formula does not consider shift of "hot" subband centers on the wave number axis or other finer phenomena, due to which growth of the width parameter with increase in temperature is accelerated. The quantum-mechanical approach of [18] is thus obtained:

$$\gamma = \gamma_0 (T/T_0)^m, \quad m = a + bT.$$

At moderate temperatures the increase in exponent m may be considered by means of the same quantity ξ :

$$m = 0.5 \frac{1}{\xi} + m_* \frac{\xi - 1}{\xi}.$$

In the present study $m_* = 0.729$. At 1800°K , $m = 0.65$ instead of 0.5 in the first approximation. Then $\gamma_0 = 39 \text{ cm}^{-1}$.

Rotational Structure Parameter.

The formula for the rotational structure parameter is taken from studies of the Edwards group:

TABLE 1. Integral Absorption in Fundamental Band of Carbon Monoxide Spectrum, cm^{-1} . Comparison of Calculations and Experiment

Experiment					Calculation					
T, K	P, bar	x , $\text{cm} \cdot \text{bar}$	(*)-[1] (**)-[3]	[2]	[7]	[8]	authors			
							A	A _r	A _{st}	
300	0,51	0,5	27(*)	22,0	27,5		23,1	23,1	25,0	
		2,5	60	58,2	60		51,3	51,3	47,2	
		5	80	89,0	78,6		71,3	71,3	61,1	
	1,02	10	105	122	99,6		97,5	97,5	78,3	
		1	53	48,5	53,9		45,2	45,2	44,2	
		5	110	112	99,6		95,8	95,8	79,2	
	2,04	10	130	148	126		127	127	99,7	
		20	155	169	152		161	161	124	
		2	95	90	93,2		84,6	84,6	73,6	
	3,06	10	150	159,2	152		155	155	122	
		20	170	184	188		184	184	147	
		3	125	127,2	122		116	116	95,7	
			15	180	193,5	187		182	182	150
	900	0,25	2,5		26,3	29,4	26,7	30,0	28,6	32,1
			5		37,8	39,7	40,4	41,6	40,7	42,9
0,51			2,5		38,0	39,7	40,4	41,9	40,4	44,3
1,02		5		55,0	69,7	56,5	58,0	57,4	58,9	
		10		66,0	67,5	78,8	79,4	80,8	77,4	
		1		27,7	30	35,2	35,7	33,4	39,2	
2,04		5		82,0	82,3	80,2	79,0	79,2	78,7	
		10		106,2	114	112	108	111	102	
		20		134	124	142	145	153	132	
3,06		2		57,6	60,3	71,1	67,8	65,8	70,8	
		10		134,3	124	142	143	150	132	
		20		176	160	178	188	202	167	
3,06		40		226	202	223	241	262	208	
		3		90,5	89,5	103	96,8	96,6	97,1	
		15		191	168	188	193	207	173	
		30	234	210	230	245	266	214		
		60	273	258	279	297	322	259		
1200	1,02	5		46,6			79,9	78,1	81,7	
	2,04	10		119,4			147	155	139	
	3,06	15		187,2			198	212	185	
		20					221	240	203	
		30		255			255	281	231	
		40					281	311	252	
	60		294			317	353	284		
1800	1,02	10	129(**)		97,7	117	115	112	117	
		20	159		140	158	156	160	154	
	1,53	15	172		146	169	162	165	161	
		30	221		202	217	216	231	208	
	2,04	20	195		192	208	204	214	199	
		40	268		264	262	267	294	253	
	2,55	25	247		238	243	241	259	232	
		50	317		316	300	312	349	292	
	3,06	30	278		278	270	275	300	261	
		60	347		368	335	350	396	326	

$$b/d = (b/d)_0 \sqrt{T_0/T} P_* \xi(T). \quad (10)$$

The quantities b_0 and d_0 depend on the wave number in different manners. Line half-width also depends on the nature of the molecule with which collisions occur. In the present study the parameter b/d was averaged over the wave number. In the case of a mixture of CO-N_2 at $T_0 = 300^\circ\text{K}$, according to [11, 12], $b_0 = 0.063 (\text{cm} \cdot \text{bar})^{-1}$. On the average $d_0 \approx 2B_e = 3.8 \text{ cm}^{-1}$. We then have $(b/d)_0 = 0.01675 \text{ bar}^{-1}$. The details of this parameter are of significance only in exact (quantum-mechanical) computation. In the given case the parameters of the rotational structure can be considered to be the quantities $(b/d)/z_r$ and $(b/d)/z_{st}$, appearing in Eqs. (4) and (5). The numbers z_r and z_{st} are correlation parameters used to describe experimental data on integral absorption in a spectral band. For the carbon monoxide band we have $z_r = 0.07$ and $z_{st} = 0.04$. The effective pressure is determined from the well-known formula

$$P_* = P + 0.02 p.$$

TABLE 2. Spectroscopic Data for Carbon Monoxide Fundamental Band and Three Overtones Used in Present Study

j	$S_{0j}, \text{cm}^{-1}(\text{cm} \cdot \text{bar})$	ω_j, cm^{-1}
1	237,12	2130
2	1,67	4200
3	0,183	6270
4	0,02	8340

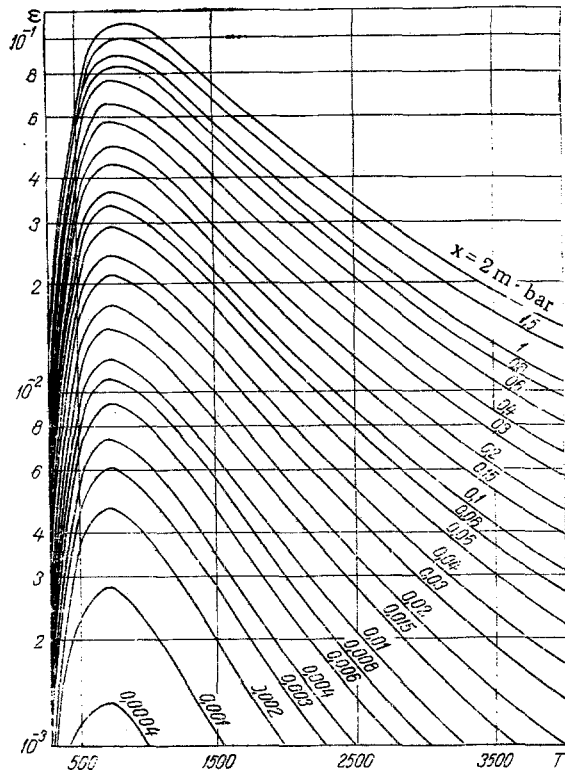


Fig. 1. Nomogram of carbon monoxide emissivity from present calculations. Effective pressure equal to unity.

Integral Absorption in a Spectral Band.

The entire group of formulas presented above is necessary for the calculation: Eqs. (9), (5), (4), (10), and others. Aside from the spectroscopic constants presented, we note the integral intensity of the fundamental band $S_0 = 237.12 \text{ cm}^{-1}/(\text{cm} \cdot \text{bar})$. The same value was taken in the studies cited herein.

Table 1 presents a comparison of experimental and calculated data. Also shown are the terms A_r and A_{st} , combined in [9]. As is evident, at 1800°K the statistical model still does not make the total contribution to integral intensity. It can be concluded that at this temperature some regularity in line distribution along the wave number axis is significant.

On the whole, the present calculations give the best description of experimental data. Moreover, they are much simpler than those presented by the Greif group.

The effect of pressure on absorption is also important in evaluating the calculation. According to experimental data obtained in [19], at $x = 1.356 \text{ cm} \cdot \text{bar}$ and $T = 300^\circ\text{K}$ with pressure increase from 1 to 2, 20, ∞ bars, absorption in the band increases 1.68, 4.5, and 4.8 times, respectively. Such a great pressure effect contradicts the later experimental studies employed herein. The present calculation gives increases of 1.35, 2.48, and 2.67 times, which are significantly higher than the calculation of [2]. Unfortunately, the studies of the Greif group offer no analogous results.

Emissivity of Carbon Monoxide.

Calculation was performed by Eq. (1) with consideration of the fundamental band and three overtones. Spectroscopic data are presented in Table 2. Values of S_{0j} for $j = 3$ and 4

TABLE 3. Contributions to Carbon Monoxide Emissivity of Fundamental Band and Three Overtones ($P_* = 1$ bar, $x = 100$ cm·bar. Values in table are multiplied by 10^4)

i	T, K				
	500	1000	2000	3000	4000
1	553	837	330	148	79,8
2	1,3	28,6	42,1	29,8	19,5
3	0	1,08	4,87	7,0	6,9
4		0	1,62	2,86	2,9

are doubtful, but for the majority of practical problems these overtones play no role. Only at $T > 3000^\circ K$ and $x > 100$ cm·bar does their contribution to emissivity become significant. Figure 1 presents a nomogram of emissivity in the usual engineering form. Table 3 shows the contribution of individual spectral bands to integral emissivity. It may also be used for control of the present algorithm.

NOTATION

ϵ , gas emissivity; σT^4 , integral radiation density of black body, W/m^2 ; πI_{0j} , spectral density of black body radiation on wave number scale, $cm \cdot W/m^2$; A_w , spectral absorptive power; A_j , integral absorption in band j , cm^{-1} ; $\bar{A} = A/\gamma$; γ , width parameter, cm^{-1} ; ω_j , center of band j on wave number axis, cm^{-1} ; \bar{W} , mean integral absorption in single line, cm^{-1} ; b and d , half-width of line and mean distance between lines, cm^{-1} ; s , S , integral intensities of line and band, $cm^{-1}/(cm \cdot bar)$; I_0 , Bessel function with imaginary argument; L , Laudenberg and Reiche function; α , numerical coefficient; $\xi = F(T)/F(T_0)$; F , function describing increase in number of lines per unit interval of wave number axis; Γ , gamma function; B_e , rotational constant, cm^{-1} ; p , P , P_* , partial, total, and effective pressures, bar; T , temperature, $^\circ K$; x , optical thickness, $cm \cdot bar$.

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