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 $\nu_1 = 1342.86$ cm^{-1}, $\nu_2 = 667.30$ cm^{-1}, $x_{11} = -2.20$ cm^{-1}, $x_{22} = -0.75$ cm^{-1}, $x_{12} = 3.76$ cm^{-1}, and $x_{ll} = 1.03$ cm^{-1}, given by Taylor, Benedict, and Strong [5], with $\nu_3 = 2349.15$ cm^{-1}, $x_{13} = -18.54$ cm^1, and $x_{23} = -12.48$ cm^{-1}, as indicated in a private communication from Benedict, and $x_{33} = -12.46$ cm^{-1}, chosen to fit the observed 11496.5 cm^{-1} at $v_3 = 5$. 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 0.132×10^{-6} cm^{-1} was used on the ground that it was not ruled out by a preliminary empirical value of $(0.165$ cm$^{-1} \pm 0.02$ cm$^{-1})$ $\times 10^{-6}$ of Plyler. For rotational-vibrational interaction, the values $\alpha_1 = 0.00056$ cm^{-1} and $\alpha_2 = -0.00062$ cm^{-1} were given by Herzberg [6], and $\alpha_3 = 0.0031$ 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 $\omega_2 = \nu_2 - x_{ll}$. 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 $B + x_{ll}$ 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

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

allowed tabular integration to give the other functions, duplicating the directly calculated values to about one in the fourth decimal place up to 1,000° K and satisfactorily at higher temperatures. $S°/R$ is given as the sum of $(H°-E_0°)/RT$ and $-(F°-E_0°)/RT$, as tabulated. The translational contribution to the latter is $(5/2) \ln T + (3/2) \ln M + \ln (2\pi^{3/2}) k^{5/2}/(h^3 N_0^{3/2} P_0)$, evaluated as $(5/2) \ln T + 2.0121$, based on $M = 44.01$ for molecular weight and values for the physical constants. The value used for hc/k is 1.43847 cm deg.

4. Thermodynamic Functions

The thermodynamic functions calculated for carbon dioxide include heat capacity, enthalpy, free energy, and entropy for the standard ideal gas state. The properties are listed in the dimensionless forms $C_p°/R$, $(H°-E_0°)/RT$, $-(F°-E_0°)/RT$, and $S°/R$ in table 1. The corrections added to the harmonic-oscillator rigid-rotator functions based on ν_1, ν_2, and ν_3, to obtain $C_p°/R$, $(H°-E_0°)/RT$, and $-(F°-E_0°)/RT$ for $C^{12}O_2^{16}$, are given in table 2.

The amounts by which the functions for the natural mixture (omitting entropy of isotope mixing and of nuclear spin) exceed those for $C^{12}O_2^{16}$ are given in table 3.

Although it was desired to produce an accurate table of thermodynamic functions, the new values have considerable uncertainty. Using some arbitrarily assigned uncertainties for some of the constants, rough estimates of the magnitude of the uncertainties for the functions $C_p°/R$, $(H°-E_0°)/RT$, and $-(F°-E_0°)/RT$ are listed in table 4 for 300°, 1,000°, 3,000°, and 5,000° K. Uncertainties of 0.1 cm^{-1} for ν_2 and x_{22} have been taken arbitrarily and may be too small. A 2-percent uncertainty in the Fermi effect as computed is consistent with the order of magnitude of the 1.3−cm^{-1} difference in different values of W_0. For α_1 and α_2 Herzberg

TABLE 1. *"Ideal gas" thermodynamic properties of CO₂ (natural isotopic mixture)*

T	$C_p°/R$	$(H°-E_0°)/RT$	$-(F°-E_0°)/RT$	$S°/R$	T	$C_p°/R$	$(H°-E_0°)/RT$	$-(F°-E_0°)/RT$	$S°/R$	T	$C_p°/R$	$(H°-E_0°)/RT$	$-(F°-E_0°)/RT$	$S°/R$
°K					°K					°K				
50	3.5001	3.4963	15.5922	19.0885	550	5.5371	4.3602	24.3981	28.7583	1,250	6.826	5.453	28.415	33.868
60	3.5002	3.4969	16.2297	19.7266	560	5.5691	4.3815	24.4769	28.8584	1,300	6.872	5.506	28.630	34.136
70	3.5006	3.4974	16.7688	20.2662	570	5.6006	4.4026	24.5546	28.9572	1,350	6.913	5.558	28.839	34.397
80	3.5020	3.4979	17.2358	20.7337	580	5.6315	4.4235	24.6314	29.0549	1,400	6.952	5.607	29.042	34.649
90	3.5055	3.4985	17.6479	21.1464	590	5.6618	4.4443	24.7072	29.1515	1,450	6.988	5.654	29.239	34.893
100	3.5128	3.4995	18.0165	21.5160	600	5.6915	4.4648	24.7820	29.2468	1,500	7.021	5.699	29.432	35.131
110	3.5249	3.5013	18.3501	21.8514	610	5.7207	4.4852	24.8560	29.3412	1,600	7.082	5.783	29.802	35.585
120	3.5432	3.5039	18.6549	22.1588	620	5.7494	4.5053	24.9291	29.4344	1,700	7.134	5.861	30.155	36.016
130	3.5680	3.5079	18.9355	22.4434	630	5.7775	4.5253	25.0013	29.5266	1,800	7.180	5.933	30.492	36.425
140	3.5995	3.5133	19.1957	22.7090	640	5.8052	4.5451	25.0728	29.6179	1,900	7.222	6.000	30.815	36.815
150	3.6372	3.5202	19.4383	22.9585	650	5.8324	4.5647	25.1434	29.7081	2,000	7.258	6.062	31.124	37.186
160	3.6804	3.5289	19.6657	23.1946	660	5.8591	4.5841	25.2132	29.7973	2,100	7.291	6.120	31.421	37.541
170	3.7282	3.5392	19.8800	23.4192	670	5.8853	4.6033	25.2823	29.8856	2,200	7.320	6.174	31.707	37.881
180	3.7800	3.5511	20.0826	23.6337	680	5.9110	4.6223	25.3506	29.9729	2,300	7.347	6.224	31.983	38.207
190	3.8347	3.5646	20.2750	23.8396	690	5.9363	4.6412	25.4183	30.0595	2,400	7.371	6.271	32.249	38.520
200	3.8916	3.5795	20.4582	24.0377	700	5.9611	4.6599	25.4852	30.1451	2,500	7.393	6.316	32.506	38.822
210	3.9502	3.5957	20.6332	24.2289	710	5.9855	4.6784	25.5514	30.2298	2,600	7.414	6.358	32.754	39.112
220	4.0097	3.6132	20.8009	24.4141	720	6.0094	4.6967	25.6170	30.3137	2,700	7.433	6.397	32.995	39.392
230	4.0695	3.6317	20.9619	24.5936	730	6.0329	4.7149	25.6819	30.3968	2,800	7.451	6.435	33.228	39.663
240	4.1296	3.6512	21.1169	24.7681	740	6.0559	4.7328	25.7461	30.4789	2,900	7.468	6.470	33.455	39.925
250	4.1892	3.6716	21.2663	24.9379	750	6.0786	4.7506	25.8098	30.5604	3,000	7.484	6.503	33.675	40.178
260	4.2484	3.6926	21.4107	25.1033	760	6.1009	4.7682	25.8728	30.6410	3,100	7.499	6.535	33.888	40.423
270	4.3068	3.7143	21.5505	25.2648	770	6.1228	4.7857	25.9353	30.7210	3,200	7.513	6.566	34.096	40.662
280	4.3643	3.7365	21.6860	25.4225	780	6.1442	4.8030	25.9971	30.8001	3,300	7.526	6.595	34.299	40.894
290	4.4208	3.7591	21.8175	25.5766	790	6.1653	4.8201	26.0584	30.8785	3,400	7.539	6.622	34.496	41.118
300	4.4763	3.7821	21.9453	25.7274	800	6.1860	4.8370	26.1192	30.9562	3,500	7.551	6.649	34.688	41.337
310	4.5307	3.8054	22.0697	25.8751	810	6.2064	4.8538	26.1794	31.0332	3,600	7.563	6.674	34.876	41.550
320	4.5840	3.8289	22.1909	26.0198	820	6.2264	4.8704	26.2390	31.1094	3,700	7.575	6.698	35.059	41.757
330	4.6361	3.8525	22.3091	26.1616	830	6.2460	4.8869	26.2982	31.1851	3,800	7.586	6.721	35.238	41.959
340	4.6871	3.8763	22.4244	26.3007	840	6.2653	4.9032	26.3568	31.2600	3,900	7.597	6.743	35.413	42.156
350	4.7371	3.9002	22.5371	26.4373	850	6.2843	4.9193	26.4149	31.3342	4,000	7.608	6.765	35.584	42.349
360	4.7859	3.9241	22.6473	26.5714	860	6.3029	4.9353	26.4725	31.4078	4,100	7.618	6.786	35.751	42.537
370	4.8335	3.9481	22.7552	26.7033	870	6.3212	4.9511	26.5297	31.4808	4,200	7.628	6.806	35.915	42.721
380	4.8801	3.9720	22.8608	26.8328	880	6.3392	4.9668	26.5863	31.5531	4,300	7.638	6.825	36.075	42.900
390	4.9257	3.9959	22.9643	26.9602	890	6.3569	4.9823	26.6426	31.6249	4,400	7.647	6.843	36.233	43.076
400	4.9704	4.0197	23.0657	27.0854	900	6.3742	4.9977	26.6983	31.6960	4,500	7.657	6.861	36.387	43.248
410	5.0140	4.0434	23.1653	27.2087	910	6.3913	5.0129	26.7536	31.7665	4,600	7.666	6.879	36.538	43.417
420	5.0566	4.0670	23.2630	27.3300	920	6.4080	5.0280	26.8085	31.8365	4,700	7.676	6.896	36.686	43.582
430	5.0983	4.0905	23.3590	27.4495	930	6.4244	5.0429	26.8629	31.9058	4,800	7.685	6.912	36.831	43.743
440	5.1392	4.1139	23.4533	27.5672	940	6.4406	5.0577	26.9169	31.9746	4,900	7.694	6.928	36.974	43.902
450	5.1792	4.1371	23.5460	27.6831	950	6.4565	5.0723	26.9705	32.0428	5,000	7.702	6.943	37.114	44.057
460	5.2183	4.1602	23.6372	27.7974	960	6.4721	5.0868	27.0237	32.1105					
470	5.2566	4.1831	23.7269	27.9100	970	6.4874	5.1012	27.0765	32.1777					
480	5.2942	4.2059	23.8152	28.0211	980	6.5025	5.1154	27.1289	32.2443					
490	5.3310	4.2285	23.9022	28.1307	990	6.5173	5.1295	27.1809	32.3104					
500	5.3671	4.2509	23.9878	28.2387	1,000	6.5318	5.1434	27.2325	32.3759					
510	5.4024	4.2731	24.0722	28.3453	1,050	6.601	5.211	27.485	32.696					
520	5.4371	4.2952	24.1554	28.4506	1,100	6.664	5.276	27.729	33.005					
530	5.4711	4.3170	24.2374	28.5544	1,150	6.723	5.337	27.965	33.302					
540	5.5044	4.3387	24.3183	28.6570	1,200	6.776	5.396	28.193	33.589					

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

T	C_p°/R	H°/RT	$(-F^\circ/RT)$
$^\circ K$			
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 CO_2 for the natural isotopic mixture exceed those for $C^{12}O^{16}_2$*

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

T	C_p°/R	$(H^\circ - F_0^\circ)/RT$	$-(F^\circ - F_0^\circ)/RT$	S°/R
$^\circ K$				
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 ± 0.00010 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	$C_p^\circ R$ (calculated)	$C_p^\circ R$ (experimental)
$^\circ K$		
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/R	H/RT	$(-F/RT)$
Temperature 300° K			
ν_2	0.0002	0.0001	0.00004
x_{22}	.0002	.00006	.00002
W_0	.00002	.000005	.000001
α	.0003	.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_0	.00007	.00004	.00002
α	.001	.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 x	.001	.0002	.0001
W_0	.0002	.0001	.0001
α	.004	.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 x	.0047	.0012	.0004
W_0	.0004	.0002	.0002
α	.007	.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 $B + x_{ll}$ 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°/R with change of spectroscopic constants*

Values given are $10^3 c_j d(C_p^\circ/R)/dc_j$.

T	$c_j = x_{11}$	x_{22}	x_{33}	x_{12}	x_{13}	x_{23}	α_1	α_2	α_3	$B+x_{ll}$
$^\circ K$										
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 $(H° - E_0°)/RT$ with change of spectroscopic constants*

Values are $10^3 c_j d[(H° - E_0°)/RT]/dc_j$.

T	$c_j = x_{11}$	x_{22}	x_{33}	x_{12}	x_{13}	x_{23}	α_1	α_2	α_3	$B + x_{11}$
°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 $-(F° - E_0°)/RT$ with change of spectroscopic constants.*

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

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	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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