RADIATION PROPERTIES OF CARBON MONOXIDE

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Nomograms are given to determine the degree of blackness and other characteristics of carbon monoxide by using the "from line to line" method.

Radiation properties of carbon monoxide have been studed by many researchers. The gas is charac acterized by a simple structure and by available spectral data and, therefore, it can serve as a convenient means for comparison of methods. Its practical value is determined by its frequent occurrence in industry and nature. However, the known radiation characteristics are unsatisfactory with respect to accuracy and range of arguments. In this paper, we present results of calculations by the "from line to line" algorithm published in [1, 2]. The method can be used for other diatomic gases without modifications if there is initial data.

A nomogram of the degree of blackness was proposed in 1954 by Hottel [3] based on calculations that were in good agreement with observations of Ulrich. In [4] and other subsequent publications, including Soviet publications, changes were introduced only concerning conversion to different units. The nomogram is limited to a temperature of 1300 K and is insufficient even for conventional combustion furnaces and chambers. For devices with low-temperature plasmas the degrees of blackness are required up to the complete dissociation of molecules about 7500 K under normal pressure.

In the literature it was noted that the estimates of the observed degrees of blackness were too high, apparently, as a result of the formation of carbon dioxide. The reaction $2CO = C_{sol} + CO_2$ is exothermic. Its equilibrium constant $K = P^2_{CO}/P_{CO_2}$ is published in many handbooks. From the equation $\xi c_0 = (1 - c_0)^2$, where $c_0 = p_{CO_2}/P$, $\xi = K/P$ it follows that $c_0 = 0.999$; 0.660; 0.019 and 0.001 respectively, at T = 600, 900, 1200 and 1500 K. Equilibrium in the observation cell is not attained. However, the reaction is accelerated with increasingtemperature, therefore, observations can show an increase in the concentration of CO_2 in spite of the decrease in the equilibrium value of c_0. A catalytic acceleration of the reaction is also possible.

Our results agree well with calculations in [5, 6] conducted with the use of new spectral datda. In [5], cited more often, we also can notice an anomaly in absorption on the wing of the R⁻ branch of the fundamental band. It increases with an increase in temperature and pressure. Here we also can suggest the formation of carbon dioxide and the overlap with its 4.3 μ band, the strongest in the spectra of the combustion products. Apparently, this does not lead to a considerable distortion of results.

In the handbook [7], the basic data are given only for the fundamental band. However, even these data should be considered obsolete [2]. The curve of the spectral absorption from [7, p. 307] agrees well with the observations in [5]; however, our checking for different arguments does not show a good fit. The wide-band method of Edwards [8, p. 490] is partially used in ⌊9⌋ when describing radiation properties of sulfur dioxide; however, it is not considered here.

Tables 1 and 2 show good agreement between our calculations of the integral absorption in the fundamental band and in the first overtone with the experimental data. Discrepancies are within the error limits of the method. The integral intensity of the fundamental band in [5] is $S_0 = 237$; we used $S_0 = 257.5$ cm⁻¹/(cm·atm) at $T_0 = 300$ K. However, this fact does not play a significant role, especially when the optical thickness increases, because calculations in [5] are corrected in agreement with observations. If S_0 is too low, this is compensated partially by other values when processing experimental data. In our calculations the S_0 are chosen more rigorously since they do not contain adjusting coefficients.

TABLE 1. Comparison between the Calculated Integral Absorption in the Fundamental Band A, cm^{-1} and Experimental Values [5]

T, K	x, cm·atm	P, atm	Data [5]	Calculations	Data after Barch and Williams [6]
300	0,5	0,5	22,0	26,6	27
	1,0	1,0	48,5	51,7	53
	2,0	2,0	90,0	93,9	95
	3,0	3,0	127,2	124,1	125
	1,25	0,25	30,2	31,3	
	2,5	0,5	58,5	60,2	60
	5,0	1,0	112,0	106,7	110
	10,0	2,0	159,2	157,0	150
	15,0	3,0	193,5	178,2	180
	2,5	0,25	45,0	44,3	
	5,0	0,5	89,0	82,5	80
	10,0	1,0	148,0	134,9	130
	20,0	2,0	184,0	177,5	170
	30,0	3,0	205,0	194,7	
	5,0	0,25	66,0	61,7	
	10,0	0,5	122,0	109,1	105
	20,0	1,0	169,0	160,1	155
	40,0	2,0	210,0	194,3	
	60,0	3,0	226,0	209,8	
600	0,5	0,5	27,4	17,6	
	1,0	1,0	44,0	34,8	
	2,0	2,0	84,4	67,6	
	3,0	3,0	120,6	97,2	
	2,5	0,5	36,4	42,3	
	5,0	1,0	82,8	81,0	
	10,0	2,0	160,0	143,7	
	15,0	3,0	206,0	186,2	
	2,5	0,25	28,0	31,1	
	5,0	0,5	56,2	60,5	
	10,0	1,0	115,2	112,2	
	20,0	2,0	184,0	183,5	
	30,0	3,0	232,0	221,7	
	5,0	0,25	44,4	44,4	
	10,0	0,5	90,0	84,8	
	20,0	1,0	151,6	149,1	
	40,0	2,0	224,8	219,5	
	60,0	3,0	262,0	249,5	
900	1,0	1,0	27,7	19,3	
	2,0	2,0	57,6	57,2	
	3,0	3,0	90,5	83,5	
	2,5	0,5	38,0	36,8	
	5,0	1,0	82,0	71,2	
	10,0	2,0	134,3	131,2	
	15,0	3,0	191,0	178,9	
	2,5	0,25	26,3	27,2	
	5,0	0,5	55,0	53,1	
	10,0	1,0	106,2	100,5	
	20,0	2,0	176,0	176,1	
	30,0	3,0	234,0	227,5	
	5,0	0,25	37,8	39,2	
	10,0	0,5	66,0	75,5	
	20,0	1,0	134,0	138,1	
	40,0	2,0	226,0	224,0	
	60,0	3,0	273,0	270,5	
1200	5,0	1,0	46,6	66,4	
	10,0	2,0	119,4	123,9	
	15,0	3,0	187,2	172,1	
	10,0	1,0	77,5	94,9	
	20,0	2,0	150,0	170,1	
	30,0	3,0	255,0	226,4	
	20,0	1,0	127,4	132,3	
	40,0	2,0	233,0	223,3	
	60,0	3,0	294,0	280,2	
1500	5,0	1,0	40,0	63,5	
	10,0	2,0	117,0	119,2	
	15,0	3,0	190,0	167,0	
	10,0	1,0	58,6	91,6	
	20,0	2,0	141,0	166,1	
	30,0	3,0	232,0	224,5	
	20,0	1,0	121,0	128,9	
	40,0	2,0	236,0	222,1	
	60,0	3,0	306,0	285,0	

TABLE 2. Comparison between the Calculated Integral Absorption in the First Overtone A, cm^{-1} and Experimental Values [5]

T, K	x, cm·atm	P, atm	Data [5]	Calculation
300	20,0	1,0	18,8	16,2
	40,0	2,0	33,5	36,5
	60,0	3,0	50,0	52,9
600	20,0	1,0	10,8	11,5
	40,0	2,0	21,6	22,8
	60,0	3,0	33,9	33,8
900	20,0	1,0	9,48	9,02
	40,0	2,0	19,36	17,72
	60,0	3,0	31,4	26,3
1200	20,0	1,0	7,07	7,81
	40,0	2,0	14,8	15,13
	60,0	3,0	29,0	22,5
1500	40,0	2,0	15,1	13,5
	60,0	3,0	24,0	19,96
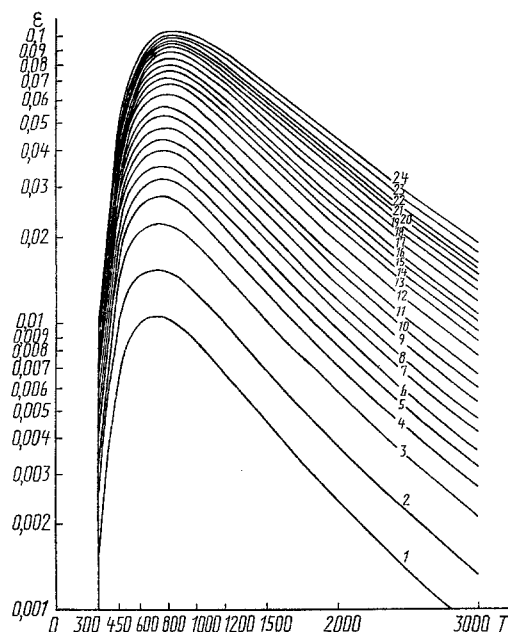
Fig. 1. Degree of blackness of carbon monoxide up to 3000 K for $P_* = 1$ atm (normal pressure and infinite dilution by nitrogen). The curve numbers correspond to optical thickness, cm·atm: 1) 1; 2) 2; 3) 4; 4) 6; 5) 8; 6) 10; 7) 13; 8) 16; 9) 20; 10) 25; 11) 30; 12) 40; 13) 50; 14) 60; 15) 70; 16) 80; 17) 100; 18) 120; 19) 140; 20) 160; 21) 180; 22) 200; 23) 250; 24) 300. T, K.

In Fig. 1, a new nomogram of the degree of blackness is shown for conventional thermotechnical calculations, and in Fig. 2, up to 7000 K. The contribution of the first overtone is shown. The maximal contribution of the second overtone does not fall within the nomogram field, it is equal to 9.3×10^{-5} for 300 cm·atm and a temperature of about 2000 K.

In [5], the degrees of blackness were compared with the data of Li and Happel (1964), Penner (1959) and Oppenheim (1959). Better agreement is noted with Li and Happel, and there is a great overestimation of the results of Ulrich as compared with all others. In Fig. 2, our results are compared with calculations in [5, 6] for 1 and 30 cm·atm. The data in [6]
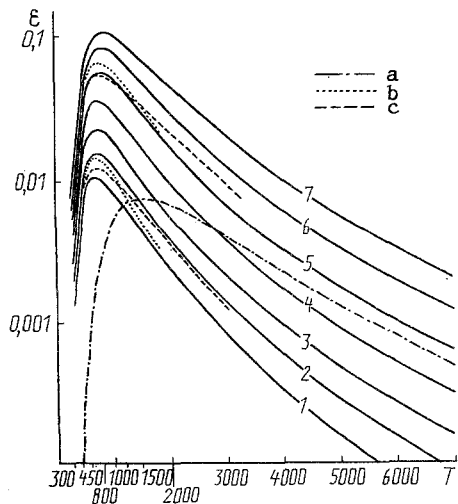
Fig. 2. Degree of blackness of carbon monoxide up to 7000 K at $P_* = 1$ atm. Curve numbers correspond to optical thicknesses, cm·atm: 1) 1; 2) 2; 3) 4; 4) 10; 5) 30; 6) 100; 7) 300; a) contribution of the first overtone at 300 cm·atm for all different isotopes; for comparison the degrees of blackness are shown for 1 and 30 cm·atm; b) according to [5]; c) according to [6].
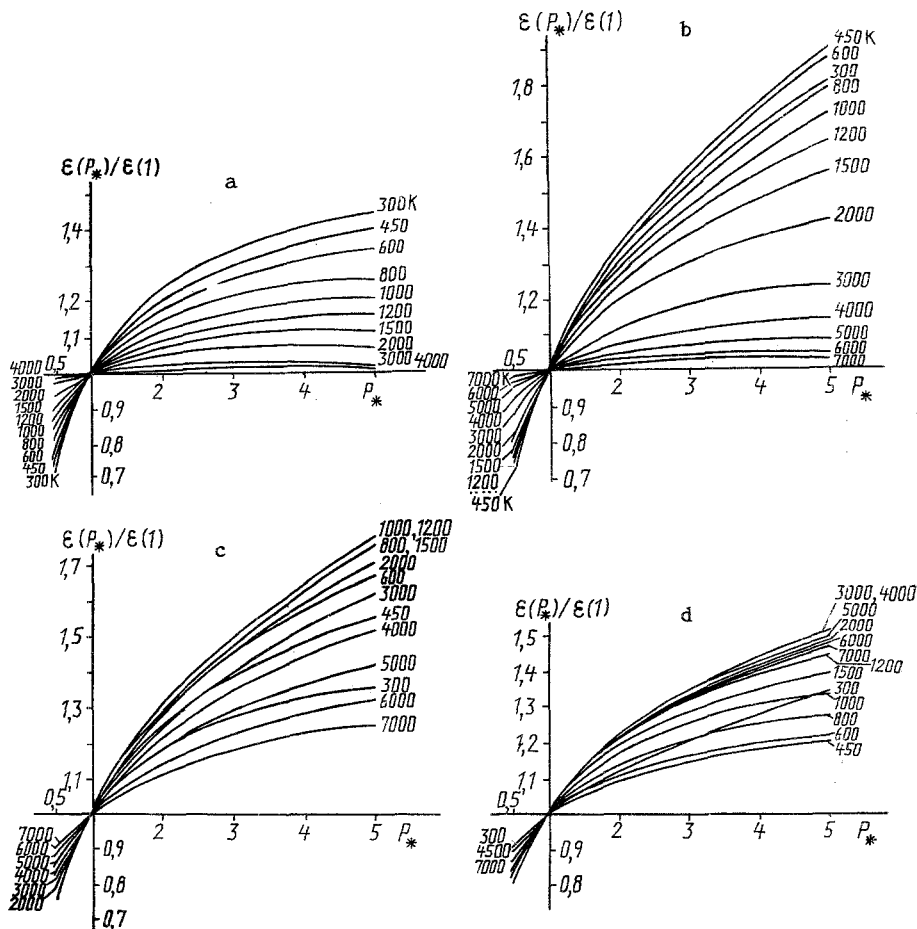

Fig. 3. Correction on effective pressure, $c = \varepsilon(P_*)/\varepsilon(P_* = 1)$; a) $x = 0.1$; b) 1; c) 10; d) 100 cm·atm. P_*, atm.

are obtained from a wide-band model with a crude extrapolation of parameters with respect to the temperature. The extrapolation in the given algorithm is not free from flaws: however, it is more reliable.

In Fig. 3, the influence of the effective pressure on the degree of blackness is shown. It is stronger than for the three-atom gases H_2O and CO_2 because of the large distance between the lines.

We now pass to the consideration of peculiarities of fragments of the algorithm. We made a separate program to calculate the parameter s/d. We assume that the spectral degree

of blackness $\varepsilon_\omega = 1 - \exp(-xs/d)$ and its integral over the spectrum represents the limit that cannot be exceeded under any pressure. However, this cannot be true for our calculations. We bound the band by lines, intensities of which are larger than the given values $s_0 = 10^{-6}$ $cm^{-1}/(cm \cdot atm)$. We discarded weaker lines outside the band; however, the wings of the lines with centers within the band were located there. At 300 K the absorption on far wings appeared to be unexpectedly high, which is explained by the maximal intensity, compact arrangement, and a large line width at low temperatures. The Voigt contour, which we assume in the given calculations, agrees with the dispersion contour in proportion to the distance from the central line, especially when the pressure increases. The real wings are distorted. In [10], an empirical correction is offered, according to which the contour beginning with $|\omega - \omega_0| = 4$ cm^{-1} is multiplied by $\exp[-0.015(|\omega - \omega_0|-4)]$ and the far wings decrease quickly to zero. Up to now the correction has been discussed, and it has been shown in [11] that it does not improve explicitly the accuracy for carbon monoxide. The "generalized contour," which is rather complicated, is more appropriate. However, when the temperature increases to a level that is substantial for thermotechnical calculations, the role of the far wings become negligibly small, and the noted peculiarity can be neglected.

If we exclude low temperatures when the number of lines is small and they overlap at sufficiently large x, then, when the optical thickness increases, the curves on the plot of corrections in the coordinates $\varepsilon(P_x)/\varepsilon(1) = f(x)$ with T = const, which we omitted, pass from unity to unity through a maximum for $P_x > 1$ and a minimum for $P_s < 1$.

Below we list distinctive features of the algorithm as compared with previous publications.

1. In our calculations four bands are considered, as in [6], but with modified parameters. For all bands, the algorithm is similar to the "from line to line" algorithm.

2. The integral intensities of the fundamental bands differ for isotopic versions. In order of predominance of molecular weight, they are: 283, 267, 268, 283 $cm^{-1}/(cm \cdot atm)$ as calculated per 100 mass % at 273.2 K. For overtones, they are: 1) 2.09; 2) $1.39 \cdot 10^{-2}$; 3) $4.12 \cdot 10^{-5}$ $cm^{-1}/(cm \cdot atm)$. These values are distributed among the varieties of molecules in correspondence with the mass fraction.

3. The dispersion contour of the line is replaced by the Voigt contour.

4. The collision broadening is calculated by the method presented below.

Calculation of the half-width of the lines is based on values of b_0 at 300 K, represented in Fig. 4. For $m \le 25$, they are adopted from [12], and for $m > 25$ they are obtained from the theory of K. B. Panfilovich. According to the theory, the temperature affects the half-width through the coefficients of dynamic viscosity and the population of rotational levels. However, in our algorithm a different simplified dependence is assumed. For a mixture of gases with additive broadening

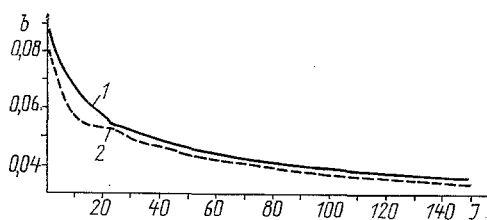$$b = P \sum_l b_{0l} c_l (T_0/T)^{\chi_l}, \quad c_l = p_l/P, \quad \sum_l c_l = 1.$$

$$(1)$$

Fig. 4. Collison half-widths of lines for $T_0 = 300$ K and P = 1 atm for pure monoxide (1) and in a mixture with nitrogen at infinite dilution (2). b_0, $cm^{-1} \cdot atm^{-1}$.

TABLE 3. Coefficients of Broadening, Averaged over
the Lines for CO–N_2 Mixture According to Versions
(5)

T, K	Version I	Version II	T, K	Version I	Version II
300	0,146	0,147	3000	0,153	0,144
600	0,155	0,151	4000	0,156	0,147
1000	0,154	0,146	5000	0,159	0,151
1500	0,152	0,143	6000	0,162	0,154
2000	0,152	0,142	7000	0,163	0,157

We introduce an effective pressure

$$b = P_* b_{01} (T_0/T)^{X_1}, \quad P_* = P \left(1 + \sum_{l \neq 1} B_l c_l \right), \tag{2}$$

where index 1 corresponds to nitrogen; B, to the coefficient of broadening.

For the binary mixture CO–N_2 from (1) and (2) it follows that

$$B_2 = (b_{02}/b_{01})(T_0/T)^{-(X_2 - X_1)} - 1, \tag{3}$$

where index 2 corresponds to carbon monoxide; $X_1 = 0.66$ and $X_2 = 0.69$. The relationship is written for a separate line and does not introduce an error in accurate calculations. When using nomograms of integral values, for example, in Figs. 1-3, it is necessary to average $\bar{B}_\ell$. For the binary mixture

$$P_* = P (1 + \bar{B}_2 c_2), \quad c_2 = p_{CO}/P, \tag{4}$$

the relationship

$$\bar{B}_2 = (\bar{b}_2/\bar{b}_1) - 1$$

and two methods for averaging $\bar{b}$:

$$\bar{b}_I = (\Sigma s_i b_i)/\Sigma s_i, \quad 1/\bar{b}_{II} = (\Sigma s_i/b_i)/\Sigma s_i. \tag{5}$$

Summation encompasses all the quantum numbers. Results are given in Table 3. For all the temperatures, and irrespective of the method of averaging, we can assume that $\bar{B}_2 = 0.15$. According to complete calculations of the degree of blackness "from line to line," we obtain $\bar{B}_2 = 0.12$ with the same weak dependence on temperature. We did not succeed in explaining the difference of 0.03. In the literature, only one value of $\bar{B}_2 = 0.02$ [5] is encountered.

Nomograms of corrections in Fig. 3 are obtained with the normal pressures P; however, on the x-axis the effective values are shown with the simple replacement $P \to P_*$. For the mixture of CO–N_2 the value of P_* is calculated from (4) with $\bar{B}_2 = 0.12$. For other gases we can use Eqs. (5), according to which calculations of s_i and b_i are incomparably simpler than according to the complete algorithm.

The algorithm "from line to line" gives all the values necessary for practical calculations of the heat exchange by radiation with participation of gases. For carbon monoxide it is fairly reliable because of the precision and completeness of spectral data. Calculated nomograms of the degrees of blackness and corrections to them exceed the actual nomograms in the range of arguments and the magnitude of the error. Certain elements of the calculations are introduced for the first time. The use of the algorithm for other two-atom gases is limited only by the availability of the source data.

NOTATION

b, half-width of the line, cm^{-1}; $c_\ell = p/P$, mole fraction of the active gas; d, distance between the lines, cm^{-1}; m, combined rotational quantum number; p and P, partial pressure and total pressure, atm; s and S, integral intensities of lines and the band, $cm^{-1}/(cm \cdot atm)$;

B, dimensionless coefficient of self-broadening; T, temperature, K; ε, degree of blackness; ω, wave number, cm^{-1}. Indices: 0, at 300 K; ω, spectral value; *, effective value.

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