

Thermodynamic Data for Carbon Dioxide at High Pressure and Temperature

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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-

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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

$$H(P, T) = \int_{T_0}^T Cp(0, T)dT + \int_0^P [V - T(\partial V/\partial T)_P]dP$$

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,Cp, etc. | Misc. | Misc. |
| 1937 | Michels, A., others | (25,29) | PV | 0-150 | 18-3117 |
| 1937 | Michels, A., others | (27) | PV | 2.85-40.08 | 36.32-98.45 |
| 1937 | Michels, A., others | (20) | H,S,etc. | 25-150 ^a | 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 ^a | 0-2000 |
| 1948 | Michels, A., de Groot, S. R. | (22) | H,S,Cp, etc. | 25-150 ^a | 1-600 |
| 1948 | Michels, A., de Groot, S. R. | (23) | H,S,PV, etc. | 25-150 ^a | 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,Cp,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,Cp,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. | (7) | 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

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

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. The actual form used for the computation of the enthalpy data was

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

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. In Equation 3, c is a correction factor inserted so that the zero of enthalpy occurs at 0°C. and 1 atm.

$$c = \int_0^1 \{V - T(\partial V/\partial T)_p\} dP \text{ at } T = T_0 = 273.16^\circ \text{K.}$$

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

| T, °C. | Pressure Atmospheres | | | | | | | | | | | | | | | | | | | | | | | | | | |
|-----------|----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|------|------|------|------|------|------|------|------|------|------|
| | 0 | 1 | 2 | 3 | 4 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 60 | 70 | 80 | 90 | 100 | 110 | 125 | 150 | 175 | 200 | | |
| 150 | 1415.0 | 1410.1 | 1405.2 | 1400.3 | 1395.4 | 1390.5 | 1365.9 | 1341.4 | 1316.8 | 1292.3 | 1267.8 | 1243.2 | 1218.7 | 1194.2 | 1169.6 | 1120 | 1071 | 1022 | 973 | 924 | 875 | 802 | 769 | 556 | 433 | | |
| 160 | 1515.9 | 1511.3 | 1506.6 | 1502.0 | 1497.3 | 1492.7 | 1469.4 | 1446.1 | 1422.9 | 1399.6 | 1376.3 | 1353.1 | 1329.8 | 1306.5 | 1283.3 | 1237 | 1190 | 1144 | 1097 | 1051 | 1004 | 934 | 818 | 702 | 585 | | |
| 170 | 1617.6 | 1613.2 | 1608.8 | 1604.3 | 1599.9 | 1595.5 | 1573.3 | 1551.2 | 1529.0 | 1506.9 | 1484.7 | 1462.6 | 1439.4 | 1414.2 | 1396.1 | 1352 | 1307 | 1263 | 1219 | 1175 | 1064 | 1004 | 953 | 842 | 731 | | |
| 180 | 1720.1 | 1715.9 | 1711.7 | 1707.5 | 1703.3 | 1699.1 | 1678.0 | 1656.9 | 1635.8 | 1614.8 | 1593.7 | 1572.6 | 1551.5 | 1530.5 | 1509.4 | 1467 | 1425 | 1383 | 1341 | 1299 | 1256 | 1193 | 1088 | 982 | 877 | | |
| 190 | 1823.4 | 1819.4 | 1815.4 | 1811.4 | 1807.3 | 1803.3 | 1783.2 | 1763.1 | 1743.1 | 1723.0 | 1702.9 | 1682.8 | 1662.7 | 1642.6 | 1622.5 | 1582 | 1542 | 1502 | 1462 | 1422 | 1381 | 1321 | 1221 | 1120 | 1020 | | |
| 200 | 1927.4 | 1923.6 | 1919.8 | 1915.9 | 1912.1 | 1908.3 | 1889.1 | 1869.9 | 1850.7 | 1831.6 | 1812.4 | 1793.2 | 1774.1 | 1754.9 | 1735.7 | 1697 | 1659 | 1621 | 1582 | 1544 | 1506 | 1448 | 1352 | 1256 | 1161 | | |
| 210 | 2032.2 | 2028.5 | 2024.9 | 2021.2 | 2017.6 | 2013.9 | 1995.7 | 1977.4 | 1959.2 | 1940.9 | 1922.6 | 1904.4 | 1886.1 | 1867.9 | 1849.6 | 1813 | 1777 | 1740 | 1704 | 1667 | 1630 | 1576 | 1484 | 1391 | 1302 | | |
| 220 | 2137.7 | 2134.2 | 2130.7 | 2127.3 | 2123.7 | 2120.3 | 2102.9 | 2085.5 | 2068.1 | 2050.7 | 2033.3 | 2015.8 | 1998.4 | 1981.0 | 1963.6 | 1929 | 1894 | 1859 | 1824 | 1790 | 1755 | 1703 | 1616 | 1529 | 1442 | | |
| 230 | 2243.9 | 2240.6 | 2237.3 | 2233.9 | 2230.6 | 2227.3 | 2210.7 | 2194.1 | 2177.6 | 2161.0 | 2144.4 | 2127.8 | 2111.2 | 2094.6 | 2078.1 | 2045 | 2012 | 1979 | 1945 | 1912 | 1879 | 1829 | 1746 | 1663 | 1581 | | |
| 240 | 2350.9 | 2347.7 | 2344.5 | 2341.8 | 2338.2 | 2335.0 | 2319.2 | 2303.4 | 2287.5 | 2271.7 | 2255.9 | 2240.1 | 2224.2 | 2208.4 | 2192.6 | 2161 | 2129 | 2098 | 2066 | 2034 | 2003 | 1955 | 1876 | 1797 | 1718 | | |
| 250 | 2458.5 | 2455.5 | 2452.4 | 2449.4 | 2446.4 | 2443.3 | 2428.2 | 2413.0 | 2397.9 | 2382.8 | 2367.6 | 2352.5 | 2337.3 | 2322.2 | 2307.0 | 2277 | 2246 | 2216 | 2186 | 2156 | 2125 | 2080 | 2004 | 1928 | 1853 | | |
| 260 | 2566.8 | 2563.9 | 2561.0 | 2558.0 | 2555.1 | 2552.2 | 2537.7 | 2523.2 | 2508.6 | 2494.1 | 2479.6 | 2465.0 | 2450.5 | 2436.0 | 2421.4 | 2392 | 2363 | 2334 | 2305 | 2276 | 2247 | 2203 | 2131 | 2058 | 1985 | | |
| 270 | 2675.7 | 2672.9 | 2670.1 | 2667.3 | 2664.6 | 2661.8 | 2647.8 | 2633.9 | 2620.0 | 2606.1 | 2592.1 | 2578.2 | 2564.3 | 2550.4 | 2536.4 | 2509 | 2481 | 2453 | 2425 | 2397 | 2369 | 2328 | 2258 | 2188 | 2119 | | |
| 280 | 2785.3 | 2782.6 | 2779.9 | 2777.3 | 2774.6 | 2771.9 | 2758.6 | 2745.2 | 2731.8 | 2718.4 | 2705.7 | 2691.7 | 2678.3 | 2665.0 | 2651.6 | 2625 | 2598 | 2571 | 2545 | 2518 | 2491 | 2451 | 2384 | 2317 | 2251 | | |
| 290 | 2895.5 | 2893.0 | 2890.4 | 2887.8 | 2885.3 | 2882.7 | 2869.9 | 2857.1 | 2844.3 | 2831.5 | 2818.7 | 2805.9 | 2793.1 | 2780.3 | 2767.5 | 2742 | 2716 | 2691 | 2665 | 2639 | 2614 | 2575 | 2511 | 2446 | 2383 | | |
| 300 | 3006.5 | 3004.0 | 3001.5 | 2999.1 | 2996.6 | 2994.1 | 2981.8 | 2969.5 | 2957.2 | 2944.9 | 2932.5 | 2920.2 | 2907.9 | 2895.6 | 2883.3 | 2859 | 2834 | 2809 | 2785 | 2760 | 2736 | 2698 | 2637 | 2575 | 2514 | | |
| 310 | 3117.9 | 3115.5 | 3113.1 | 3110.8 | 3108.4 | 3106.0 | 3094.0 | 3082.1 | 3070.2 | 3058.2 | 3046.3 | 3034.3 | 3022.4 | 3010.4 | 2998.5 | 2975 | 2951 | 2927 | 2903 | 2879 | 2855 | 2819 | 2760 | 2700 | 2640 | | |
| 320 | 3230.0 | 3227.7 | 3225.5 | 3223.2 | 3220.9 | 3218.6 | 3207.1 | 3195.7 | 3184.2 | 3172.7 | 3161.3 | 3149.8 | 3138.4 | 3126.9 | 3115.4 | 3093 | 3070 | 3047 | 3024 | 3001 | 2978 | 2944 | 2886 | 2829 | 2772 | | |
| 330 | 3342.7 | 3340.5 | 3338.3 | 3336.1 | 3333.9 | 3331.7 | 3320.7 | 3309.7 | 3298.8 | 3287.8 | 3276.8 | 3265.8 | 3254.8 | 3243.8 | 3232.8 | 3211 | 3189 | 3167 | 3145 | 3123 | 3101 | 3068 | 3013 | 2958 | 2903 | | |
| 340 | 3455.8 | 3453.7 | 3451.6 | 3449.4 | 3447.3 | 3445.2 | 3434.7 | 3424.1 | 3413.6 | 3403.1 | 3392.5 | 3380.2 | 3371.4 | 3360.0 | 3350.3 | 3329 | 3308 | 3287 | 3266 | 3245 | 3224 | 3192 | 3139 | 3078 | 3034 | | |
| 350 | 3569.6 | 3567.6 | 3565.5 | 3563.5 | 3561.5 | 3559.5 | 3549.4 | 3539.3 | 3529.2 | 3519.1 | 3509.0 | 3498.9 | 3488.7 | 3478.7 | 3468.6 | 3448 | 3428 | 3408 | 3388 | 3368 | 3347 | 3317 | 3267 | 3216 | 3166 | | |
| 360 | 3683.6 | 3681.7 | 3679.7 | 3677.8 | 3675.9 | 3673.9 | 3664.2 | 3654.5 | 3644.8 | 3635.1 | 3625.4 | 3615.8 | 3606.1 | 3596.4 | 3586.7 | 3567 | 3548 | 3529 | 3509 | 3490 | 3471 | 3441 | 3393 | 3344 | 3296 | | |
| 370 | 3798.5 | 3796.6 | 3794.8 | 3792.9 | 3791.1 | 3789.2 | 3779.9 | 3770.6 | 3761.3 | 3752.0 | 3742.7 | 3733.4 | 3724.1 | 3714.8 | 3705.5 | 3687 | 3668 | 3650 | 3631 | 3612 | 3594 | 3565 | 3519 | 3473 | 3426 | | |
| 380 | 3914.1 | 3912.3 | 3910.5 | 3908.9 | 3906.9 | 3905.1 | 3896.2 | 3887.2 | 3878.3 | 3869.4 | 3860.4 | 3851.5 | 3842.6 | 3833.6 | 3824.7 | 3807 | 3789 | 3771 | 3753 | 3735 | 3717 | 3691 | 3646 | 3601 | 3557 | | |
| 390 | 4030.7 | 4029.0 | 4027.4 | 4025.6 | 4023.9 | 4022.4 | 4013.6 | 4006.5 | 4005.0 | 3996.5 | 3979.7 | 3970.8 | 3962.2 | 3953.6 | 3945.0 | 3928 | 3911 | 3894 | 3876 | 3859 | 3842 | 3816 | 3774 | 3731 | 3688 | | |
| 400 | 4147.4 | 4145.7 | 4144.1 | 4142.5 | 4140.8 | 4139.2 | 4131.0 | 4122.8 | 4114.5 | 4106.3 | 4098.1 | 4089.9 | 4081.7 | 4073.5 | 4065.3 | 4049 | 4032 | 4016 | 4000 | 3983 | 3967 | 3942 | 3901 | 3860 | 3819 | | |
| 410 | 4264.3 | 4262.7 | 4261.1 | 4259.5 | 4258.0 | 4256.4 | 4248.5 | 4240.6 | 4232.8 | 4224.9 | 4217.0 | 4209.1 | 4201.3 | 4193.4 | 4185.5 | 4170 | 4154 | 4138 | 4122 | 4107 | 4091 | 4066 | 4027 | 3988 | 3949 | | |
| 420 | 4381.8 | 4380.3 | 4378.8 | 4377.3 | 4375.8 | 4374.3 | 4366.8 | 4359.3 | 4351.7 | 4344.2 | 4336.7 | 4329.2 | 4321.7 | 4314.2 | 4306.7 | 4292 | 4277 | 4262 | 4247 | 4232 | 417 | 4194 | 4157 | 4119 | 4082 | | |
| 430 | 4499.9 | 4498.5 | 4497.0 | 4495.6 | 4494.2 | 4492.7 | 4485.5 | 4478.3 | 4471.1 | 4463.9 | 4456.7 | 4449.5 | 4442.3 | 4435.1 | 4427.9 | 4414 | 4409 | 4385 | 4370 | 4356 | 4341 | 4320 | 4284 | 4248 | 4212 | | |
| 440 | 4619.4 | 4618.0 | 4616.6 | 4615.2 | 4613.8 | 4612.5 | 4605.6 | 4597.8 | 4591.7 | 4584.8 | 4577.9 | 4575.1 | 4567.4 | 4551.7 | 4550.3 | 4537 | 4523 | 4509 | 4495 | 4481 | 4467 | 4447 | 4412 | 4378 | 4343 | | |
| 450 | 4737.9 | 4736.6 | 4735.2 | 4733.9 | 4732.6 | 4731.3 | 4724.7 | 4718.0 | 4711.4 | 4704.8 | 4698.2 | 4691.6 | 4685.0 | 4678.4 | 4671.8 | 4658 | 4645 | 4632 | 4619 | 4606 | 4592 | 4573 | 4540 | 4507 | 4473 | | |
| 460 | 4856.9 | 4855.7 | 4854.4 | 4853.1 | 4851.9 | 4850.6 | 4844.3 | 4837.9 | 4831.6 | 4825.3 | 4818.9 | 4812.6 | 4806.3 | 4799.9 | 4793.6 | 4781 | 4768 | 4756 | 4743 | 4730 | 4718 | 4699 | 4667 | 4635 | 4604 | | |
| 470 | 4976.5 | 4975.3 | 4974.1 | 4972.9 | 4971.7 | 4970.5 | 4964.4 | 4958.3 | 4952.3 | 4946.2 | 4940.2 | 4934.1 | 4928.0 | 4920.2 | 4915.9 | 4904 | 4892 | 4880 | 4867 | 4855 | 4843 | 4825 | 4795 | 4764 | 4734 | | |
| 480 | 5096.7 | 5095.5 | 5094.3 | 5093.2 | 5092.0 | 5090.9 | 5085.1 | 5079.3 | 5073.5 | 5067.7 | 5061.9 | 5056.1 | 5051.3 | 5048.7 | 5043.9 | 5039.5 | 5038.7 | 5027 | 5015 | 5004 | 4992 | 4981 | 4969 | 4952 | 4923 | 4894 | 4965 |
| 490 | 5211.9 | 5210.8 | 5209.7 | 5208.6 | 5207.5 | 5206.4 | 5206.0 | 5195.3 | 5189.7 | 5184.2 | 5178.6 | 5175.3 | 5171.9 | 5167.5 | 5162.0 | 5156.5 | 5154.5 | 5154 | 5123 | 5112 | 5101 | 5090 | 5073 | 5046 | 5018 | 4990 | |
| 500 | 5338.6 | 5337.5 | 5336.4 | 5335.4 | 5334.3 | 5333.2 | 5327.9 | 5322.6 | 5317.3 | 5312.0 | 5307.0 | 5301.4 | 5296.1 | 5290.8 | 5285.5 | 5275 | 5264 | 5254 | 5243 | 5232 | 5222 | 5206 | 5179 | 5153 | 5126 | | |
| 510 | 5459.9 | 5458.9 | 5457.9 | 5456.9 | 5455.9 | 5454.8 | 5449.8 | 5444.7 | 5430.7 | 5434.6 | 5429.5 | 5424.5 | 5419.4 | 5414.3 | 540 | | | | | | | | | | | | |

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

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

Pressure, Atm.

| Temp., °C. | 0 | 1 | 10 | 50 | 100 | Source |
|------------|---------|--------|--------|--------|--------|--------|
| 150 | 1414.99 | 1410.1 | 1365.9 | 1169.6 | 924 | This |
| | 1415.05 | 1410.1 | 1366.0 | 1169.7 | | (16) |
| | 1414.9 | 1384.1 | 1209.8 | 930 | | (11) |
| | 1409.8 | | 1162.9 | 897 | | (23) |
| | 1397.6 | 1369.9 | | 892.6 | | (30) |
| 200 | 1927.42 | 1923.6 | 1889.1 | 1735.7 | 1544 | This |
| | 1927.48 | 1923.6 | | 1735.8 | | (16) |
| | 1928.5 | 1893.7 | | | 1517.5 | (30) |
| 250 | 2455.5 | 2428.2 | 2156 | | | This |
| | 2461.5 | 2433.8 | | 2116.8 | | (30) |
| 300 | 3006.46 | 3004.0 | 2891.8 | 2883.3 | 2760 | This |
| | 3006.59 | 3004.1 | | 2880.8 | | (16) |
| | 3011.9 | 2988.1 | | 2729.7 | | (30) |
| 350 | 3567.6 | 3549.4 | 3368 | | | This |
| | 2478.0 | 3558.0 | 3343.1 | | | (30) |
| 400 | 4147.38 | 4145.7 | 4131.0 | 4065.3 | 3983 | This |
| | 4147.22 | 4145.6 | | 4065.7 | | (16) |
| | 4156.7 | 4141.0 | | 3959.7 | | (30) |
| 450 | 4736.6 | 4724.7 | 4606 | | | This |
| | 4749.0 | 4735.4 | 4783.4 | | | (30) |
| 500 | 5338.55 | 5337.5 | 5327.9 | 5385.5 | 5232 | This |
| | 5339.15 | 5338.1 | | 5286.0 | | (16) |
| | 5352.5 | 5341.1 | | 5211.4 | | (30) |
| 550 | 5950.6 | 5943.1 | 5868 | | | This |
| | 5967.8 | 5958.5 | 5846.7 | | | (30) |
| 600 | 6573.50 | 6572.9 | 6567.2 | 6541.9 | 6510 | This |
| | 6573.73 | 6573.1 | | 6542.3 | | (16) |
| | 6591.7 | 6584.1 | | 6487.5 | | (30) |
| 650 | 7204.1 | 7200.1 | | 7160 | | This |
| | 7224.7 | 7218.3 | | 7134.8 | | (30) |

At 150° C., and 150 atm., $H = 679$ (This) and 683 (17). At 150° C., and 200 atm., $H = 433$ (This), 459 (11), 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 (Cal./Mole)

| 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 $B \cdot TdB/dT$ 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).

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 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 | 1.446460 | 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 |
| 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 | ... | 2.815317 | ... | 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. $A_0 = 1.00705$.

^b Normal 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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LITERATURE CITED

- (1) Baker, H. W., "Technology of Heat," p. 57, Longmans Green, London, 1956.
- (2) Cook, D., *Can. J. Chem.* **35**, 268 (1957).
- (3) Deming, W. E., Deming, L. S., *Phys. Rev.* **56**, 108 (1939).
- (4) Din, F., ed., "Thermodynamic Functions of Gases," vol. II, Butterworths, London, 1956.
- (5) Ellenwood, F. O., Kulik, N., Gay, N. R., Cornell Univ. Eng. Expt. Sta., Bull. **30** (1942).
- (6) Granet, I., Kass, P., *Petrol. Refiner* **31**, 137 (1952).
- (7) Gratch, S., Office of Technical Services, Rept. **PB124957** (1950).
- (8) Gratch, S., *Trans. Am. Soc. Mech. Engrs.* **71**, 897 (1949).
- (9) Gratch, S., Univ. of Pennsylvania Research Lab. Preprint, 1947; *Trans. Am. Soc. Mech. Engrs.* **70**, 631 (1948).
- (10) de Groot, S. R., Michels, A., *Physica* **14**, 218 (1948).
- (11) Huggill, J. A. W., Newitt, D. M., Pai, M. U., Mech. Eng. Research Lab., Gt. Brit. Dept. Sci. Ind. Research, Rept. **8** (1950).
- (12) Kendall, B. J., Sage, B. H., *Petroleum* **14**, 184 (1951).
- (13) Kennedy, G. C., *Am. J. Sci.* **252**, 225 (1954).
- (14) MacCormack, K. E., Schneider, W. G., *J. Chem. Phys.* **18**, 1269 (1950).
- (15) *Ibid.*, p. 1273.
- (16) Maron, S. H., Turnbull, D., *J. Am. Chem. Soc.* **64**, 2195 (1942).
- (17) Masi, J. F., *Trans. Am. Soc. Mech. Engrs.* **76**, 1067 (1954).
- (18) Masi, J. F., Petkof, B., Natl. Bur. Standards. Rept. **1185**, (1951); *J. Research Natl. Bur. Standards* **48**, 179 (1952).
- (19) Meyers, C. H., *Ibid.*, **29**, 157 (1942).
- (20) Michels, A., Bijl, A., Michels, C. *Proc. Roy. Soc. (London)* **A160**, 376 (1937).
- (21) Michels, A., Blaïsse, B., Michels, C., *Ibid.*, **A160**, 358 (1937).
- (22) Michels, A., de Groot, S. R., *Appl. Sci. Research* **A1**, 94 (1948) (revision of 21).
- (23) *Ibid.*, p. 103.
- (24) Michels, A., Michels, C., *Proc. Roy. Soc. (London)* **A153**, 201 (1935).
- (25) *Ibid.*, **A160**, 348 (1937).
- (26) Michels, A., Michels, C., Wouters, H., *Ibid.*, **A153**, 214 (1935).
- (27) Michels, A., Stryland, J. C., *Physica* **16**, 813 (1950).
- (28) Michels, A., Wassenaar, T., Zweitering, T., Smits, P., *Ibid.*, **16**, 501 (1950).
- (29) Michels-Veraart, C. M., thesis, Amsterdam, 1937.
- (30) Natl. Bur. Standards, Circ. **564**, Chap. 4 (1955).
- (31) Natl. Bur. Standards-Natl. Advisory Comm. for Aeronaut., "Tables of Thermal Properties of Gases," Table 13.10, 1950.
- (32) Natl. Defense Research Comm., Summary Technical Rept., Division 11, 1946.
- (33) Oishi, J., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **A3**, 22 (1949).
- (34) Pfeifferle, W. C., Goff, J. A. Miller, J. G., *J. Chem. Phys.* **23**, 509 (1955).
- (35) Price, D., *Ind. Eng. Chem.* **47**, 1649 (1955).
- (36) Price, D., Naval Ordnance Lab. NAVord Rept. **2876** (1933).
- (37) *Ibid.*, **3846** (1954).
- (38) Quinn, E. L., Jones, C. L., "Carbon Dioxide," Reinhold, New York, 1936.
- (39) Reamer, H. H., Olds, R. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.* **36**, 88 (1944).
- (40) Roebuck, J. R., Murrell, T. A., Miller, E. E., *J. Am. Chem. Soc.* **64**, 400 (1942).
- (41) Schneider, W. G., Chynometh, A., *J. Chem. Phys.* **19**, 1607 (1951).
- (42) Schrock, V. E., Natl. Advisory Comm. Aeronaut., Tech. Note **2838** (1952).
- (43) Smallwood, J. C., *Ind. Eng. Chem.* **34**, 863 (1942).
- (44) Sweigert, R. L., Weber, P., Allen, R. L., *Ibid.*, **38**, 185 (1946).
- (45) Wentorf, R. H., Jr., Univ. Wis. Naval Research Lab., Rept. CM **724** (1952); *J. Chem. Phys.* **24**, 607 (1956).
- (46) Woolley, H. W., *Can. J. Phys.* **31**, 604 (1953).
- (47) Woolley, H. W., *J. Research Natl. Bur. Standards* **52**, 289 (1954).

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Measurement of the Thermal Properties of Carbonaceous Materials

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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.

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).

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