

Thermodynamic Data for Carbon Dioxide at High Pressure and Temperature

P. E. LILEY¹

Imperial College of Science and Technology, London, S.W.7, England

During a research program undertaken to investigate the thermodynamic properties of certain mixtures containing carbon dioxide as one component, it was discovered that very few data for pure carbon dioxide were available at temperatures above 150° C. Table I lists recent work on the thermodynamic properties of this vapor. At the period of compilation of these data, the only information available for temperatures above 150° C. was that provided by Sweigert, Weber, and Allen (44) [which had been questioned by Granet and Kass (6)], the original NBS-NACA values of properties at zero pressure only (37), and the experimental investigation of MacCormack and Schneider (14) to 50-atm. pressure from which thermodynamic functions were computed (15) using the same basic spectroscopic data (8) as those used by the National Bureau of Stand-

¹Present address, Purdue University, Lafayette, Ind.

ards. It was therefore decided to tabulate values at much closer temperature and pressure intervals than the data then available, and to extend the tabulation to 200-atm. pressure. This led to the work described below.

ENTHALPY DATA

If the virial equation

$$PV = A + BP = CP^2 + DP^3 + \dots \quad (1)$$

is a valid equation of state for the gas, then it is easily shown that the general thermodynamic relation

$$H(P, T) = \int_{T_0}^T C_p(0, T) dT + \int_0^P \{V - T(\partial V / \partial T)_p\} dP$$

Table I. Some Recent Work on Thermodynamic Properties of Carbon Dioxide

Year	Author(s)	Ref.	Function(s)	Temp., Range, °C.	Pressure Range, Atm.
1935	Michels, A., Michels, C.	(24)	PV	0-150	16-250
1935	Michels, A., others	(26)	PV	0-150	70-3000
1936	Quinn, E. L., Jones, C. L.	(38)	H, S, C _p , etc.	Misc.	Misc.
1937	Michels, A., others	(25, 29)	PV	0-150	18-3117
1937	Michels, A., others	(21)	PV	2.85-40.08	36.32-98.45
1937	Michels, A., others	(20)	H, S, etc.	25-150°	0-600 amagats
1939	Deming, W. E., Deming, L. S.	(3)	f/p	0(5)30(10)50(25)150	1(25)100(50)200.2500
1942	Ellenwood, F. O., others	(5)	C _p , C _v	0-4000° F.	0-10000 p.s.i.a.
1942	Maron, S. H., Turnbull, D.	(16)	...	137, 198, 258	1000
1942	Meyers, C. H.	(19)	P, V	Critical temp.	...
1942	Roebuck, J. R., others	(40)	...	-75(25)0(10)100(25)150(50)300	1-200
1942	Smallwood, J. C.	(43)	C _p
1944	Reamer, H. H., others	(39)	P, V, T	100(60)460° F.	0-10000 p.s.i.a.
1946	N.D.R.C. Summ. Tech. Rep.	(32)
1946	Sweigert, R. L., others	(44)	H, S, V	75-1800° F.	0.15-3000 p.s.i.a.
1948	Gratch, S.	(9)	Review	0-150	0-3000
1948	de Groot, S. R., Michels, A.	(10)	μ, C _p	25-150°	0-2000
1948	Michels, A., de Groot, S. R.	(22)	H, S, C _p , etc.	25-150°	1-600
1948	Michels, A., de Groot, S. R.	(23)	H, S, PV, etc.	25-150°	1-2000
1949	Gratch, S.	(8)	C _p , etc.	100(misc.) 5000° R.	0
1949	Oishi, J.	(33)	P, V, T	0, 100	0.57 to 1.23
1950	Gratch, S.	(7)	C _p	100(misc.) 5000° R.	0
1950	Huggill, J. A. W., others	(11)	H, S, V	-80(10)150	1-3000
1950	MacCormack, K. E., Schneider, W. G.	(14)	P, V, T	0(50)200(100)600	0-50
1950	MacCormack, K. E., Schneider, W. G.	(15)	H, S, C _p , etc.	0(50)200(100)600	0(10)50 and 1
1950	Michels, A., Stryland, J. C.	(27)	C _v	20-40	140 to 425 amagats
1950	Michels, A., others	(28)	Vapor pressure	-56 to 3	5-37
1950	N.B.S.-N.A.C.A. Tables	(31)	H, S, C _p , etc.	60(10)800(50) 2700° K.	0
1951	Kendall, B. J., Sage, B. H.	(12)	P, V, T	40-460° F.	200-100000 p.s.i.a.
1951	Schneider, W. G., Chynometh, A.	(41)	C _v	Critical temp.	...
1952	Granet, I., Kass, P.	(6)	C _p	100-1500° F.	0-2000 p.s.i.a.
1952	Masi, J. F., Petkof, B.	(18)	C _p	-30, 0, 50, 90	0.5, 1, 1.5
1952	Schrock, V. E.	(42)	C _p	35-350	1-67
1952	Wentorf, R. H., Jr.	(45)	P, V, T	31.02-31.10	72.723-72.974
1953	Price, D.	(36)	H, S, PV, C _p , etc.	0-1000	0-40 amagats (< 100)
1953	Woolley, H. W.	(46)	C _p /C _v	23.8	0-22.22
1954	Kennedy, G. C.	(13)	P, V, T	0(10)1000° K.	25-1400 bars
1954	Masi, J. F.	(17)	C _p , review	250-1500° K.	1
1954	Price, D.	(37)	H, S, PV, C _p , etc.	100(50)500(100)1000	50-1400 bars
1954	Woolley, H. W.	(47)	H, S, C _p	50(10)1000(50)1500(100)5000° K.	0
1955	N.B.S.	(30)	H, S, C _p , etc.	50(10)1000(50)1500(100)5000° K.	0-100
1955	Pfefferle, W. C., others	(34)	P, V, T	30	3.684-53.633
1955	Price, D.	(35)	P, V, H, S	100(50)500(100)1000	50-1400 bars
1956	Baker, H. W.	(1)	H	-140	-1400 p.s.i.a.
1956	Din, F., ed.	(4)	H, S, V, etc.	-80(10)150, etc.	0.5-3000
1956	Wentorf, R. H., Jr.	(45)	P, V, T	31.02-31.10	72.723-72.974
1957	Cook, D.	(2)	P, V, T	-60 to 30	0.5-2.5
1957	This work	...	H, V	150(10)650	1-200

^aTabulated principally at 25° C. intervals.

reduces to

H(P,T) = H(0,T) + (B - TdB/dT)P + (C - TdC/dT)P^2/2 + (D - TdD/dT)P^3/3 + ... (2)

so that, from a knowledge of the zero pressure function H(0,T), the virial coefficients and their temperature derivatives, the enthalpy at any pressure, P, and temperature, T, can readily be computed.

H(P,T) = H(0,T) + (B - TdB/dT)P - c (3)

i.e., it has been assumed that all virial coefficients higher than the second are negligible. This assumption was postulated by Schneider (14) from experimental work and has also been shown to be valid by analysis of a few compressibility measurements made by the author in a similar pressure and temperature range.

c = integral from 0 to 1 of {V - T(delta V / delta T)_P} dp at T = T_0 = 273.16° K.

According to MacCormack and Schneider (15), c = -12.53 cal. per mole.

The zero pressure data of Gratch (8) as tabulated by Woolley (31) have been interpolated to give values of H(0,T) for every 10° from 150° to 650°C.

The data of Table II are compared with other work in Table III. Despite the numerous tabulations of thermodynamic functions listed in Table I, only MacCormack and Schneider listed zero pressure values in 1952, apart from the source values (37).

The agreement of the data for higher pressures is fairly satisfactory except possibly for the highest pressures at 150° C. The divergence in values here can be taken as indicative of the uncertainty existing in the virial coefficients and shows that high

Table II. Enthalpy of Carbon Dioxide (Units: Calories per mole. Enthalpy zero, 0° C., 1 atm.)

Table with 21 columns representing pressure in atmospheres (0 to 200) and 21 rows representing temperature in degrees Celsius (150 to 650). The cells contain numerical values for enthalpy.

precision is necessary if accurate virial derivatives are to be obtained. The estimated uncertainty of these values is given in Table IV; with the exception mentioned above, all the published values fall inside the limits assigned in Table IV.

VOLUMETRIC BEHAVIOR

Values are given, in Table V, of the first and second virial coefficients for the temperature range 150° to 650° C., so that

volumetric data can readily be obtained by applying the virial equation

$$PV = A + BP \quad (4)$$

These values were obtained by interpolation of those quoted by MacCormack and Schneider (14) for six temperatures from 150° to 650° C. A few compressibility measurements made by the author in this temperature range gave virial values in excellent agreement with those quoted in Table V. Since completion of this work, a discussion of such data has appeared (30) which will enable the agreement between the values of MacCormack and Schneider (14) and other data to be assessed. The fuller

Table III. Comparison of Enthalpy Data^a for Carbon Dioxide

Temp., °C.	Pressure, Atm.					Source
	0	1	10	50	100	
150	1414.99	1410.1	1365.9	1169.6	924	This (16)
	1415.05	1410.1	1366.0	1169.7		
		1414.9	1384.1	1209.8	930	
		1409.8		1162.9	897	
200		1397.6	1369.9		892.6	This (16)
	1927.42	1923.6	1889.1	1735.7	1544	
	1927.48	1923.6		1735.8		
		1928.5	1893.7		1517.5	
250		2455.5	2428.2	2156		This (30)
		2461.5	2433.8		2116.8	
300	3006.46	3004.0	2891.8	2883.3	2760	This (16)
	3006.59	3004.1		2880.8		
		3011.9	2988.1		2729.7	
350		3567.6	3549.4		3368	This (30)
		2478.0	3558.0		3343.1	
400	4147.38	4145.7	4131.0	4065.3	3983	This (16)
	4147.22	4145.6		4065.7		
		4156.7	4141.0		3959.7	
450		4736.6	4724.7		4606	This (30)
		4749.0	4735.4		4783.4	
500	5338.55	5337.5	5327.9	5385.5	5232	This (16)
	5339.15	5338.1		5286.0		
		5352.5	5341.1		5211.4	
550		5950.6	5943.1		5868	This (30)
		5967.8	5958.5		5846.7	
600	6573.50	6572.9	6567.2	6541.9	6510	This (16)
	6573.73	6573.1		6542.3		
		6591.7	6584.1		6487.5	
650		7204.1	7200.1		7160	This (30)
		7224.7	7218.3		7134.8	

At 150° C., and 150 atm., $H = 679$ (This) and 683 (17). At 150° C., and 200 atm., $H = 433$ (This), 459 (17), and 374 (23).

^aEnthalpy unit, cal./mole.

Enthalpy zero, 0° C. 1 atm.

One amagat unit of energy = $RT_0/A_0 = 539.02$ cal./mole.

$R = 1.98718$ cal./mole °K. $T_0 = 273.16$ °K.

$A_0 =$ volume per mole of CO_2 /volume per mole perfect gas.

Table IV. Estimated Uncertainties in Values of Table II for the Enthalpy of Carbon Dioxide Vapor^a

Pressure Atm.	Temp., °C.						
	150	200	250	300	400	500	600
1	0.15	0.15	0.15	0.18	0.20	0.25	0.30
10	2.6	2.1	1.8	1.4	1.0	0.8	0.6
50	13	10	7.7	6.5	4.1	2.7	1.8
100	25	20	15	13	8	6	3.5
150	38	30	23	19.5	12	9	5.3
200	51	40	30	26	16	11	7

^aThese uncertainties are those introduced in interpolation of original NBS zero pressure data (37) and in estimation of coefficients $B-TdB/dT$ at various temperatures from a plot of values deduced from Equation 3. Zero pressure data have been revised (47) since this material was completed, and uncertainties do not include differences between two sets of zero-pressure tabulations (37,47).

Table V. Virial Coefficients of Carbon Dioxide Interpolated from the Work of MacCormack and Schneider (15).

T., °C.	A_T^a		$PV(P = 50)^a$		$-10^3 B_T^a$	
	McC&S	This	McC&S	This	McC&S	This
150	1.560050	1.560050	1.44640	1.446400	2.273	2.273
160	...	1.596917	...	1.491267	...	2.113
170	...	1.633784	...	1.535784	...	1.951
180	...	1.670560	...	1.582050	...	1.772
190	...	1.707517	...	1.624017	...	1.670
200	1.744383	1.744380	1.66785	1.667880	1.531	1.530
210	...	1.781250	...	1.710000	...	1.425
220	...	1.818120	...	1.752070	...	1.321
230	...	1.854980	...	1.793580	...	1.228
240	...	1.891850	...	1.835500	...	1.127
250	...	1.928720	...	1.877070	...	1.033
260	...	1.965580	...	1.918430	...	0.943
270	...	2.002450	...	1.959750	...	0.854
280	...	2.039320	...	2.007270	...	0.781
290	...	2.076183	...	2.041583	...	0.692
300	2.113050	2.113050	2.08257	2.082400	0.610	0.613
310	...	2.149920	...	2.122870	...	0.541
320	...	2.186783	...	2.163333	...	0.469
330	...	2.223650	...	2.203650	...	0.400
340	...	2.260520	...	2.243720	...	0.336
350	...	2.297380	...	2.283180	...	0.284
360	...	2.335250	...	2.322400	...	0.237
370	...	2.371117	...	2.360417	...	0.194
380	...	2.407983	...	2.400533	...	0.149
390	...	2.444850	...	2.439500	...	0.107
						$10^3 B_T^a$
400	2.481717	2.481720	2.47818	2.478220	-0.071	-0.070
410	...	2.518584	...	2.517134	...	-0.029
420	...	2.555450	...	2.555900	...	-0.009
430	...	2.592320	...	2.594620	...	0.046
440	...	2.629184	...	2.633284	...	0.082
450	...	2.666050	...	2.673900	...	0.117
460	...	2.702910	...	2.710410	...	0.150
470	...	2.739784	...	2.748934	...	0.183
480	...	2.776650	...	2.787300	...	0.213
490	...	2.813517	...	2.825717	...	0.244
500	2.850384	2.850383	2.86400	2.864033	0.272	0.273
510	...	2.887250	...	2.902350	...	0.302
520	...	2.924120	...	2.904620	...	0.330
530	...	2.960383	...	2.978383	...	0.362
540	...	2.997850	...	3.017350	...	0.391
550	...	3.034717	...	3.055467	...	0.415
560	...	3.071583	...	3.036983	...	0.442
570	...	3.108449	...	3.131849	...	0.468
580	...	3.145317	...	3.170017	...	0.494
590	...	3.182183	...	3.208133	...	0.519
600	3.219050	3.219050	3.2465	3.246250	0.544	0.544
610	...	3.255917	...	3.284367	...	0.569
620	...	3.292784	...	3.322434	...	0.593
630	...	3.329650	...	3.360550	...	0.618
640	...	3.366517	...	3.398567	...	0.641
650	...	3.403384	...	3.436634	...	0.665

^a A_T, B_T, PV are in amagat units. $A_0 = 1.00705$.

^bNormal volume = 22258.2 cc./mole.

discussion of the NBS tabulation by Masi (30) has not yet appeared.

OTHER WORK

Since the above computations were completed, extensive tables of thermodynamic properties (4, 30, 35-37) have appeared. Some (4, 30) are revisions of tables (11, 31) incorporated in the comparisons above, while the data of Price (35-37) are based upon volumetric determinations of Kennedy (13). Values given by Kennedy do not appear to be sufficiently accurate for comparison of virial coefficients with those of Table V. The newer tabulation (30) contains zero pressure values for carbon dioxide (47) which differ from the original data (31). The second portion of Table III compares the data of Table II and (30). Except at the higher pressures and at 150° C. agreement to 1% exists.

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Measurement of the Thermal Properties of Carbonaceous Materials

J. D. BATCHELOR, P. M. YAVORSKY and EVERETT GORIN
Research and Development Division, Consolidation Coal Co., Library, Pa.

Many processes for the treatment of coal involve thermal conversion. In process development, thermal data on the materials are desirable. This work was designed to supply such thermal data for carbonaceous materials. Heat capacity measurements were made on a bituminous coal from the Pittsburgh seam and its low-temperature char. Thermal conductivity was measured on a coal-char-pitch briquet. Finally, an estimate was made of the heat transfer film coefficient from a fluidized heating medium to a spherical briquet. This latter work was carried out so that the thermal parameters could be applied to the calculation of heating rates for carbonaceous briquets, an application which is described in an article in the July issue of *I/EC* on heat transfer in the carbonization of briquets (17).

The companion article on "Heat Transfer and Thermal Stresses in Carbonization of Briquets" appears in the July issue of *Industrial and Engineering Chemistry*, Vol. 51, page 833.

LITERATURE SURVEY

The heat capacity data for coal and coke were reviewed by Clendenin and others (3). A correlation equation for the specific heat capacity of moisture-free coal is presented, based on data for 23 American bituminous coals. The equation expresses heat capacity as a linear function of temperature and volatile matter content, but is not expected to hold into the temperature range in which coal becomes plastic. In fact, the very limited data included in the correlation for temperatures above 100° C. make its use above about 150° C. an unjustifiable extrapolation.

The heat capacity of a material undergoing thermal decomposition such as bituminous coal in the plastic range loses