

Thermodynamic Functions for Carbon Dioxide in the Ideal Gas State

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The thermodynamic functions C_p°/R , $(H^\circ - E_0^\circ)/RT$, $-(F^\circ - E_0^\circ)/RT$, and S°/R for carbon dioxide in the ideal gas state are given from 50° to 5,000° K, based on the latest spectroscopic data.

1. Introduction

Thermodynamic functions for carbon dioxide were computed by Kassel [1],¹ whose values were corrected to more recent values of the physical constants and extended from 3,500° to 5,000° K by Wagman, et al. [2]. Values by H. L. Johnston have been given by Ellenwood, Kulik, and Gay [3]. A subsequent calculation by Gratch [4] differed appreciably, showing a somewhat different behavior at elevated temperature. With improved spectroscopic constants, it has become possible to carry out a recalculation of greater accuracy. Values obtained for the specific heat in the main are intermediate between the previous calculations.

2. Spectroscopic Constants

The spectroscopic constants used for $C^{12}O_2^{16}$ with the vibrational energy formula are $\nu_1=1342.86\text{ cm}^{-1}$, $\nu_2=667.30\text{ cm}^{-1}$, $x_{11}=-2.20\text{ cm}^{-1}$, $x_{22}=-0.75\text{ cm}^{-1}$, $x_{12}=3.76\text{ cm}^{-1}$, and $x_{11}=1.03\text{ cm}^{-1}$, given by Taylor, Benedict, and Strong [5], with $\nu_3=2349.15\text{ cm}^{-1}$, $x_{13}=-18.54\text{ cm}^{-1}$, and $x_{23}=-12.48\text{ cm}^{-1}$, as indicated in a private communication from Benedict, and $x_{33}=-12.46\text{ cm}^{-1}$, chosen to fit the observed 11496.5 cm^{-1} at $\nu_3=5$. The rotational constant B_0 was taken as 0.39038 cm^{-1} , received in a private communication from Earle K. Plyler, of the Bureau, as a preliminary value. For the stretching constant D_0 , a theoretical value of $0.132 \times 10^{-6}\text{ cm}^{-1}$ was used on the ground that it was not ruled out by a preliminary empirical value of $(0.165\text{ cm}^{-1} \pm 0.02\text{ cm}^{-1}) \times 10^{-6}$ of Plyler. For rotational-vibrational interaction, the values $\alpha_1=0.00056\text{ cm}^{-1}$ and $\alpha_2=-0.00062\text{ cm}^{-1}$ were given by Herzberg [6], and $\alpha_3=0.0031\text{ cm}^{-1}$ was obtained from Plyler's newer data. The Fermi resonance constant W_0 was taken as 51.01 cm^{-1} , correcting for a $\sqrt{2}$ factor in the publication of Taylor, Benedict, and Strong.

3. Method of Calculation

The calculation was performed by computing the harmonic-oscillator rigid-rotator thermodynamic functions and adding corrections for deviations from this simple model. Corrections were made for anharmonicity, rotational-vibrational interac-

tion, azimuthal quantum effects, rotational stretching, and Fermi resonance. The first three of these corrections are an extension of a method indicated by Mayer and Mayer [7] for diatomic molecules and used for polyatomic molecules by Stockmayer, Kavanagh, and Mickley [8]. The general formulas as now extended are given in another paper [9]. The constants as given in section 2 are in form for this use, with the exception of ν_2 , for which the derived formulas require $\omega_2=\nu_2-x_{11}$. In the present application to carbon dioxide the anharmonicity formulas were carried through the second-power terms (including cross products) but not through the third-power terms. The rotational-vibrational interaction was carried through the first power, second-power terms being omitted. The azimuthal $B+g_{22}$ or $B+x_{11}$ terms were carried through the second power, third-power terms being omitted. No correction was made for the small splitting associated with azimuthal l -type doubling, on the basis that its effect is entirely negligible. Cross-product terms between azimuthal and rotational-vibrational interaction, between azimuthal and anharmonic, and between rotational-vibrational interaction and anharmonic constants were found to have small effect below 1,500° K and were omitted throughout. It may be supposed that a complete and exact representation of the energy levels would include corresponding interaction terms, so that the lack of such empirical constants may help justify the omission of related cross-product terms. In addition, the considerable uncertainty in many of the available constants provides a greater uncertainty in the resulting table than the effects of the omitted cross-product terms. The procedure used in calculating the effect of Fermi resonance and the results of that calculation are given in a separate publication [10]. No corrections were introduced for either vibrational or rotational cutoff.

The correction quantities contributing to the thermodynamic functions were calculated for $C^{12}O_2^{16}$ at 300°, 600°, 1,000°, 1,200°, 1,500°, 2,000°, 3,000°, 4,000°, and 5,000° K, and for the specific heat at several lower temperatures. The harmonic oscillator contributions were computed at closer intervals and adjusted to frequencies representing a weighted average according to the relative abundance of the isotopes. The molecular weight and rotational constant were similarly taken for the natural isotopic mixture. The values of C_p°/R interpolated to the intervals given in the final table

¹ Figures in brackets indicate literature references at the end of this paper.

TABLE 2. Corrections added in obtaining table 1, due to x_{ij} , x_{ij} , α_i , x_{11} , W_0 , and $\Delta\nu_2 = \nu_2 - \omega_2$

T	C_p^0/R	H^0/RT	$(-F^0/RT)$
°K			
50	0.00012	-0.0037	0.0039
100	.00016	-.0018	.0021
150	-.00026	-.0012	.0014
200	-.00072	-.0010	.0011
250	-.0004	-.0009	.0009
300	-.0001	-.0008	.0007
400	+.0006	-.0006	.0006
500	.0018	-.0002	.0005
600	.0038	+.0003	.0005
700	.0071	.0010	.0006
800	.0112	.0020	.0008
900	.0161	.0033	.0011
1,000	.0213	.0048	.0015
1,200	.0325	.0085	.0027
1,500	.0495	.0150	.0053
2,000	.0775	.0271	.0112
2,500	.1055	.0400	.0187
3,000	.1338	.0533	.0272
3,500	.1631	.0669	.0364
4,000	.1935	.0808	.0462
4,000	.2252	.0951	.0565
5,000	.2584	.1097	.0673

TABLE 3. Amounts by which the thermodynamic functions for CO₂ for the natural isotopic mixture exceed those for C¹²O¹⁶O₂

[The entropy of mixing of the different isotopic molecules and nuclear-spin entropies have been omitted.]

T	C_p^0/R	$(H^0 - F_0^0)/RT$	$-(F^0 - F_0^0)/RT$	S^0/R
°K				
100	0.00006	0.00001	0.00092	0.00093
200	.0007	.0002	.0010	.0012
300	.0009	.0004	.0011	.0015
400	.0009	.0005	.0013	.0018
500	.0008	.0006	.0014	.0020
600	.0008	.0006	.0015	.0021
700	.0008	.0007	.0016	.0023
800	.0008	.0007	.0017	.0024
900	.0007	.0007	.0018	.0025
1,000	.0007	.0007	.0018	.0025
1,200	.0006	.0007	.0019	.0026
1,500	.0005	.0007	.0021	.0028
2,000	.0003	.0006	.0023	.0029
2,500	.0002	.0005	.0024	.0029
3,000	.0002	.0005	.0025	.0030
3,500	.0001	.0004	.0026	.0030
4,000	.0001	.0004	.0026	.0030
4,500	.0001	.0003	.0027	.0030
5,000	.0001	.0003	.0027	.0030

indicates an uncertainty of $\pm 0.00010 \text{ cm}^{-1}$, or about one-sixth of their values. For each temperature the sum of the separate uncertainties has been obtained. It is to be recognized that the actual uncertainty is probably considerably greater in view of the arbitrary values assigned and the neglect of part of the constants in making these estimates.

A comparison of table values with the experimental values reported by Masi and Petkof follows:

Temperature	C_p^0/R (calculated)	C_p^0/R (experimental)
°K		
243.16	4.1483	4.148
273.16	4.3250	4.324
323.16	4.6005	4.604
363.16	4.8009	4.804

TABLE 4. Partial list of uncertainties

Constants	C_p^0/R	H^0/RT	$(-F^0/RT)$
Temperature 300° K			
ν_2	0.0002	0.0001	0.00004
x_{22}0002	.00005	.00002
W_000002	.000005	.00001
α0003	.00007	.00002
Sum.....	0.0007	0.0002	0.00008
Temperature 1,000° K			
ν_2	0.00004	0.0001	0.0002
x_{22}002	.0007	.0004
W_000007	.00004	.00002
α001	.0006	.0003
Sum.....	0.003	0.0015	0.001
Temperature 3,000° K			
ν_2	0.000006	0.00004	0.0003
Linear x_{22}006	.003	.002
Quadratic x_{22}001	.0003	.0001
Cubic x001	.0002	.0001
W_00002	.0001	.0001
α004	.002	.002
Sum.....	0.012	0.006	0.005
Temperature 5,000° K			
ν_2	0.000002	0.00003	0.0003
Linear x_{22}01	.005	.004
Quadratic x_{22}003	.0009	.0004
Cubic x0047	.0012	.0004
W_00004	.0002	.0002
α007	.003	.003
Sum.....	0.025	0.01	0.008

Values of coefficients of change of thermodynamic properties with respect to small changes of spectroscopic constants are given in tables 5, 6, and 7, for the anharmonicity, rotation-vibration interaction, and the azimuthal $B+x_{11}$ constants. If ensuing revisions of these constants involve only small changes, the corresponding revised thermodynamic functions can be adequately approximated with small proportionate changes.

TABLE 5. Coefficients for change of C_p^0/R with change of spectroscopic constants

Values given are $10^6 c_{ij} d(C_p^0/R)/dc_i$.

T	$c_i = x_{11}$	x_{22}	x_{33}	x_{12}	x_{13}	x_{23}	α_1	α_2	α_3	$B+x_{11}$
°K										
300	0.008	1.26	0	-0.19	0	0.012	0.10	-1.57	0.013	-3.6
600	.59	6.9	.09	-3.6	.45	2.6	.70	-3.9	.92	-5.4
1,000	2.3	13.8	1.78	-9.8	3.9	14.3	1.42	-6.6	3.54	-8.4
1,200	3.2	17.2	3.4	-12.6	6.2	21	1.74	-7.9	4.8	-9.9
1,500	4.5	22	6.3	-16.8	9.9	31	2.2	-9.9	6.5	-12.0
2,000	6.5	31	11.6	-23	15.9	48	3.0	-13.3	9.1	-15.4
3,000	10.3	49	23	-36	28	83	4.5	-20	14.0	-21
4,000	14.0	69	35	-50	41	122	5.9	-27	18.8	-26
5,000	17.9	92	49	-64	55	165	7.4	-33	23	-30

TABLE 6. Coefficients for change of $(H^\circ - E_0^\circ)/RT$ with change of spectroscopic constants

Values are $10^3 c_i d[(H^\circ - E_0^\circ)/RT]/dc_i$.

T	$c_1 = x_{11}$	x_{22}	x_{33}	x_{12}	x_{13}	x_{23}	α_1	α_2	α_3	$B+x_{11}$
$^\circ K$										
300	0.001	0.22	0	-0.022	0	0.001	0.015	-0.45	0.001	-1.48
600	.105	2.1	.009	-.82	.056	.38	.20	-1.61	.161	-3.0
1,000	.64	5.4	.30	-3.2	.80	3.4	.55	-3.1	.98	-4.5
1,200	1.00	7.1	.67	-4.5	1.51	5.8	.72	-3.8	1.51	-5.3
1,500	1.57	9.6	1.51	-6.6	2.8	9.9	.97	-4.8	2.3	-6.4
2,000	2.5	13.8	3.4	-9.9	5.4	17.4	1.37	-6.5	3.7	-8.3
3,000	4.5	23	8.0	-16.6	10.9	33	2.2	-9.9	6.3	-11.7
4,000	6.4	32	13.2	-23	16.8	51	2.9	-13.2	8.9	-14.7
5,000	8.3	41	18.9	-30	23	69	3.6	-16.6	11.3	-17.4

TABLE 7. Coefficients for change of $-(F^\circ - E_0^\circ)/RT$ with change of spectroscopic constants.

Values given are $10^3 c_i d[-(F^\circ - E_0^\circ)/RT]/dc_i$.

T	$c_1 = x_{11}$	x_{22}	x_{33}	x_{12}	x_{13}	x_{23}	α_1	α_2	α_3	$B+x_{11}$
$^\circ K$										
300	0	0.039	0	-0.002	0	0	0.002	-0.136	0	-0.60
600	.018	.70	.001	-.188	.007	.058	.060	-.81	.029	-2.1
1,000	.182	2.5	.049	-1.13	.169	.84	.24	-1.98	.280	-4.0
1,200	.33	3.7	.134	-1.83	.38	1.67	.36	-2.6	.51	-4.9
1,500	.61	5.5	.37	-3.1	.85	3.40	.55	-3.6	.93	-6.2
2,000	1.20	8.9	1.05	-5.4	2.0	7.3	.88	-5.2	1.80	-8.3
3,000	2.6	16.1	3.3	-10.7	5.2	17.3	1.59	-8.4	3.8	-12.3
4,000	4.2	24	6.2	-16.4	9.2	29	2.3	-11.7	6.0	-16.1
5,000	5.8	32	9.8	-22	13.5	43	3.0	-15.1	8.2	-19.7

5. References

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